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Spectroscopy of Hydrothermal Solutions 18: pH-Dependent Kinetics of Itaconic Acid Reactions in Real Time

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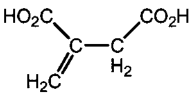
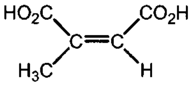
The kinetics of decarboxylation of the α-substituted acrylic acid itaconic acid were analyzed at 280−330 °C, 275 bar, and solution $pH_{25} = 0.8-5.75$ using an FTIR spectroscopy flow reactor. As the pH was increased, the observed rate constant initially decreased to a minimum at $pH_{25} = 1.82$, then increased and reached its maximum at $pH_{25} = 3.75$, and then decreased again up to the limit of study at $pH_{25} = 5.75$. The decarboxylation rate depends on the molecular form of itaconic acid in the order of itaconate monoanion > protonated itaconic acid > neutral itaconic acid ≈ itaconate dianion. Insight into possible reasons for this trend was obtained from geometry-optimized structures using density functional theory with the B3LYP method at the 6-31+G* level.

Introduction

Dicarboxylic acids are important components in subterranean waters.[1] Detailed studies of the pH dependence of decarboxylation of one such acid, malonic acid, have been reported recently.[2] Itaconic acid (I) is another dicarboxylic acid that has attracted attention in the hydrothermal regime.[3−6] It was first known as a byproduct of the pyrolysis of citric acid.[7] It is produced industrially by fermentation of *Aspergillus terreus* and has been of interest in polymer industry as a monomer and a copolymer component in part because of its availability from a renewable nonpetroleum resource[8,9] and in part because it enhances the properties of polymer coatings.[10]


I

The hydrothermal chemistry of itaconic acid is potentially rather complex as a result of the presence of three functional groups, each of which contributes to the reaction pathways. Decarboxylation, isomerization (e.g., formation of citraconic acid (II) and mesaconic acid (III)), and hydration are known to occur at high temperature.[3,5,6] In addition, protonation occurs in highly acidic solution,[4] and polymerization can be initiated in aqueous solution.[9]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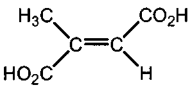
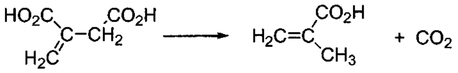

III

The reaction scheme of itaconic acid was outlined in some detail by Carlsson et al.[3] and by Cody et al.[5] in the research on the conversion of citric acid to itaconic acid. Carlsson et al. found that decreasing the solution pH reduced the rate of decarboxylation of itaconic acid but favored the undesirable decarbonylation reaction, while a high pH also quenched the decarboxylation reaction. A solution with an itaconic acid-to-base of ratio between 5:1 and 10:1 at $T = 350-375$ °C exhibited approximately 70% conversion to methacrylic acid by the decarboxylation reaction 1.


(1)

The work of Cody et al. dealt with hydrothermal media in which CO_2 and H_2 were added. In addition to decarboxylation reactions, the hydrogenation of itaconic acid occurred leading to methyl succinic acid. The conversions of itaconic to citraconic and mesaconic acids occurred through the methyl succinic acid. Because no H_2 was added in the present work, the conditions most closely mimic those employed by Carlsson et al.

Despite the impressive amount of knowledge that already exists about the species involved in the itaconic acid reaction network, no kinetic measurements of any of the reactions have been reported previously. The complexity of the network makes such determinations into a particularly thorny problem. Nevertheless, it appeared to be possible to establish the kinetics of at least the decarboxylation of itaconic acid because itaconic acid has been indicated to be the least stable of all of the carboxylate species in the reaction network toward decarboxylation and isomerization of the other isomers to itaconic acid preceded their decarboxylation.[3,5,6] The kinetic behavior of itaconic acid was determined in real time at hydrothermal conditions as a function of the pH by the use of an FTIR spectroscopy flow reactor.[11−14] Density functional theory calculations were also conducted to provide additional insight into the experimental data and mechanism.

Experimental Section

Itaconic acid (99%), citraconic acid (98%), methacrylic acid (99%), HCl, and NaOH were obtained from Aldrich Chemical Co. and used as received. Milli-Q deionized water was sparged with compressed Ar before use to expel the atmospheric gases. The pH values of aqueous solutions were adjusted by adding aqueous HCl or KOH solutions and were measured with an Orion model 330 pH meter. The concentrations of aqueous itaconic acid, citraconic acid, and methacrylic acid solutions were controlled to be 0.5 *m* as the pH was adjusted.

