Tuning Alkylation Reactions with Temperature in Near-Critical Water

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Quantitative kinetics for the alkylation reactions of phenol and p-cresol with tert-butyl alcohol in near-critical water as a function of temperature are reported. The reaction products of the alkylation reactions were ortho- and para-substituted phenols, which are used extensively as antioxidants in numerous polymer systems. A new experimental reaction apparatus was designed, constructed, and successfully operated to allow pressure control and sampling of the reaction systems, which provided rate constants in the temperature range 250 – 300°C. Additionally, activation energies and heats of formation were calculated from the temperature dependence of the rate constants, and ortho-substitution was found to be exothermic whereas para-substitution was found to be endothermic. These results demonstrate that product distribution of the alkylation reactions could be tuned with temperature to produce specific products.

Introduction

The low cost and environmentally benign nature of water are incentives for using water as an alternative to organic solvents for a wide variety of organic reactions. Chemical processing is possible in water because of the favorable changes that occur in the chemical and physical properties at high temperatures and pressures. The dielectric constant of water gradually decreases from a value of 80 at ambient conditions to approximately 5 at the critical point (Uematsu and Franck, 1980), and this decrease is paralleled by an increase in the solubility of organic compounds. In the near-critical region (250–350°C), the dielectric constant can be adjusted to dissolve effectively both nonpolar and polar compounds (Connolly, 1966; Shaw et al., 1991; Gao, 1993). Near-critical water also has a strong tendency to ionize, and thus is a source of hydronium and hydroxide ions than water at ambient conditions. The dissociation constant increases by more than three orders of magnitude when going from ambient to near-critical conditions (Marshall and Franck, 1981), which allows water in the near-critical region to promote acid- and base-catalyzed reactions that do not occur readily at ambient temperatures (Kuhlmann et al., 1994; Katritzky et al., 1996).

The unique properties of water at high temperatures were first exploited for toxic waste detoxification using supercritical water as the processing medium for oxidation (Modell et al., 1982; Thomason and Modell, 1984). Since these initial investigations, numerous studies have reported oxidation reactions of a wide variety of organic compounds in supercritical water with efficiencies often greater than 99.99%, and several comprehensive reviews of these investigations have been published (Subramaniam and McHugh, 1986; Shaw et al., 1991; Savage et al., 1994).

Although oxidation reactions have received the most attention, supercritical water has also been used as a reaction solvent for fuels processing and conversion of biomass, and these areas were included in the recent review of reactions at supercritical conditions by Savage et al. (1994). Near-critical water can support a much wider variety of reactions than is possible at supercritical temperatures, because the milder reaction conditions permit synthesis as well as decomposition reactions. Much of the work reported in near-critical water has still focused on oxidation reactions, fuels processing, and conversion of biomass, but other work has also included or-

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ganic syntheses (Kuhlmann et al., 1994; Bagnell et al., 1996; Katritzky et al., 1996; Parsons, 1996; Holliday et al., 1997; Xu et al., 1997).

In this investigation, the solubilizing properties and high hydronium ion content of near-critical water were exploited to carry out typically acid-catalyzed Friedel-Crafts alkylation reactions in the absence of added acid catalysts to produce a variety of sterically hindered phenols. The advantages of synthesizing the sterically hindered phenols in near-critical water include replacement of environmentally undesirable organic solvents, replacement of environmentally undesirable acid catalysts, possible reduction of unwanted byproducts, and easier recycling of used materials. Additionally, by eliminating the acid catalysts, the need for base neutralization, catalyst regeneration, and disposal of salt byproducts is eliminated.

