Spectroscopy of Hydrothermal Reactions. 5. Decarboxylation Kinetics of Malonic Acid and Monosodium Malonate

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The kinetics of decarboxylation of 1.07 *m* malonic acid and monosodium malonate at 120–230 °C and 275 bar were determined directly in a combined microflow reactor and short-pathlength IR spectroscopy cell. Malonic acid and monosodium malonate decomposed in a single step to CO₂ and acetic acid and CO₂ and the acetate ion, respectively. The kinetics for malonic acid were modeled as an equilibrium between malonic acid and the monoanion with parallel decarboxylation of both species. The Arrhenius parameters are $E_a = 120 \pm 2 \text{ kJ/mol}$ and $\ln A (\text{s}^{-1}) = 29.4 \pm 0.1$ for the malonate monoanion and $E_a = 126 \pm 2 \text{ kJ/mol}$ and $\ln A (\text{s}^{-1}) = 31.4 \pm 0.1$ for malonic acid in a 316 stainless steel flow reactor at 120–210 °C. Decarboxylation of the monoanion is slower than that of malonic acid. The rates of decarboxylation of malonic acid are slower above 140 °C in a Pt/Ir alloy flow reactor with diamond windows than in a 316 stainless steel flow reactor with sapphire windows.

Introduction

Reactions of carboxylic acids occur in the hydrothermal environment in a broad spectrum of applications. For example, pressure and temperature are among several variables which can be manipulated to alter the properties of H₂O and, thereby, optimize the yield of desired products. Examples include the interconversion of lactic and acrylic acid,^{1,2} which has been accomplished in sub- and supercritical H₂O. The sequential conversion of citric to itaconic to methylacrylic acids in subcritical H₂O has recently been described by Antal et al.³

Sedimentary brines and ocean-based volcanic vents are hydrothermal environments where carboxylic acids are among the important organic compounds formed. Bell and Palmer⁴ describe the role of mono- and dicarboxylic acids in brines, while Shock⁵ has discussed the thermodynamics of organic acids in brines.

Carboxylic acids are present in many waste streams owing to their widespread use in industrial processes and commercial products (e.g., preparation of polymers, paper products, pharmaceuticals, dyes, formates, flavoring agents, perfumery esters, etc.). The destruction of these aqueous wastes by wet air oxidation⁶ involves hydrothermal conditions and is one approach to meeting local discharge standards for wastewater.

In none of the areas of research or application mentioned above has a real time, direct spectroscopic measurement of the rate or pathway of reaction of a carboxylic acid been reported at hydrothermal conditions. This void was one of the motivations of the research described in this article. The focus here is on the conversion of aqueous malonic acid and monosodium



malonate to acetic acid and sodium acetate. Malonic acid was chosen because it is relatively reactive and noncorrosive and has a straightforward decarboxylation reaction. Thus, the conversion takes place rapidly at subcritical conditions in H₂O without leaching the reactor walls. The pathway can be deduced with relative ease from the IR spectrum.

Decarboxylation of malonic acid and monosodium malonate has been previously studied at lower temperatures, in the batch mode, and by *ex situ* analysis of the products. Bernoulli and Wege⁷ discussed malonic acid in the 75–110 °C range at approximately 1 atm. Fairclough⁸ examined aqueous monosodium malonate at 76–120 °C in a sealed tube. Hall⁹ conducted studies of both compounds at 80–90 °C at about 1 atm.

In this paper, we have investigated malonic acid and monosodium malonate directly at 120–210 °C in a flow reactor which possessed windows suitable for transmission IR spectroscopy. The observation of the reactants and products in real time by infrared spectroscopy enables the kinetics and pathway to be determined simultaneously.

Experimental Section

A microflow reactor, which is also a precision spectroscopy cell, was used to study the reactions described herein. Controlled, constant conditions of temperature (25-450 °C), pressure (1-335 bar), and flow rate (0.03-2.5 mL/min) are available as chosen. Both a 90/10 Pt/Ir alloy cell with diamond wafer windows¹⁰ and a 316 stainless steel (SS) cell with sapphire windows¹¹ were used. A detailed description of the flow reactor (surface-to-volume ratio of 25) and operating procedures is given elsewhere.^{10,11} For the studies described herein, kinetics were determined at flow rates at 2.00-0.05 mL/min, which translates to residence times in the cell of 1.79-71.4 s. The temperature range of the study was 120-230 °C, and the pressure was maintained at a constant value of 275 bar at all times. These conditions ensured that a single fluid phase is present over the entire range of studies. Multiple determinations (three-five) were made at several sets of conditions to determine the precision of a given rate measurement. Malonic acid solutions were prepared from 99% malonic acid (Aldrich). The monosodium malonate was prepared by adding 1 equiv of NaOH to a solution of malonic acid.