The flow reactor−IR spectroscopy cell constructed from titanium with sapphire windows and gold foil seals has been described in detail elsewhere.[11−14] The temperature and pressure

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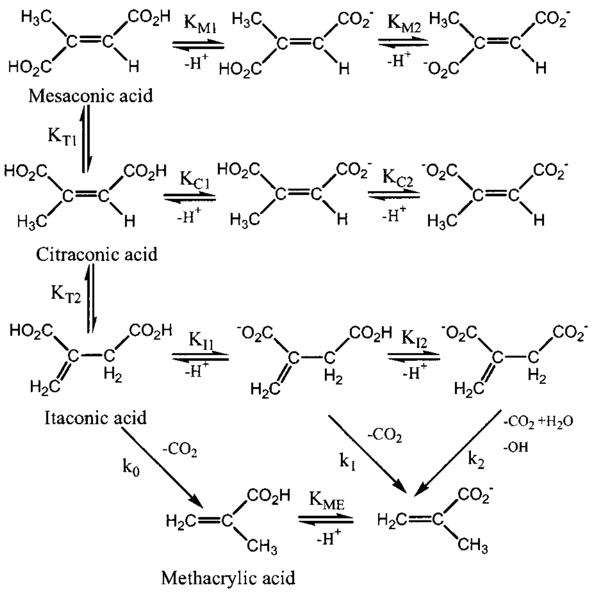
SCHEME 1



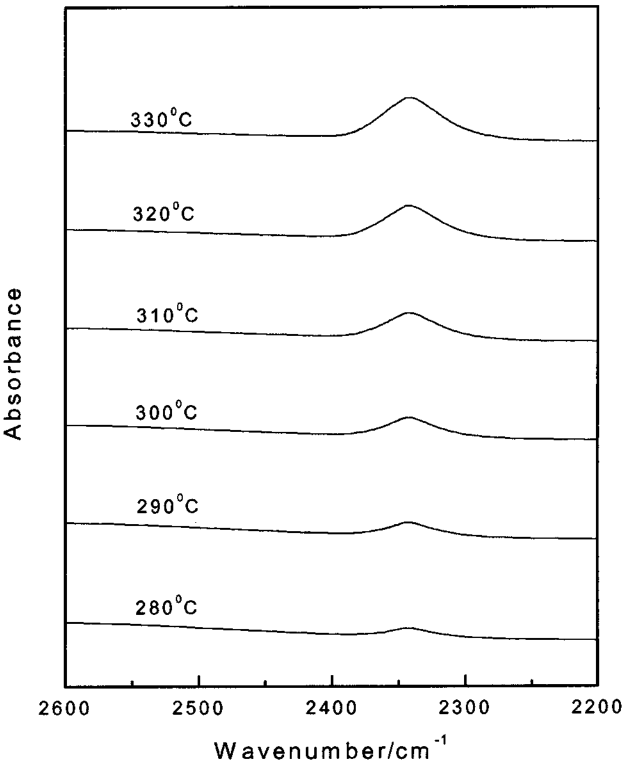


Figure 1. FTIR spectra for the formation of CO_2 (ν_3) from decarboxylation of 0.5 *m* itaconic acid at different temperatures, where the pressure is 275 bar, the reactor residence time is 37 s, and the $pH_{25} = 2.31$ (natural value).

were controlled within ±1 °C and ±1 bar, respectively. The flow rate was controlled as desired by the use of an Isco syringe pump in the 0.01−1.0 mL/min range with an accuracy of 1%. Correction of the flow rate was made to account for the density change with temperature. Transmission IR spectra were recorded at 4 cm^{-1} resolution with a Nicolet 560 Magna FTIR spectrometer and an MCT-A detector. Background spectra recorded on pure water under the same conditions were subtracted. Thirty-two spectra were summed at each condition, and the rate data reported herein are the average of three replicated measurements. The decarboxylation kinetics were determined only up to $T = 330$ °C and $pH_{25} = 0.8-5.75$ because it was found that severe leakage at the gold foil seals frequently occurred when the cell was operated at higher solution pH (greater than 6.5) in the upper temperature range. On the other hand, the addition of HCl to create pH values below 0.8 caused corrosion of the cell at hydrothermal conditions.

During the decarboxylation reaction, only the asymmetric stretch of aqueous CO_2 centered at 2343 cm^{-1} was observed in the band-pass of sapphire windows. To obtain the kinetic parameters, the band area of CO_2 was converted to concentration at each condition by using the Beer−Lambert Law and the previously determined molar absorptivity of aqueous CO_2.[15] Weighted least-squares regression[16] was performed in which the statistical weight was set to be $1/\sigma^2$, where σ is the standard deviation of the variables.

