Effects of Water in the Decarboxylation of Aromatic Carboxylic Acids in Supercritical Water

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Abstract

Supercritical water (SCW), due to its ability to dissolve organics and tunable properties, has been considered to have a great potential as a substitute for toxic organic solvents. To clarify its roles in hydrothermal reactions, the effect of water on reactions was investigated. In this research, decarboxylation reaction, a ubiquitous reaction both in degradation and synthesis, in SCW was examined. Water density was varied to investigate the effect of the changed properties of water to the reaction. Phthalic acid decarboxylation was used as a model.

Kinetic studies at 400 °C and pressures of 25 MPa to 40 MPa revealed that the reaction is in first-order. The resulting rate constants were plotted against pressure and revealed a decrease in rate when pressure was increased. Kirkwood's expression was employed to investigate a possible relationship between the rate and solvent dielectric constant which varies with pressure. Plotting the log k and the Kirkwood dielectric function, $(\varepsilon - 1)/(2\varepsilon + 1)$, showed good linear dependence suggesting that solvation effect is dominating the kinetics of the reaction in the given conditions.

Keywords

Supercritical water, Decarboxylation, Effect of Water

1. Introduction

Supercritical water is defined as water above its critical point (374 °C, 22.1 MPa). Because of its ability to dissolve organic, in addition to almost zero toxicity, it has been deemed as a feasible alternative to toxic organic solvents used in organic synthesis. In addition, by merely changing the temperature and pressure, its properties could be finely tuned. This has also resulted to numerous studies about using only one solvent to play the role of a

reactant/product, a catalyst, or a reaction medium, depending on the conditions.[1]–[4] In fact, several classes of organic reactions have already been conducted in subCW/SCW, including total oxidations, eliminations, condensations, additions, redox reactions, and so on.

One reaction where the effects of water have been investigated is the decarboxylation reaction. Compared to other reactions, decarboxylation reactions are straightforward, involve only a few products which make analyses easier (as there are possibly fewer side products to deal with), and has almost no side reactions; therefore, it is easier to isolate the effect of water on the reaction and exclude other possible contributing factors. Moreover, the behavior of aromatic carboxylic acids in sub- and supercritical water is important both synthesis and decomposition reactions. Its significance is found in at least three different areas: in plastics and fiber industries, in fuel processing, and in waste treatment.[5]

Kinetic, mechanistic, and stability studies of decarboxylation reactions in aqueous media are several, but research gaps and discrepancies still exist. For example, computational simulations of the mechanism of benzoic acid decarboxylation and its derivatives illustrated 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.[6], [7]   Based on these calculations, it could be said that water acts as a catalyst. However, sufficient experimental data is still needed to confirm this. On the other hand, in a study performed by Fuji, et al., experimental results showed that near the critical pressure, the rates of formic acid decarboxylation decreased with increasing pressure. They also concluded that solvation effect is dominating in the near critical state.[8] Pressure is related with density, and it could be said that with increasing pressure, and consequently density, the effect of water would also increase. Unfortunately, the effect of pressure and density, which affects many SCW reactions[8], has only been minimally discussed and demonstrated experimentally in previous literatures.

In this research, the effect of water in the decarboxylation is further investigated. Decarboxylation of phthalic acid at varying densities is used as a model.

2. Experimental

2.1. Materials and Flow Reactor

For the preparation of the phthalic acid (purchased from Kanto Chemical Co., Inc.) solution, the weighed amount was dissolved in heated water (about 60 ºC) to aid dissolution. HPLC analysis of the prepared solution showed no signs of decomposition at this temperature. The distilled water used for all experiments was purified using an Aquarius (manufactured by RFD240 HAADVANTEC) distillation apparatus.   Prior to injection to the reactor, the acid solution and distilled water were degassed by bubbling with N_2 gas. Fig. 1 shows the flow

reactor diagram. The reactor is roughly divided into 3 parts: a raw material supply part, a preheating and reaction part, and a cooling / recovery part. For the reaction part, a 1/16 inch and 0.8 mm (outer and inner diameters, respectively) Hastelloy reactor was used for its good oxidation resistance, high-temperature strength, and exceptional stress-corrosion resistance. The total volume was about 0.78 mL. Other tubing parts were made from stainless steel.

2.2. Experimental Procedure

A flow reactor (specified in Section 2.1) was used to conduct decarboxylation in SCW. The two HPLC pumps injected the 0.02 M acid solution and the distilled water at a fixed flow rate (1:9 acid : water ratio). The flow rate was regularly checked throughout the progress of the experiment. The reactor was saturated for one hour, after which, few milliliters of unreacted samples were collected. The temperatures of preheater ovens (represented by OVEN in the diagram) were set such that the distilled water was sufficiently preheated to ensure that the target temperature (400 °C) was achieved at the mixing point. The oven (GC OVEN in Fig. 1) for the reactor was set so that the mixing point and the reactor was maintained at 400 °C. All temperatures were monitored using thermocouples. Pressures of 20, 25, 30, and 40 MPa were regulated using a back-pressure regulator. Once the reaction temperature was reached, 3 times of the residence time was elapsed before collecting samples at the outlet. The temperature and pressure were periodically checked to ascertain that they were constant. The temperature and pressure were kept within ± 1-2 °C and ± 0.5-1 MPa, respectively. Cooling water was flowed in parallel to the part after the reactor to quickly quench the reaction. The cooled effluent was then collected in a vial. HPLC-PDA (JASCO Corp.) was used to measure concentrations of phthalic acid and benzoic acid in solution while GC-MS (Shimadzu Corp.) for the confirmation of the identity of the contents of collected samples.
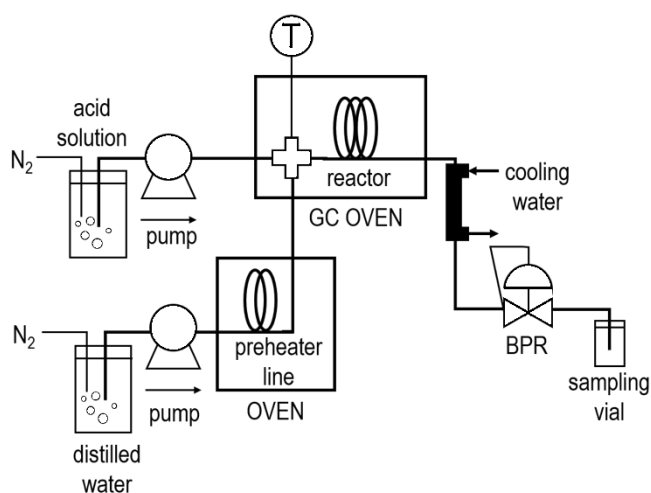