A Nicolet 60SX FTIR spectrometer with a liquid N_2 cooled MCT detector was used for cell spectral measurements. Spectra were obtained at 4 cm⁻¹ resolution by adding 32 interferograms.

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Figure 1. Mid-IR spectra of 1.07 m malonic acid at 200 °C and 275 bar at several residence times in the Pt/Ir-diamond flow cell.

Absorbance areas were determined by curve fitting the baseline-corrected spectra using Peakfit (Jandel Scientific).

Results and Discussion

The major reaction of dicarboxylic acids is decarboxylation to produce CO2 and the monocarboxylic acid in which the backbone has one fewer carbon atoms.⁴ Figure 1 shows several of the many IR spectra of 1.07 m ($m = \text{mol kg}^{-1}$ of solvent) malonic acid recorded with the Pt/Ir-diamond cell at different residence times. Because the temperature of this data set is 200 °C, significant conversion to CO₂ has taken place, as evidenced by $\nu_3(CO_2)$ at 2345 cm⁻¹. Also, the overlapping C-O stretch and COH in-plane bending modes characteristic of malonic and acetic acid are observed at 1100-1300 cm⁻¹. The C=O stretch at about 1750 cm⁻¹ overlaps the ν_2 bending mode of H₂O, which is difficult to subtract completely from the spectrum under these conditions. All of the absorbances observed could be attributed to malonic acid, acetic acid, and CO₂, which is valuable information because it eliminates the existence of other major reaction channels. A total carbon balance, however, was not determined because of spectral overlap of the acids and their anions. It was confirmed that decomposition of the acetic acid and acetate ion products is not detected by IR spectroscopy at the temperatures and residence times used here. This is not surprising given the stability of acetic acid against hydrothermal decomposition.¹²⁻¹⁴ As a result, the absorbance of $\nu_3(CO_2)$ forms the basis of the kinetic analysis.

The studies were conducted in both the 316 SS–sapphire cell and the Pt/Ir–diamond cell. Sapphire permits only the rate of conversion to CO_2 to be discerned. However, the absence of secondary and side reactions means that knowledge about the concentration of CO_2 enables the decarboxylation of malonic acid to be specified unambiguously. One problem remains: malonic acid is in equilibrium with the malonate ion(s). As a result, two sources of CO_2 exist, (i.e., decarboxylation of malonic acid and the malonate monoanion^{4,9}). Under the



Figure 2. First-order rate plots for decarboxylation of 1.07 m monosodium malonate.

TABLE 1: Rate Constants (1.07 m Solutions) under 275 bar^a

| | NaCO ₂ - | HCO ₂ CH ₂ CO ₂ H | | | |
|--|---|---|---|-----------------------------------|-----------------------------------|
| | CH ₂ CO ₂ H | SS-sapphire cell | | Pt/Ir-diamond cell | |
| °C | $10^{3}k_{1},$ s ⁻¹ | $10^{3}k_{1},$ s ⁻¹ | $10^{3}k_{2},$ s ⁻¹ | $10^{3}k_{1},$ s ⁻¹ | $10^{3}k_{2},$ s ⁻¹ |
| 120 140 160 170 180 190 200 210 220 230 | $13 27 55 \pm 7 114 \pm 62 242 \pm 76 611$ | $\begin{array}{c} 0.5 \\ 2.6 \\ 16 \\ 74 \pm 13 \\ 128 \pm 1 \\ 220 \pm 62 \\ 490 \pm 86 \end{array}$ | $\begin{array}{c} 0.515 \\ 4.17 \\ 22.3 \\ 110 \pm 25 \\ 243 \pm 1 \\ 377 \pm 111 \\ 703 \pm 250 \end{array}$ | 70 147 209 295 375 | 113 201 334 573 831 |

^a Rates without standard deviations are single measurements.

conditions of this study, the ionization constant of malonic acid and the rates of decarboxylation of the malonic acid and its monoanion are unknown. Therefore, the relative roles of these two species in producing CO_2 are not known. Hence, determination of this rate of decarboxylation of the monosodium malonate solution at hydrothermal conditions is essential to determining the kinetics of decarboxylation of malonic acid.

Monosodium Malonate. The malonate monoanion is in equilibrium with malonic acid and the malonate dianion. However, on the basis of an isocoulombic form of the equilibrium constant,¹⁵ the amount of diacid and dianion in a 1.07 *m* monosodium malonate solution is negligible within the uncertainty of our kinetic measurements (i.e., a % dianion range of $(1.7-1.1) \times 10^{-1}$ and a % diacid range of $(0.48-1.0) \times 10^{-2}$ assuming an ionic strength of 1) from 160 to 210 °C.^{16,17} Therefore, decarboxylation of the aqueous malonate monoanion is considered to be the single-step, first-order reaction shown in eq 1. In eq 1 the concentration (α) *m* of CO₂ is a simple

$$HOOCCH_2COO^{-} \xrightarrow{\kappa_1} CO_2 + CH_3COO^{-}$$
(1)

function of the concentration $(1.07 - \alpha) m$ of the monoanion. The area of $\nu_3(CO_2)$ was converted to concentration by using the external calibration results for aqueous CO_2 described earlier under the same pressure and temperature conditions.¹¹ Selected concentration-time data are plotted in Figure 2 as a first-order