The qualitative feasibility of carrying out alkylation reactions of phenol and *p*-cresol with tertiary, secondary and primary alcohols has been studied previously in near-critical water at 275°C in the absence of added acid catalysts (Chandler et al., 1997); here, we report the quantitative kinetics for the reactions of phenol and *p*-cresol with *tert*-butyl alcohol. A new experimental reaction apparatus was designed, constructed, and successfully operated to allow the accurate determination and control of the reaction pressure, and to ensure only one liquid phase was present during the reaction. The new reaction apparatus also allowed the system to be sampled as a function of time, which provided reaction kinetics as well as product distribution information. The alkylations of phenol and *p*-cresol were carried out in the temperature range 250–300°C, and the data provide insight on how reaction conditions might be tuned to produce specific products, such as sterically hindered phenols.

Commercial Importance of Alkylation Reactions

Alkylation reactions of phenol and cresol with *tert*-butyl alcohol provide simple, model reactions to investigate Friedel-Crafts alkylation chemistry in near-critical water, but the products, sterically hindered phenols, are also of great commercial importance. Hindered phenols are used extensively as antioxidants during fabrication, storage, processing, and end-use of many polymer systems (Pospisil, 1988). Polymer degradation often takes place in the presence of oxygen, and, therefore, oxidation reactions are the most significant means of structural breakdown of many polymer systems. Heat and light initiate the generation of free radicals during polymer degradation, and these free radicals react with atmospheric oxygen to produce peroxy radicals ROO·. The peroxy radicals are very reactive and will abstract hydrogen atoms from the organic substrate forming new free radicals. Since new free radicals are generated by each reaction step, more oxygen is incorporated into the system and a chain reaction proceeds (Ranney, 1979).

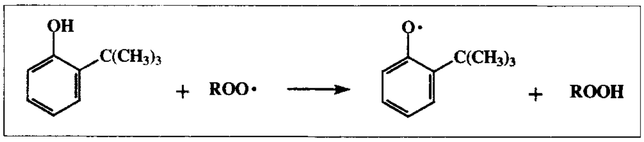

Figure 1. Antioxidant mechanism of sterically hindered phenols (Ranney, 1979).

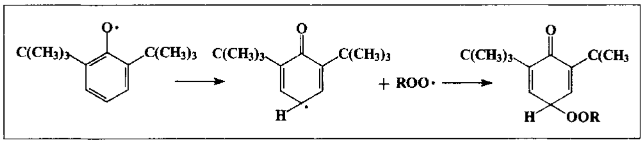

Figure 2. Reaction of phenoxy radical from antioxidant mechanism with a second free radical (Ranney, 1979).

Sterically hindered phenols act as free-radical scavengers and are used to inhibit oxidation of many polymers, including polyolefins, styrenes, and vinyls (Murphy, 1996). A sterically hindered phenol reacts with a peroxy radical by donating a hydrogen atom to the peroxy radical to form a nonradical substrate and a phenoxy radical, as shown in Figure 1. If the antioxidant is well stabilized, or sterically hindered from reacting further by bulky substituents in the ortho positions, it will not act as an initiator for further reactions. Depending on the stability, the hindered phenol might even react with a second free radical as shown in Figure 2 (Ranney, 1979).

The effectiveness of hindered phenols as antioxidants not only depends on stability but also on the ability of the phenols to interact with the peroxy radicals. Thus, electron withdrawing groups reduce the interactions when present as substituents on the aromatic ring, whereas electron donating groups, such as methyl and *tert*-butyl groups, activate the hydroxyl group and increase efficiency (Chirinos-Padron and Allen, 1992). Because of both stability and activity, a simple compound that is used extensively as an antioxidant is 2,6-di-*tert*-butyl-4-methylphenol, which is commonly known as butylated hydroxytoluene (BHT) (Murphy, 1996). This compound, which is shown in Figure 3, is very stable because of the bulky *tert*-butyl groups in the ortho positions and is activated by the methyl group in the para position.

