

# Investigation of the Roles of Water in the Decarboxylation of Aromatic Carboxylic Acids in Supercritical Water

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## 1. Research Background

Supercritical water (SCW) is defined as water above its critical point (374 °C, 22.1 MPa). This medium has attracted much attention because of its many advantages over other solvents – it is nontoxic, abundant, and has tunable physical and transport properties.<sup>1,2</sup> By varying the temperature and pressure, many properties of water, e.g., density, dielectric constant, viscosity, ion product ( $K_w$ ), diffusion coefficient, substantially change. As a result, water plays different roles in hydrothermal reactions depending on the conditions.<sup>3</sup> If as a reactant or product, water can participate in elementary reaction steps. As a catalyst, it can act as an acid or base catalyst via self-dissociation or as a molecule that modifies and stabilizes transition states. It can also affect the kinetics of reactions through the changes in its intermolecular molecular interactions with solutes at near-critical to critical regions. As a medium, physical effects are observed even in the absence of intermolecular interactions.<sup>4</sup> By understanding these properties and the roles water play, reactions in SCW can be controlled to enhance conversion and selectivity.

One reaction where the roles of water could be studied is the decarboxylation reaction. Other than it is simple and straightforward, the behavior of aromatic carboxylic acids in high-temperature water (HTW) is significant in at least three different areas: in plastics and fiber industries, in fuel processing, and in waste treatment.<sup>5</sup> It is therefore unsurprising that decarboxylation in aqueous conditions has been studied extensively, including kinetic, mechanistic, and stability studies, among others. From previous studies, it was found that the unsubstituted benzoic acid was the least reactive among substituted ones, and as various substituents are added, its reactivity is enhanced.<sup>5,6</sup> Computational simulations of the mechanism of benzoic acid decarboxylation and its derivatives showed how water interacts with the carboxylic acid portion to form a transition state through which the activation energy of the reaction is lowered, and consequently facilitates  $-COOH$  removal.<sup>3,7</sup> Based on these calculations, it could be said that water acts as a catalyst. However, not enough data is present to support this. Moreover, other possible roles of water have not been explored yet. Thus, in light of the aforementioned research results, an explanation of how water interacts with the carboxylic portion still needs to be understood to be able to predict experimental results and make generalized conclusions.

Among the properties of water, density seems to have a greater effect in hydrothermal reactions than others. In oxidation in SCW, decomposition rate of compounds such as CO, methanol, and phenol are functions of water density. Additionally, reactions such as hydrolysis, dehydration, and retro-aldol reactions are said to be affected by water density according to other numerous studies.<sup>8</sup> There have also been literatures mentioning the effect of density on decarboxylation reaction. Somewhere else, it has been concluded that as pressure is increased, which consequently increases density, the conversion of benzoic acid also increased.<sup>5,9</sup> Although it has been mentioned, an in-depth explanation as to why and how the increased density affects the reaction is not available. Thus, in this research, I focused on the effect of density and used it to deduce the roles of water in decarboxylation reactions.

## 2. Purpose of the study

The goal of this research is to identify the roles of water in the decarboxylation of aromatic acids by investigating the effect of density. Phthalic acid decarboxylation was used as the model reaction (Fig. 1). Specifically, the aim of this research are 1) to measure the conversion and yield of phthalic acid decarboxylation at different densities by varying the pressure, 2) to calculate the rate constant and to relate it to pressure, 3) to propose a numerical relationship between pressure and

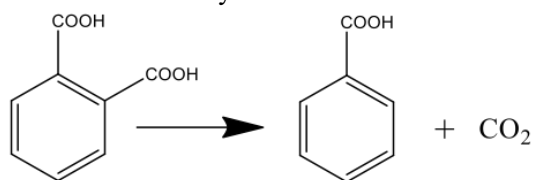


Fig.1. Decarboxylation of phthalic acid to benzoic acid and carbon dioxide.

reaction rate, and 4) to propose possible roles of water in the reaction based on conclusions derived from experimental data.

### 3. Research Plan

#### 3.1. Preliminary investigation

To examine the effect of density, the pressure of the system was varied to 20, 25, 30, 35 and 40 MPa at 400 °C and flow rate of 1 ml/min. At this temperature, density varies greatly. Conversion and yield were then plotted against density and pressure.

#### 3.2. Kinetic study

To be able to measure the effect of pressure to the rate of the reaction, the rate constants were calculated from first order rate plots. They were constructed by measuring the conversion of phthalic acid at 400 °C at varying residence times. The slope of the linear plot was taken as the rate constant for the given conditions. Flow rate was adjusted from 2 ml/min to 4 ml/min at 0.5-minute intervals.

### 4. Experimental Section

The reactor is made up of Hastelloy with internal diameters of 0.80 mm and outer diameter of 1/16 in. (Figure 2), and total reactor volume of about 0.7 ml. A GC oven was used to maintain the reactor at the desired temperature. Two HPLC pumps were used to inject the acid solution and the distilled water at a fixed flow rate. A pre-heater made of stainless steel was connected to the distilled water line to ascertain that the target temperature was achieved at the mixing point. Pressure was regulated using a back-pressure regulator. Cooling water was flowed in parallel with the reactor after the reactor part to quickly quench the reaction. The cooled sample was then collected in a vial. For analysis, HPLC-PDA was used for quantitative measurements while GC-MS for the confirmation of the identity of the contents of collected samples. No sample preps were performed prior to analysis.