Results and Discussion

Reaction Pathway of Itaconic Acid. The detailed decomposition pathway of itaconic acid was described by Carlsson et al.[3] and Cody et al.[5] at various hydrothermal reaction conditions. The experimental conditions used here most closely resemble those of Carlsson et al. The dominant pathways are shown in Scheme 1. Hydration of the unsaturated reactants and products (itaconic acid, citraconic acid, mesaconic acid, and methacrylic acid) and isomerization of methacrylic acid to crotonic acid were ignored because they are slow compared with the decarboxylation of itaconic acid.[3] According to Carlsson et al.[3] and Sakai,[6] very fast isomerization equilibria among itaconic acid, citraconic acid, and mesaconic acid exist at high temperature relative to the other reactions. It is therefore reasonable to assume that these three diacids are in equilibrium before the dominant reaction occurs, which is liberation of CO_2 from itaconic acid. The product methacrylic acid was confirmed to be unreactive at the experimental conditions used here by running the flow reactor at 340 °C and at the longest residence time. In Scheme 1, k_0, k_1, and k_2 are the decarboxylation rate constants of neutral itaconic acid, the itaconate monoanion, and the itaconate dianion, respectively. The rate of formation of CO_2 from citraconic acid at its natural pH is lower than that from itaconic acid at the same temperature and pressure conditions, which supports the occurrence of both fast equilibration among itaconic acid, citraconic acid, and mesaconic acid and the fact that decarboxylation of citraconic acid occurs only after first converting to itaconic acid. It is known from experiment that the decarboxylation rate is slower than the isomerization rate.[3] The reactivity of the diacids (saturated and unsaturated) toward decarboxylation is being analyzed theoretically and experimentally in a separate study. The position of the carbon−carbon double bond in the diacids plays an important role in the decarboxylation rate.

Kinetics of Decarboxylation. The decarboxylation reactions of neutral itaconic acid, itaconate monoanion, and itaconate dianion are shown in eqs 2−4.

$$HO_2CC(CH_2)CH_2CO_2H \xrightarrow{k_0} CH_3C(CH_2)CO_2H + CO_2 \quad (2)$$

$$^-O_2CC(CH_2)CH_2CO_2H \xrightarrow{k_1} CH_3C(CH_2)CO_2^- + CO_2 \quad (3)$$

$$^-O_2CC(CH_2)CH_2CO_2^- + H_2O \xrightarrow{k_2} CH_3C(CH_2)CO_2^- + CO_2 + OH^- \quad (4)$$

As an illustration, Figure 1 displays the extent of CO_2 formation from FTIR spectra of itaconic acid with the natural solution

TABLE 1: Observed First-Order Rate Constants (k in $s^{-1} \times 10^3$) and Arrhenius Parameters of Decarboxylation of 0.5 m Itaconic Acid Solution at Different Temperatures

	pH_{25}									
T (° C)	0.8	1.25	1.82	2.05	2.31	3.25	3.75	4.25	5.25	5.75
280	0.89 ± 0.08	0.62 ± 0.04	0.37 ± 0.02	0.44 ± 0.02	0.76 ± 0.02	4.76 ± 0.07	13.35 ± 0.34	8.71 ± 0.11	4.33 ± 0.19	1.58 ± 0.05
290	1.49 ± 0.08	0.96 ± 0.04	0.65 ± 0.03	0.78 ± 0.03	1.35 ± 0.05	7.45 ± 0.10	21.16 ± 0.59	13.94 ± 0.14	6.37 ± 0.21	2.33 ± 0.08
300	2.57 ± 0.10	1.73 ± 0.08	1.02 ± 0.08	1.40 ± 0.05	2.29 ± 0.06	11.76 ± 0.17	36.57 ± 0.79	21.70 ± 0.19	10.34 ± 0.46	3.94 ± 0.19
310	4.03 ± 0.13	2.58 ± 0.09	1.54 ± 0.07	1.94 ± 0.07	3.57 ± 0.07	17.93 ± 0.33	57.34 ± 1.14	33.16 ± 0.32	17.89 ± 0.82	5.88 ± 0.33
320		3.75 ± 0.11	2.71 ± 0.11	3.30 ± 0.12	4.65 ± 0.13	28.38 ± 0.51	81.65 ± 2.80	49.82 ± 0.58	22.73 ± 1.40	
330		5.39 ± 0.18	3.87 ± 0.07	4.98 ± 0.12	6.71 ± 0.16	42.25 ± 1.34	107.22 ± 4.50			
E_a (kJ•mol^{-1})			128.3 ± 2.5				122.6 ± 5.7			
ln(A/s^{-1})			20.0 ± 0.5				22.4 ± 1.3			