Experimental Methods

Materials

HPLC Grade water was obtained from Aldrich Chemical Company, and nitrogen (High Purity Grade) used to deoxygenate the water was obtained from Air Products. The reactants, phenol (99+%, ACS Reagent), *p*-cresol (99%), and *tert*-butyl alcohol (99.5%, HPLC Grade), were obtained from Aldrich Chemical Company and were used without further

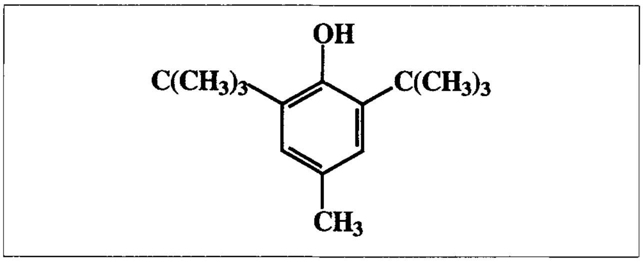

Figure 3. 2,6-di-*tert*-butyl-4-methylphenol or butylated hydroxytoluene (BHT).

purification. Methanol (99.9+%, HPLC Grade) and the calibration standard, benzoic acid (99+%, ACS Reagent), were also obtained from Aldrich Chemical Company.

Experimental procedure

Figure 4 shows the near-critical water reaction apparatus. The batch reaction vessel was a commercially available sample cylinder (Whitey Company) constructed of 316 stainless steel with a pressure rating of 340 bar at elevated temperatures. The cell had an internal volume of 300 mL and was heated in an aluminum heating block. The temperature of the heating block was controlled to within ±1°C of the reaction temperature (250–300°C) using three heavy insulated heating tapes (Omega Engineering, Inc.), which were suitable for direct contact with conductive surfaces, and a temperature controller (Omega Engineering, Inc., Model CN9000A). Unless otherwise noted, all fluid transfer lines were 316 stainless steel with an outside diameter of 1.59 mm and an internal diameter of 0.762 mm.

One end of the reactor was connected to a digital pressure transducer (Heise, Model 901B), which was used to monitor constantly the system pressure to within ±0.3 bar. A pressure relief valve was connected to this line. Also, this end of the cell was connected to a high-pressure syringe pump (Isco, Inc., Model 260D) that was filled with deoxygenated water. The other end of the cell was used to sample the reaction system. Small internal diameter tubing (0.508 mm), which extended approximately 2 cm into the reactor, was used as the sample-withdrawal port.

The experimental procedure was similar to the procedure used previously with the smaller batch reactors and heating block (Chandler et al., 1997) with a few important improvements. The batch reactor used in this investigation was 300 mL, which was scaled up 100 times from the small reactors used previously (3 mL). Therefore, the reactor volume was very large compared to the required sample size and the reactor could be sampled as a function of time to provide reaction kinetics. Additionally, the larger reactor volume allowed the pressure to be monitored and controlled during the reactions, because the reactor volume was large compared to the pressure transducer volume. Thus, reactions could be carried out at various temperatures while the pressure was held constant.

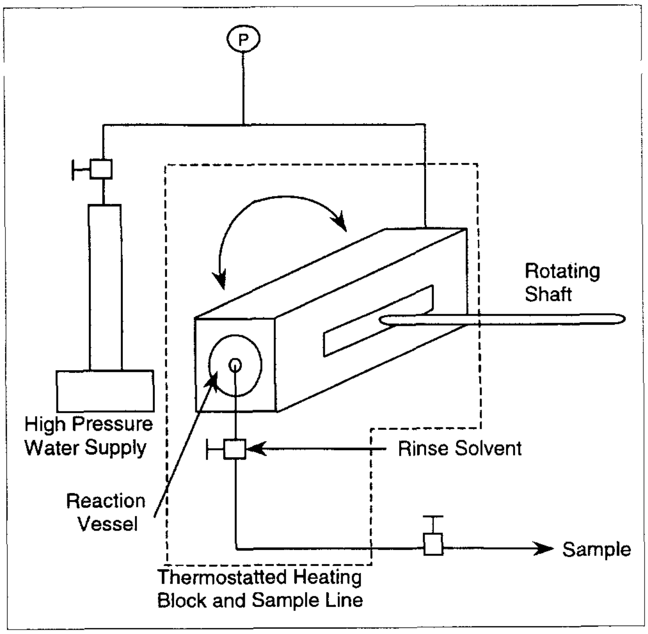

Figure 4. Near-critical water reaction apparatus.