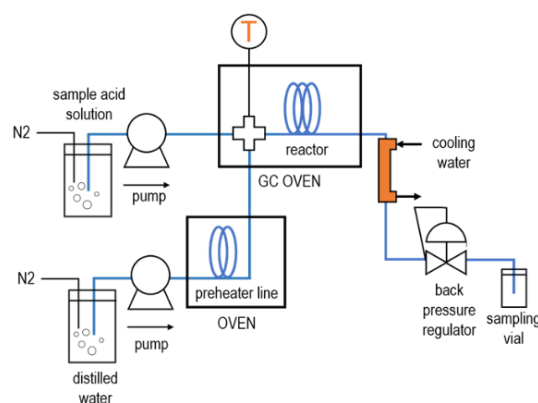


Fig. 2. Schematic diagram of the flow reactor.

### 5. Results

#### 5.1. Preliminary investigation

Figure 3 shows the results of the conversion and yield of phthalic acid decarboxylation. From these data, it can be seen that conversion and yield initially decreased from 20 to 25 MPa then started to slowly increase with pressure and density from 25 to 40 MPa. During this time, the residence time, along with pressure, also increases due to the changes in density. However, the conversion and yield did not follow suit. This result initially demonstrates a different effect of water at play that cannot be described using the assumption that water interacts with the transition state.

#### 5.2. Kinetic studies

Shown in Figure 4 is a representative graph of the conversion and yield of phthalic acid decarboxylation at 40 MPa. Most of the graphs show good agreement between the conversion and yield values, indicating that the reaction proceeded in a 1:1 stoichiometry and that there are no side products. A graph. The time

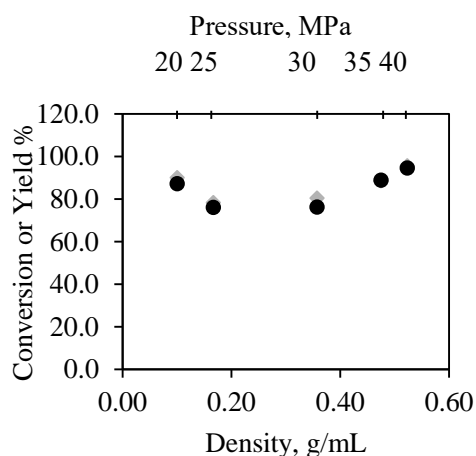


Fig. 3. Conversion of phthalic acid (circle) and yield of benzoic acid (triangle) at 400°C and flow rate of 1 ml/min.

profiles for each pressure were also used to obtain the rate order of the reaction. The conversion was expressed in terms of  $-\ln(1-x)$  where  $x$  is the conversion and plotted against residence time to obtain first-order plots. A sample graph is shown in Figure 5. The graphs showed great linear dependence and thus indicates that the reaction follows first order kinetics. The rate constants were obtained from the slope of the line. Figure 6 presents the rate constants for the decarboxylation of phthalic acid at different pressures. From the figure, it can be seen that there is a steep decrease from 20 to 25 MPa then slowly continues to decrease further from 25 to 40 MPa, clearly indicating that as pressure is increased, the rate decreases. Data for 35 MPa was not available due to instrumental errors. This trend supported the results from the preliminary investigation. As the mechanism approach cannot be used to explain the trend, a different one was considered in accounting the plausible effects of water on the observed pressure dependence.

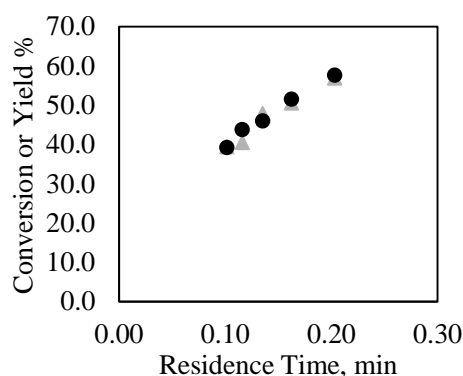
### 5.3. Solvation effects

Two perspectives were considered: by considering the dielectric constant, and by the activation volume. Both considers the differences in the polarity of the reactants, transition states, and the products and how they are affected by solvation. However, as we will see later, relating the rate to dielectric constant is more direct in this case.