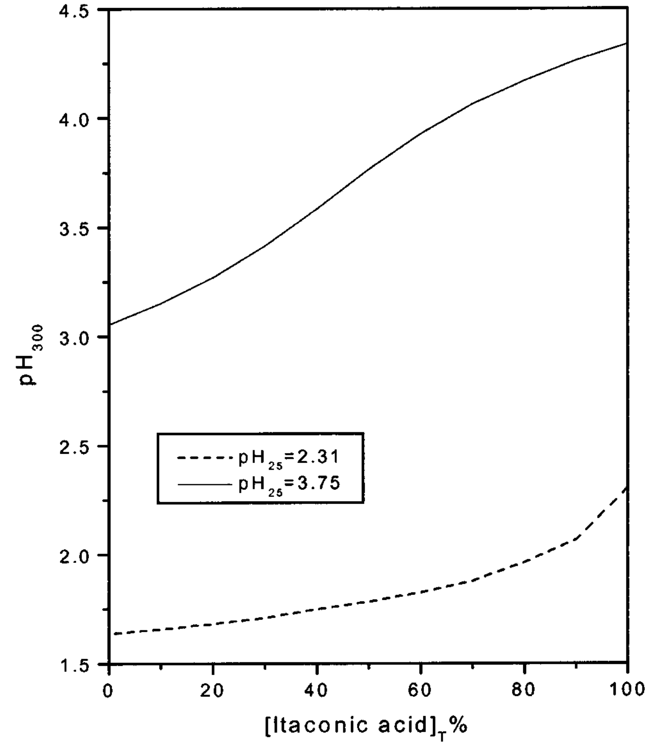


Figure 2. The pH change as a function of the percentage of total itaconic acid in an itaconic acid−citraconic acid solution at 300 °C.

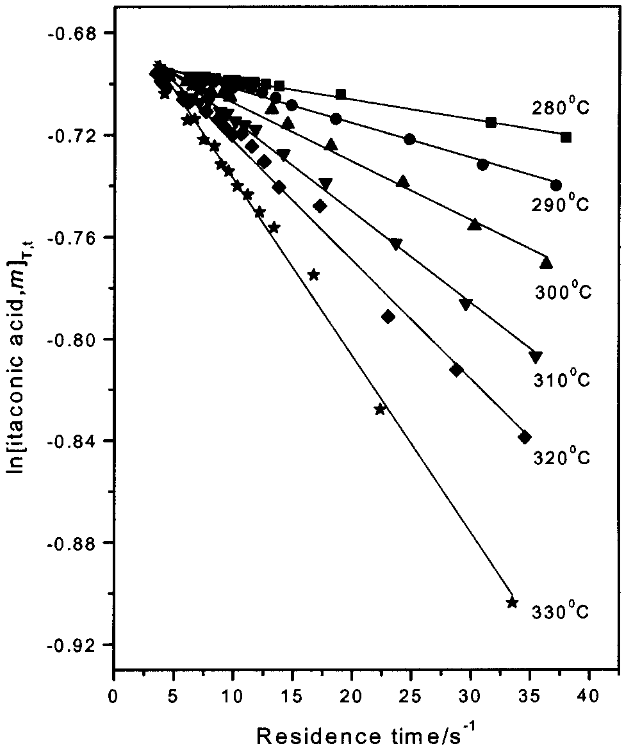


Figure 3. The rate plot for decarboxylation of 0.5 m itaconic acid at the natural solution $pH_{25} = 2.31$ and 275 bar.

$pH_{25} = 2.31$ at a constant reactor residence time of about 37 s but at different temperatures. The rate constants for decarboxylation were extracted from the time dependence of these spectra at each constant temperature subject to the following considerations. First, the concentration of itaconic acid at time t was obtained from eq 5, where [itaconic acid]$_0$ is the initial concentration of itaconic acid and $[CO_2]_{T,t}$ is the total CO_2 concentration (eq 6).

$$[\text{itaconic acid}]_{T,t} = [\text{itaconic acid}]_0 - [CO_2]_{T,t} \tag{5}$$

$$\begin{aligned}[CO_2]_{T,t} &= [CO_2]_{obs} + [HCO_3^-] + [CO_3^{2-}] \\ &= [CO_2]_{obs}\left(1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a1}K_{a2}}{[H^+]^2}\right)\end{aligned} \tag{6}$$

The calculation of $[CO_2]_{T,t}$ requires that the dissociation constants K_{a1} and K_{a2} for the hydrolysis/ionization of CO_2 in aqueous solution (eqs 7 and 8) and the solution pH are known at the reaction temperature.

$$CO_2 + H_2O \overset{K_{a1}}{\rightleftharpoons} HCO_3^- + H^+ \tag{7}$$

$$HCO_3^- \overset{K_{a2}}{\rightleftharpoons} CO_3^{2-} + H^+ \tag{8}$$

The dissociation constants of CO_2 were obtained from Butler[17] but have not been measured in the temperature range of interest in this paper. However, the equilibrium constant of any acid−base reaction in aqueous solution at high temperature can be calculated by the use of iso-Coulombic extrapolation[18] given the specific volume[19] and the dissociation constant[20] of water.

