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Effects of Water in the Decarboxylation of Aromatic Carboxylic Acids in Supercritical Water
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Abstract (less than 300 words)
<p>Organic solvents, although indispensable in organic syntheses and chromatography, are mostly toxic to the environment, urging the search for greener alternatives. Supercritical water (SCW), able to dissolve many organic compounds, has become a popular candidate. However, despite the decades-long investigation of SCW, there is still lacking information about the processes occurring in SCW, thereby limiting its applications. In this research, decarboxylation reaction, a ubiquitous reaction both in degradation and synthesis, was investigated to study the effects of water. Utilizing a flow reactor, water density was varied by changing the pressure, which simultaneously affects other water properties. Phthalic acid decarboxylation was chosen as the model reaction due to its ease of dissolution and higher reactivity compared to other carboxylic acid derivatives.</p> <p>Kinetic studies revealed that the reaction is in first-order. The resulting rate constants were plotted against pressure, which revealed a rather half-parabolic decrease in rate when pressure was increased. In an attempt to explain the trend, solvation effects were considered. For a nonionic reaction like decarboxylation, the rate increases with density when the transition state is more polar than the reactant(s).[1] The observed inverse relationship between rate and density suggests that the conversion of phthalic acid to benzoic acid passes through a transition state that is less polar than the reactant. Kirkwood's expression was employed to investigate a possible relationship between the rate and solvent dielectric constant which varies with density. Plotting the $\log k$ and the Kirkwood dielectric function, $(\epsilon - 1)/(2\epsilon + 1)$ using the rate constants and literature values of the dielectric constants, ϵ, of SCW at different pressures at 400 °C, an inverse relationship was observed. Good linear dependence between the two constants was observed, supporting the conclusion that the effect of water is through solvation.</p>
References
[1] N. Akiya, & PE Savage, ChemRev., 102, (2002) 2725 – 2750.

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