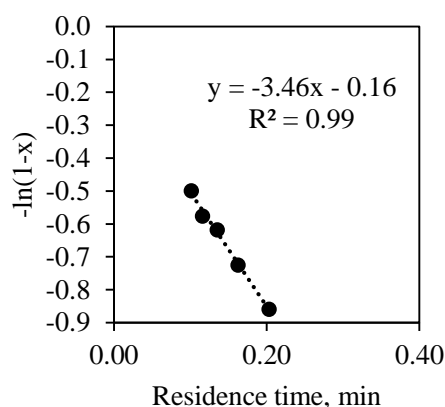
In supercritical water, the dielectric constant increases with pressure. For a nonionic reaction like decarboxylation, the changes in the dielectric constant and hydrogen bonding of water differs depending on the polarity between the reactant and the transition state. Much like an ionogenic reaction, the rate of a nonionic reaction increases with density when the transition state is more polar than the reactant(s)<sup>4</sup>. Considering the inverse relationship between rate and density seen in Figure 6, it could be presumed that the conversion of phthalic acid to benzoic acid passes through a transition state that is less polar than the reactant. For a more quantitative approach, Kirkwood's expression was employed. It expresses the free energy of transfer of a dipole moment of  $\mu$  from a medium having  $\epsilon = 1$  to a medium of dielectric constant,  $\epsilon$ ,

$$\Delta G_{tr}^0 = -\frac{\mu^2}{r^3} \left( \frac{\epsilon-1}{2\epsilon+1} \right) \text{ (Eqn. 1)}$$

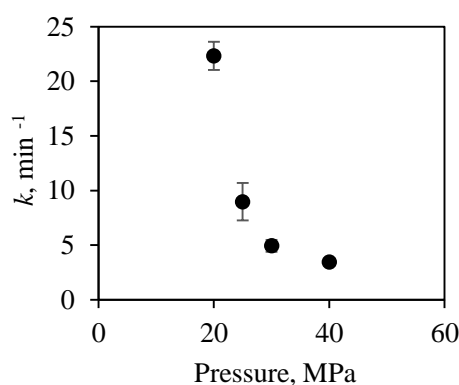
where  $r$  is the molecular radius. From the equation, a relationship between the rate constant and the solvent dielectric constant could be derived resulting to a linear equation.<sup>10</sup> Plotting the log  $k$  and  $(\epsilon -$



**Fig. 4.** Conversion of phthalic acid (circle) and yield of benzoic acid (triangle) at varying residence times at 40 MPa and 400°C.



**Fig. 5.** First order plots for rate of phthalic acid decarboxylation at 400 °C and 40 MPa.



**Fig. 6.** First order rate constants for phthalic acid decarboxylation as a function of pressure at 400 °C.

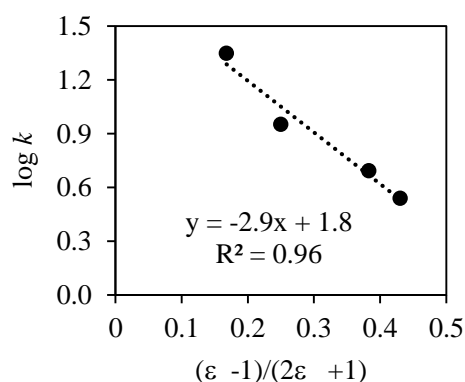
$1)/(2\epsilon + 1)$  using the rate constants from different pressures and the dielectric constants of SCW at different pressures at 400 °C, an inverse linear relationship was observed, i.e., as the dielectric constant increases, the rate decreases (Figure 7). Based on the initial assumption that an increase in solvent polarity will increase the rate when a more polar product is produced, it could be anticipated that the conversion from phthalic acid to benzoic acid resulted to a decrease in overall polarity, and an increase in solvent polarity in this reaction resulted to an opposite effect. This could be supported by examining the dielectric properties of the reactants, transition states, and products by performing molecular simulations and calculation. For the time being, it remains a topic in the future. Finally, since there is good agreement between the reaction rate and dielectric constant, it could be said that the role of water is mostly as a participant in the intermolecular interactions through solvation effects.

The other perspective is by relating the rate constant with the activation volume used by Fujii, et al.<sup>8</sup> This involves deriving an equation relating pressure and rate since there is no equation directly relating the two. Thus, comparatively, it is the more tedious approach considering, Fujii, et al.<sup>8</sup> who investigated the effect of pressure on formic acid decomposition at sub- and supercritical water, also arrived at the same conclusion. They also found out that pressure negatively affects the rate of the decomposition through solvation effects of water.<sup>8</sup>

## 6. Summary and Conclusion

In this study, the roles of the water in the decarboxylation of aromatic carboxylic acids in SCW were investigated. The density was varied by varying the reactor pressure at 400 °C. Kinetic studies showed a first-order kinetics for the reaction. The rate constants plotted against pressure showed that as the pressure and density is increased, the reaction rate decreased. The results were interpreted using the Kirkwood expression which revealed an inverse relationship between the rate constant and the dielectric constant. Thus, it was concluded that solvation effects of water were the dominant factor contributing to the rate changes in the decarboxylation of phthalic acid in SCW.

Finally, Fujii, et al.,<sup>8</sup> also studied the ionic effects in the reaction which revealed that SCW positively affects the reaction at higher pressures. Thus, as a recommendation, ionic effects could also be investigated for this reaction to explore the effect of water as an acid- and base-catalyst varying the pH of the system.



**Fig. 7.** Log of the rate constant of the decarboxylation of phthalic acid at varying pressures at 400 °C versus the Kirkwood dielectric function.

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