Second, calculation of species distribution of CO_2 in aqueous solution as a function of the pH indicated that the hydrolysis of CO_2 is sharply reduced with increasing temperature, e.g., at 300 °C only 1.09% of the CO_2 is in the form of HCO_3^- and 4.3×10^{-6}% is in the form of CO_3^{2-} at $pH_{300} = 6$. By combining

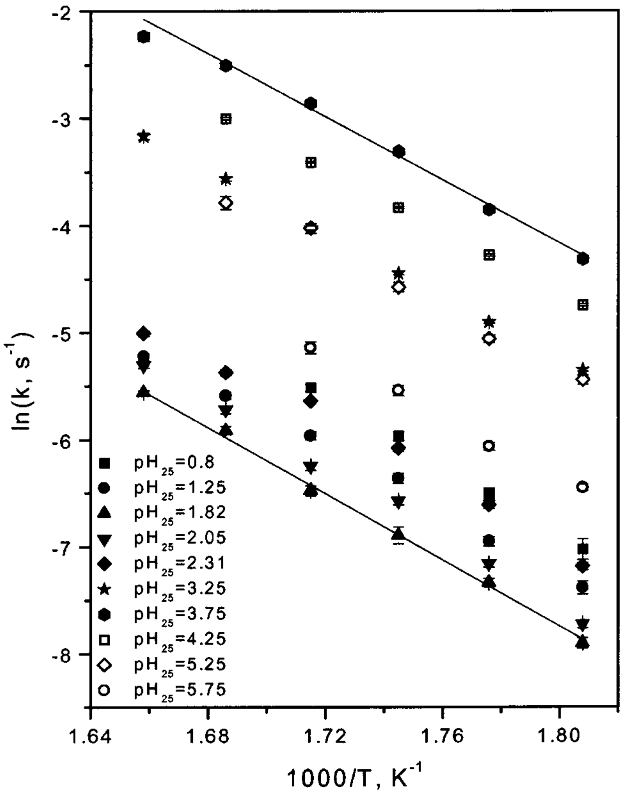


Figure 4. An Arrhenius plot for the decarboxylation of 0.5 *m* itaconic acid solution at different values of the pH.

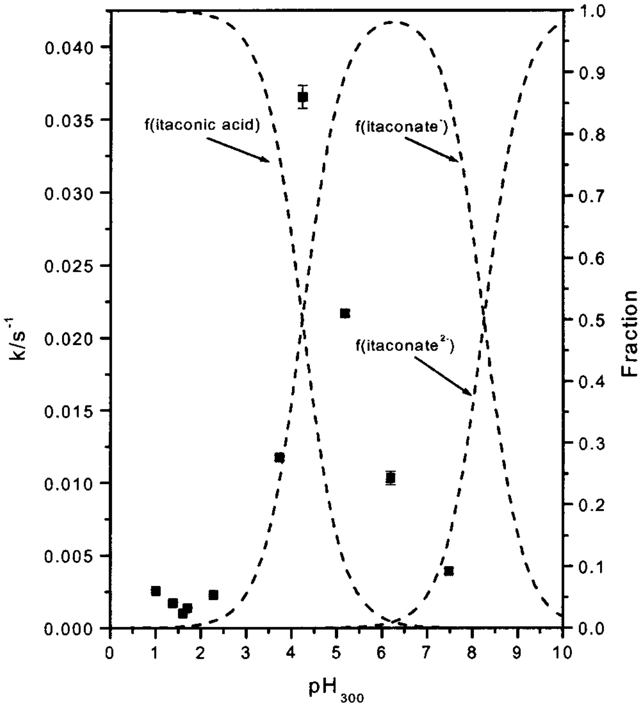


Figure 5. The observed rate constants as a function of the pH and the distribution of itaconic acid species at 300 °C and 275 bar.

these two calculations, it is acceptable to replace $[CO_2]_{T,t}$ with $[CO_2]_{obs}$ in eq 5 within the experimental uncertainty.