The new reactor design also allowed agitation of the reactor vessel. The aluminum heating block was attached to a free rotating shaft, which allowed the reaction vessel to be rotated lengthwise 180°, and small stainless steel balls were used in the reactor to facilitate mixing. The shaft could be attached through a series of arms to a motor which provided continuous mixing at a rate of approximately 60 rpm. However, the reactions studied in this investigation proceeded very slowly over several days and were carried out in a single liquid phase, and, thus, the effects of diffusional limitations were assumed to be negligible. Therefore, the runs reported in this investigation were agitated only periodically because fatigue of the fluid transfer line leading to the pressure transducer was a safety concern for the long times required for these reactions. To verify the assumption that diffusional limitations were negligible, the reaction of phenol with *tert*-butyl alcohol was carried out at 275°C with constant agitation for 48 h, and the results were within the experimental error of the runs carried out with only periodic agitation at the same reaction conditions.

In each run, 10 g (approximately 0.1 mol) of the limiting reactant, either phenol or *p*-cresol, was introduced into the reactor. Using the same apparatus described above, the solubility limit of phenol and *p*-cresol at the reaction conditions was determined to be well above the concentrations used in these reactions (Chandler et al., 1997). A 3-to-1 molar ratio of *tert*-butyl alcohol was also added to the limiting reactant. Approximately 150 mL of water was then added to the reactor leaving enough headspace for thermal expansion on heating. To ensure that no oxygen was present during the reactions, the water was first deoxygenated with nitrogen for at least 1 h before it was added to the reactor, and the headspace in the reactor was replaced with nitrogen. No significant wall effects have been observed in near-critical water when the stainless steel reactors were not new reactors (Torry et al., 1992; Kuhlmann et al., 1994), and all of the stainless steel reactors used in this investigation had been used previously.

In each run, the reactor was heated to the desired reaction temperature (250–300°C) and water was added to the reactor with the high-pressure syringe pump to bring the reaction pressure to 172 bar. Because the near-critical water was essentially incompressible, the pressure control was no better than ±4 bar. The pressure was held constant for each of the three temperatures and was above the vapor pressure of the reaction system at all three temperatures so that only one liquid phase was present. Approximately 1 h was required for the system to reach the desired reaction temperature and pressure.

At a given reaction time, three samples were removed from the system. For each set of samples, the sample loop was flushed with approximately three volumes of reaction fluid to ensure representative samples were obtained. Each sample was collected in a 250 μL sample loop (Valco Instruments

Co. Inc.), and the samples were depressurized into 5 mL of cold methanol. The sample lines were rinsed with an additional 5 mL of methanol to ensure all of the reaction products were collected in each sample. The pressure drop of the system with each sample was approximately 3 bar and water was added from the high-pressure syringe pump to maintain a constant reaction pressure.

Sample analysis

Initially, the reaction products were analyzed by gas chromatography (GC) and mass spectroscopy (MS). Once each reaction product had been identified from the mass spectral fragmentation pattern, the possible isomers were purchased from Aldrich Chemical Company with a stated purity of 98% or higher. Routine analysis was performed using GC (Varian Associates, Model 3400) with a flame ionization detector (FID) by matching the retention times of the reaction products to the retention times of the known compounds using a 15 m×0.53 mm DB-17 column with a 1.0 μm film thickness (J&W Scientific Inc.). The methanol solvent used to collect each sample contained a known amount of benzoic acid as a calibration standard. The reaction products to benzoic acid mass ratios for a given sample were calculated from the resulting GC area ratios by comparison to previously prepared calibration curves. All product yields are given as mol. % of starting limiting reactant (phenol or *p*-cresol).