Figure 3. Comparison of the experimental CO_2 concentrations (points) and the optimization of the rates in the model (lines) for eqs 1-3.

rate function at several temperatures. The slope of each line is the rate (k_1) for decarboxylation of the monoanion at that temperature. Although the difference in the ionic strength was not taken into account, the values of k_1 compiled in Table 1 are useful to complete the analysis of malonic acid. The uncertainty given for the values of k is the standard deviation based on multiple determinations.

Malonic Acid. The same measurements of the concentration of CO_2 were made on 1.07 *m* malonic acid as were made for monosodium malonate. In principle, according to eq 3, the

$$HOOCCH_2COOH \stackrel{k_f}{\underset{k_r}{\leftrightarrow}} HOOCCH_2COO^- + H^+ \qquad (2)$$

$$HOOCCH_2COOH \xrightarrow{k_2} CO_2 + CH_3COOH$$
(3)

$$HOOCCH_2COO^{-} \xrightarrow{k_1} CO_2 + CH_3COO^{-}$$
(1)

concentration of malonic acid can be obtained directly from the concentration (α) of CO₂. However, the equilibrium (eq 2) produces a small amount of the malonate monoanion which contributes to the concentration of CO_2 (eq 1) by the rate constant k_1 . Consequently, the best fit of the coupled differential rate equations for eqs 1-3 with the experimental data was achieved by minimizing the residuals with a multilevel, singlelinkage optimization routine. The optimization procedure took into account the estimation of the malonic acid concentration as well as k_1 for the malonate monoanion described above. Figure 3 shows the fit of the experimental concentration data at 190 °C with those predicted by the model. The resulting values of k_2 are tabulated in Table 1. The values of k_f and k_r are not reported because of their random behavior. However, their ratio was fairly constant and the calculated values of k_1 and k_2 were rather insensitive to k_f and k_r . Consistent with previous reports,^{4,7-9} the rate of decarboxylation of the malonate monoanion is observed to be slower than that of malonic acid. This finding may be explained by the existence of a cyclic transition state (shown below) for the decarboxylation reaction $(\Delta S^{\ddagger} = 1 \text{ eu at } 200 \text{ °C}).$



This transition state is statistically less favored for the monoanion. As a result, a lower A factor is expected and found (*vide infra*) for the monoanion ($\Delta S^{\ddagger} = -3$ eu at 200 °C). With regard



Figure 4. Arrhenius plots for the available experimental data for decarboxylation of monosodium malonate. Where no error bar is shown, the rate is based on a single measurement.



Figure 5. Arrhenius plots of the available experimental data for decarboxylation of malonic acid. Where no error bar is shown, the rate is based on a single measurement.

to the total carbon balance, it is noteworthy that the final CO_2 concentration in Figure 3 (1.05 *m*) is close to the initial concentration of malonic acid (1.07 *m*) as required by the stoichiometry of eqs 1-3.

Figures 4 and 5 are Arrhenius plots of the rate data in Table 1 for the monosodium malonate and malonic acid, respectively. Also shown are the Arrhenius data obtained previously^{7–9} for these compounds at lower temperature and pressure, in the batch mode, and by post-reaction analysis. It is not surprising that differences exist among all of these data. The rates measured by Hall⁹ at 80–90 °C can be roughly extrapolated to the hydrothermal regime of this study. Those of Bernoulli and Wege⁷ and Fairclough⁸ have similar activation energies, but the *A* factors are markedly different.

Although there is only anecdotal evidence from this study, it is interesting to find that the rate of formation of CO_2 in the 316 SS-sapphire cell is faster than in the Pt/Ir-diamond cell above about 140 °C. Figure 6 shows the Arrhenius plots obtained with these two cells. Wall effects and surface catalysis in these high surface-to-volume ratio reactors appear to have



Figure 6. Comparison of the Arrhenius parameters for decarboxylation of malonic acid in the 316 SS-sapphire cell and Pt/Ir-diamond cell.

some influence on the kinetics of hydrothermal decarboxylation of these dicarboxylic acids. At lower temperatures and pressures, the conditioning of a glass surface was found to affect the decarboxylation rate of malonic acid.⁷ Much stronger wall effects and catalysis appear to exist in monocarboxylic acids.^{5,18–20} At higher temperature, the rate of decarboxylation of acetic acid is faster on SS than on gold.²¹ In contrast, the decomposition rate of urea, for which the pH is higher than malonic acid, only minimally depends on whether the material of construction of the cell is SS or Pt/Ir alloy.¹⁰

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