Third, the solution pH at high temperature was calculated from the charge balance equation of the system,[2,21] which can be obtained from the reactions in Scheme 1. Again, the necessary dissociation constants of all acids in Scheme 1 at high temperatures must be extrapolated from those at low temperatures[22,23] using iso-Coulombic method. The ionization constants at 25 °C are as follows: itaconic acid ($pK_1 = 3.86$, $pK_2 = 5.14$), citraconic acid ($pK_1 = 2.5$, $pK_2 = 6$), mesaconic acid ($pK_1 = 3.2$, $pK_2 = 4.82$), methacrylic acid ($pK = 4.65$). The itaconic-to-citraconic acid ratio is about 4:1 at 170 °C [3] and 3:1 at 250 °C.[6] The citraconic-to-mesaconic acid ratio is about 1:1 at 360−400 °C.[3] When these isomerizations are incorporated, the solution pH of itaconic acid at 300 °C will be decreased because citraconic acid and mesaconic acid are stronger acids than itaconic acid. Unfortunately, full quantitation of the charge balance equation is not possible at this time because the isomerization equilibrium constants among itaconic acid, citraconic acid, and mesaconic acid (K_I, K_C, and K_M) and their variations with pH and temperature are not available. Therefore, an approximate calculation of the solution pH at high temperature was made using only K_{T1}. On the basis of the ratios given above,[3,6] Figure 2 shows the dependence of pH on the percentage of itaconic acid in the itaconic−citraconic acid

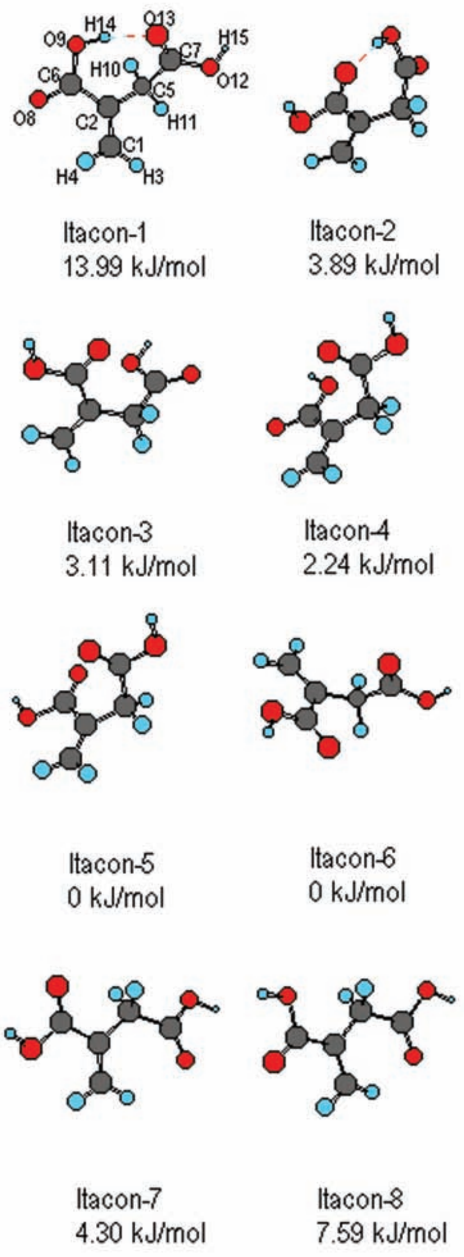


Figure 6. Conformers of itaconic acid optimized in the gas phase by B3LYP/6-31+G*.

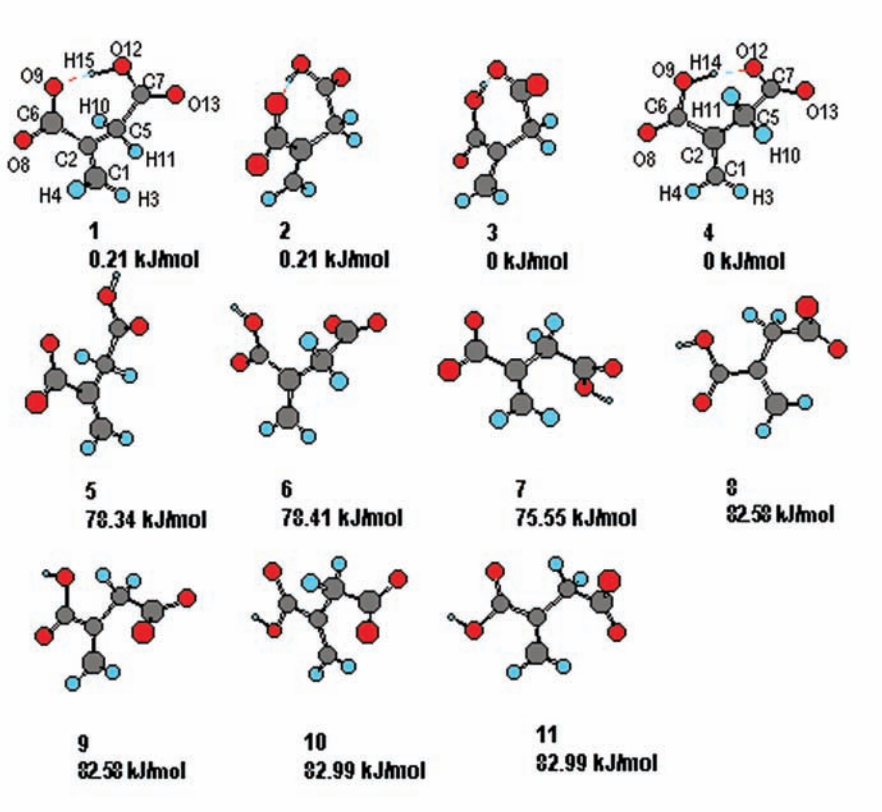


Figure 7. Conformers of itaconate monoanion optimized in the gas phase by B3LYP/6-31+G*.

