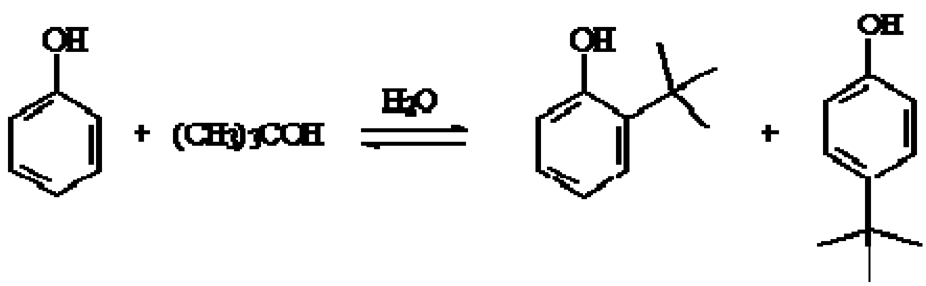
Reactions and Phase Equilibria in Near-critical Water (NCW)

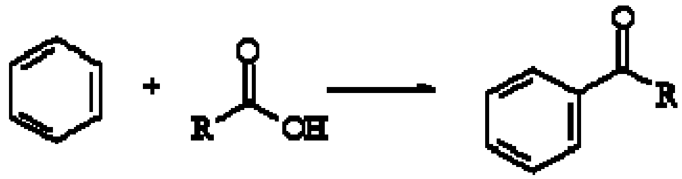
Liquid water in the temperature range of 250 to 350 °C (subsequently referred to as near-critical water) is an environmentally-benign solvent that offers tremendous opportunities for pollution prevention for a wide variety of manufacturing processes in the chemical, petrochemical, pharmaceutical, and plastics industries. NCW has a density and dielectric constant (see Figure 1) similar to that of ambient acetone, permitting the dissolution and reaction of both organic and ionic species, as well as the swelling of polymers. Unlike supercritical water, which is used for complete oxidation (usually >400 °C), the more moderate temperatures permit a wider range of useful reactions. Finally, NCW has an ionization constant (See Figure 2) which is three orders of magnitude greater than water at ambient temperatures and pressures. This latter property should facilitate promotion of acid- and base-catalyzed reactions in the absence of added mineral acids and bases.

Advantages of working in NCW are that much better solubility is available than compared to ambient liquid water, and far better control of reactions is possible at the lower temperatures as compared to supercritical conditions. The properties of ambient water are due largely to hydrogen bonding, which causes water to support ionization of salts and to be a poor solvent for nonpolar organic substances. However, because hydrogen bonding is exothermic, the equilibrium constant decreases with increasing temperature and the dielectric constant drops off dramatically from ambient temperature to supercritical conditions. Therefore, organics are much more soluble in supercritical water but there is essentially no ionizing power and salts drop out of solution. However, NCW has a dielectric constant which is greatly reduced from that of ambient water, but it still possesses a degree of ionizing potential. Thus many of the benefits of working in supercritical water are available in NCW as well, but with many additional advantages. Polar organics of any sort are completely miscible, and even hydrocarbons dissolve to a large degree (see figure 3). Note that n-heptane is five orders of magnitude more soluble in water at 350 °C than at 25 °C. Moreover, separation after reaction becomes very easy; simply lowering the temperature raises the dielectric constant enough to render organics insoluble, and products can be simply decanted.

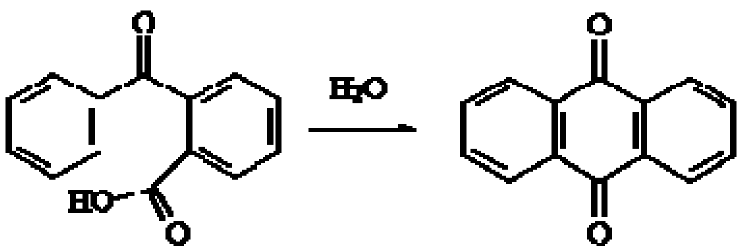
Aliphatic alcohols react with benzene in the presence of acid catalysts to form alkylbenzenes. We successfully alkylated phenol with t-butyl alcohol to produce sterically hindered phenols at 275 °C, with no added acid catalyst. The native acidity of the near-critical water (plus the phenol) was sufficient.



Also, acid chlorides, acid anhydrides, and carboxylic acids react with Lewis acids such as aluminum chloride, ferric chloride, zinc chloride, and strong protic organic acids in the presence of benzene and substituted benzenes to produce arylalkyl ketones.



A serious problem in employing Friedel-Crafts acylation reaction on an industrial scale is the necessity for the use of a stoichiometric quantity or even 2-3 times the stoichiometric amount of the acid. This, of course, results in large quantities of salt byproduct after neutralization. We have used NCW for the promotion of the acylation process, where the high temperatures and the enhanced acidity of the solvent facilitate the process. Specifically, we have run the cyclization (Friedel-Crafts acylation) reaction of o-benzoylbenzoic acid to form anthraquinone, a valuable catalyst in bleaching pulp and paper, at 275 °C successfully with only traces of acid catalyst.



We have preliminary results that indicate other acylation reactions proceed in NCW with no added acid.

An essential part of this project is a knowledge of the phase equilibria in NCW systems. In this regard, we have developed windowed vessels and techniques to observe and measure phase equilibria in aqueous-organic systems of interest. In addition to taking pertinent data for systems of interest, we are developing equations of state to characterize and extend our results.

As a result of these investigations, new processes will be available using "green chemistry" for sustainable development. NCW will

- Replace many less desirable solvents, such as aromatic hydrocarbons and chlorinated compounds
- Avoid the use of polluting mineral acids and hazardous catalysts
- Permit the minimization or even the elimination of unwanted byproducts
- Provide better control of reactions which can be run homogeneously instead of heterogeneously
- Facilitate closed processes by reuse of waste material
- Provide simple separation after reaction

Recent Publications

Chandler, K.; Liotta, C. L.; Eckert, C. A.; Schiraldi, D. "Tuning Alkylation Reactions with Temperature in Near-Critical Water." *AIChE Journal* **1998**, *44*, 2080-2087.

Chandler, K.; Deng, F.; Dillow, A. K.; Liotta, C. L.; Eckert, C. A. "Alkylation Reactions in Near-Critical Water in the Absence of Acid Catalysts." *Industrial & Engineering Chemistry Research* **1997**, *36*, 5175-5179.

Eckert, C. A.; Chandler, K. "Tuning Fluid Solvents for Chemical Reactions." *The Journal of Supercritical Fluids* **1998**, *13*, 187-195.