Fig. 1. Schematic diagram of the reactor.

3. Results and Discussion

Kinetic studies revealed that phthalic acid decarboxylation is in first order at 400°C from 20 to 40 MPa. Fig. 2 presents the rate constants for the decarboxylation of phthalic acid at different pressures.
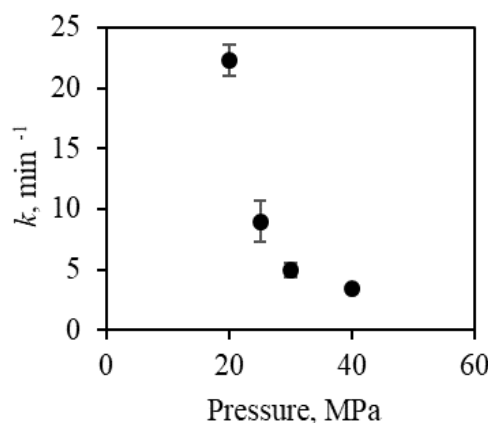

Fig. 2. First order rate constants for phthalic acid decarboxylation as a function of pressure at 400 ºC.

A steep decrease from 20 to 25 MPa was observed, then continued to slowly decrease from 25 to 40 MPa, indicating that as pressure is increased, the rate decreased. Previous research reported that gas-phase decarboxylation has a higher activation energy than the water-assisted reaction.[6], [9], [10] This is also supported by studies simulating water participating in the transition state of the reaction. [4], [7], [9], [11] The results suggest that water could be acting as a catalyst in decarboxylation. In contrast, the results of this experiment show that increasing the density of water resulted to a decreased rate, suggesting a different effect of water at play in the given conditions. In other papers[2]–[4], [8] it has been suggested that preferential solvation occurs in hydrothermal reactions, depending on the conditions. With the dielectric constant varying with temperature in sub- and supercritical state, the solvation of the reaction species could be affected throughout the progress of the reaction. The rate increases with density when the transition state is more polar than the reactant(s).[2] In this research, Kirkwood's equation was employed to relate the dielectric constant of SCW at different densities to the reaction rate. Plotting the log k and the Kirkwood dielectric function, $(\varepsilon - 1)/(2\varepsilon + 1)$ using the rate constants from different pressures and the dielectric constants, ε, of SCW at different pressures at 400 ºC, showed good linear dependence (Fig.3) suggesting that solvation effects are governing the kinetics of the reaction. More detailed explanations of solvation effects are

present in previous literature; this worked focused on demonstrating this effect empirically. These results may serve as a lead on using density to control and optimizing reactions in SCW, especially if suppressing or accelerating reaction rates is needed in a process. Moreover, although the focus of this research is on decarboxylation, using density by varying the pressure to study the effect of water may also be employed to shed more light on the mechanisms of reactions in SCW.
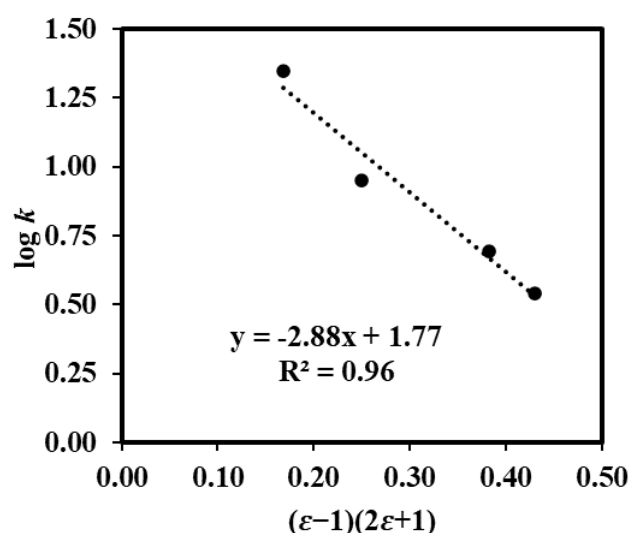

Fig. 3. Log of the rate constant of the decarboxylation of phthalic acid at varying pressures at 400 ºC versus the Kirkwood dielectric function.

6. Conclusion

The study investigated the effect of water in the decarboxylation of aromatic carboxylic acids in SCW by varying water density. The conversion and yield of phthalic acid decarboxylation at different densities were calculated and analyzed. The rate constants for each pressure were obtained and plotted against pressure. The relationship obtained was that as pressure and density is increased, the rate constant, and consequently, the rate, decreased.   The relationship was interpreted using Kirkwood's equation. Good linear dependence between the dielectric constant and rate suggested solvation effects dominate the reaction kinetics in the given conditions. In conclusion, the effect of water was successfully investigated in the given conditions (400 °C, 25-40 MPa). As these conditions is limited, it is recommended to extend the research at different conditions such as in different pH or in higher pressures.

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