solution at 300 °C. It can be seen that the solution pH is lower than that indicated by itaconic acid alone, but the true pH cannot be calculated because the complete isomerization process is not taken into account.

Given the foregoing three considerations, a plot of ln [itaconic acid]$_{T,t}$ versus the reactor residence time t indicates that the first-order rate law applies and yields the observed rate constants. Figure 3 illustrates the data at the natural pH of the solution (2.31). In the probable case that H_2O participates in the reaction, the rate law might be better referred to as pseudo-first-order. The observed first-order rate constants at different values of the pH are listed in Table 1 and shown as an Arrhenius plot in Figure 4. It is clear that with the addition of HCl the observed rate constant decreases and reaches its minimum at $pH_{25} = 1.82$ and then increases slightly with the addition of HCl. With the addition of NaOH, the rate constant increases to its maximum value at $pH_{25} = 3.75$ and then decreases again. So, the decarboxylation rate of molecular itaconic acid is slower than that of itaconate monoanion and protonated itaconic acid ($HO_2CC(CH_2)CH_2CO_2H_2^+$). The change of the rate constant with pH is shown graphically in Figure 5 in comparison with the calculated distribution of itaconic acid species. The pH values at 300 °C were used without consideration of the isomerization of itaconic acid. As was already noted above (Figure 2), inclusion of the isomerized species lowers the pH from that indicated in Figure 5, which would improve the apparent mismatch of the experimental rates and calculated concentrations of the species. If the true values of the solution pH were known, it would have been possible to fit the observed rate constants and thereby obtain the rate constants for decarboxylation of protonated itaconic acid, neutral itaconic acid, and itaconate monoanion. This procedure was successful in our recent study of α-alanine.[24] Instead, we assigned the decarboxylation rate constant at $pH_{25} = 1.82$ to reflect that of neutral itaconic acid and the value at $pH_{25} = 3.75$ to the itaconate monoanion. Values of $pH_{25} = 1.82$ and below produced by the addition of strong acid cause retardation of the isomerization of itaconic acid,[10] and hence the predominating species is the neutral itaconic acid. At the same time, the amounts of protonated itaconic acid and itaconate monoanion remain very low. For $pH_{25} = 3.75$, the rate constant for decarboxylation of the itaconate monoanion is about 25 times larger than that at $pH_{25} = 1.82$. The portion of itaconate dianion is very low at $pH_{25} = 3.75$. As the pH is raised further, the decarboxylation of the itaconate dianion takes over and, according to Figure 5, its rate constant is more comparable to that of neutral itaconic acid than to that of the monoanion.

Mechanistic Considerations. An attempt was made to understand why the itaconate monoanion decarboxylates faster than the neutral acid or the dianion by the use of density functional theory calculations (B3LYP method) with the relatively high-level basis set 6-31+G*. The Gaussian 98 program package was employed.[25] These calculations should be viewed as an estimate of the processes because no accounting was made for the existence of the water medium. After a careful structural search, eight conformers of itaconic acid and eleven conformers of the itaconate monoanion were found. The optimized structures of itaconic acid and itaconate monoanion are shown in Figures 6 and 7, respectively, along with their relative energies. The crystal structure of itaconic acid[26] is close to Itacon-6. Because of the existence of the germinal C═C bond, the C1−C2−C5−C6 dihedral angle in all structures approaches zero. The conformers of itaconate monoanion with intramolecular hydrogen bonding produce the lowest energy structures, which is not the case for itaconic acid. Because the C═C bond is electron-withdrawing, the hydrogen ion of the carboxylate group in the α position should dissociate first, but the theoretical calculation indicates that the energy difference in the position of the

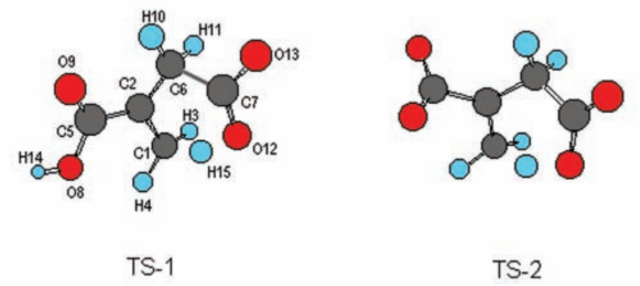


Figure 8. Transition states for the decarboxylation of neutral itaconic acid and itaconate monoanion.

TABLE 2: Atom Charges and Bond Distances

atom	itaconic acid (Itacon-5)	itaconic acid (Itacon-7)	itaconate mono-anion (3)	itaconate mono-anion (7)	transition state (TS-1)	transition state (TS-2)
			Charge (esu)			
C1	−0.41	−0.80	−0.55	−0.84	−0.90	−0.89
C2	+0.42	+0.60	+0.55	+0.66	+0.57	+0.38
C5	−0.83	−1.04	−0.88	−0.79	−0.75	−0.66
C6	+0.47	+0.59	+0.44	+0.62	+0.49	+0.48
C7	+0.52	+0.83	+0.49	+0.32	+0.53	+0.54
O8	−0.48	−0.49	−0.54	−0.64	−0.43	−0.53
O9	−0.61	−0.62	−0.64	−0.63	−0.59	−0.53
O12	−0.57	−0.59	−0.63	−0.56	−0.40	−0.51
O13	−0.43	−0.48	−0.57	−0.48	−0.43	−0.55
			Bond length (Å)			
C1−C2	1.339	1.341	1.342	1.339	1.409	1.408
C2−C5	1.507	1.514	1.515	1.526	1.426	1.478
C2−C6	1.490	1.491	1.523	1.561	1.508	1.510
C5−C7	1.520	1.513	1.564	1.501	1.754	1.608

hydrogen atom is very small. Moreover, structures 1 and 4 or structures 2 and 3 in Figure 7 represent the two lowest energy points that contain low-barrier hydrogen bonds.[27,28]

The transition states for the decarboxylation of itaconic acid from Itacon-7 (TS-1) and of itaconate monoanion from structure 7 (TS-2) were found and are displayed in Figure 8. In these two cyclic transition states, intramolecular hydrogen shift and C5−C7 bond fission are two synchronous processes. For a better comparison, the bond lengths of carbon chain and atom charges (Mulliken method) of heavy atoms in transition states and corresponding reactant states are listed in Table 2, along with the lowest energy structures for itaconic acid and itaconate monoanion. The calculated energy barrier of decarboxylation for itaconic acid is 155.27 kJ/mol if Itacon-7 is chosen as the reactant and 159.57 kJ/mol if Itacon-5 is chosen as the reactant. The experimental results in Table 1 produced $E_a = 128$ kJ/mol. The energy barrier for decarboxylation for itaconate monoanion is 60 kJ/mol from structure 7, which seems too low. However, the total energy barrier should be 135.55 kJ/mol when the decarboxylation occurs between the lowest energy structure 1 (or 2, 3, and 4) and the transition state. This value is close to the experimental value of 122 kJ/mol. Hence, the lowest energy structure may convert to structure 7 before achieving the transition state. Although the energy barriers were obtained only in the gas phase, these results could be regarded to be representative of aqueous solution because the solvent has been proposed to play a small role in the decarboxylation when an intramolecular cyclic transition state is involved.[29]

These calculations provide insight into why the itaconate monoanion decarboxylates faster than itaconic acid. When decarboxylation occurs, itaconate monoanion initially converts to its higher energy conformer 7 and then forms TS-2. According to transition-state theory, this process should be faster than that of itaconic acid for which no tautomerization initially occurs. However, the energy barriers are similar. The dianion has no transferable H atom on the carboxylate groups and thereby must decarboxylate by the participation of H_2O. As appears to be the case with the malonate dianion,[2] hydration of the carboxylate center by H_2O may be a necessary step before the reaction can occur, which reduces the rate.

The transition states of decarboxylation for itaconic acid and itaconate monoanion found computationally are supported not only by experimental results but also by the fact that the transition states of decarboxylation of β,γ-unsaturated carboxylic acids both experimentally[30] and theoretically[31] involve intramolecular cyclic structures. The average of the activation energies for decarboxylation of the neutral and monoanionic itaconic acid (Table 1) is similar to that of the same two forms of malonic acid (125 vs 120 kJ/mol), but the average exponential factor, A, is much smaller [$\ln(A/\mathrm{s}^{-1}) = 29$ vs 21.5]. Hence, the activation entropy is the main controlling factor in the decarboxylation rates of these two diacid compounds. The C−C bond scission is the common process in these reactions, but the activation energies for the decarboxylation of monocarboxylic acids, which also involves C−C bond scission, range widely (30−300 kJ/mol). The main feature that the itaconic and malonic acids have in common is the ability to form an intramolecular hydrogen bond.

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