Results and Discussion

Alkylation reactions of phenol

The reaction of phenol with *tert*-butyl alcohol (Figure 5) was carried out in the absence of added acid catalysts at 250, 275, and 300°C, and the mole fraction product yields are shown as a function of time for each temperature in Figures 6 through 8. The error bars shown in all of the figures represent the 95% confidence intervals of the average of three samples. The alkylation of phenol with *tert*-butyl alcohol produced two major products, 2-*tert*-butylphenol and 4-*tert*-butylphenol. Also, a small amount ($\leq 2\%$) of the disubstituted product, 2,4-di-*tert*-butylphenol, was formed. The major products, 2-*tert*-butylphenol and 4-*tert*-butylphenol, produced phenol when subjected to near-critical water at 275°C indicating that the reaction was reversible.

The reaction kinetics were described using a simple reaction network involving two reversible, first-order reactions. Xu et al. (1997) reported that under neutral conditions in water in the temperature range of 225–320°C *tert*-butyl alcohol undergoes rapid dehydration to form isobutylene. Thus, the reaction mechanism would involve this dehydration reaction. However, because the *tert*-butyl alcohol was present in large excess, the reaction of phenol to form both 2-*tert*-butylphenol and 4-*tert*-butylphenol was assumed to be pseudo-first-order in phenol. Additionally, 2-4-di-*tert*-butylphenol was produced in very low concentrations and was not included in the proposed reaction network. Figure 9 shows the model reaction network, where k_1 was defined as the pseudo-first-order rate constant of the reaction of phenol to form 2-*tert*-butylphenol and k_{-1} was the pseudo-first-order rate constant of the reverse reaction. Likewise, k_2 was defined as the pseudo-first-order rate constant of the reaction of phenol to form 4-*tert*-butylphenol and k_{-2} was the pseudo-first-order rate constant of the reverse reaction.

Kinetic analysis was used to summarize the experimental data in terms of the four pseudo-first-order rate constants,

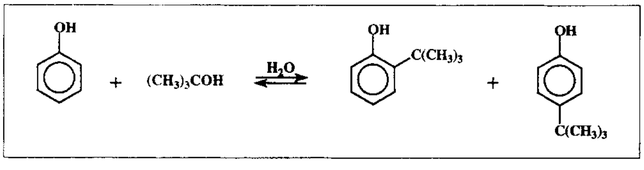

Figure 5. Reaction of phenol with *tert*-butyl alcohol in near-critical water.

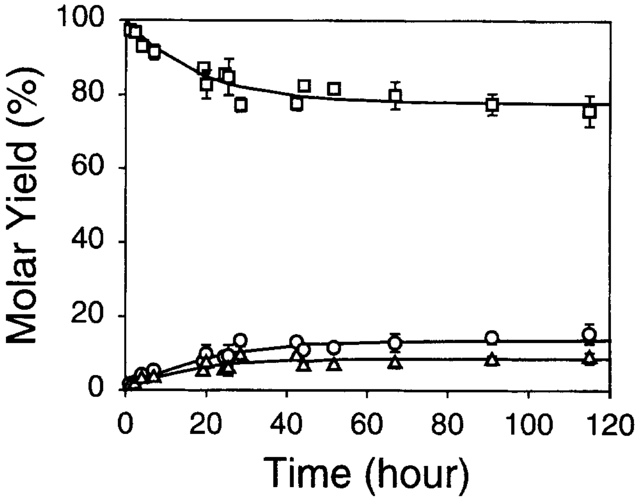

Figure 6. Mole fraction product yields as a function of time for the reaction of phenol with *tert*-butyl alcohol in water at 250°C and 172 bar.

(□) Phenol; (○) 2-*tert*-butylphenol; (△) 4-*tert*-butylphenol.

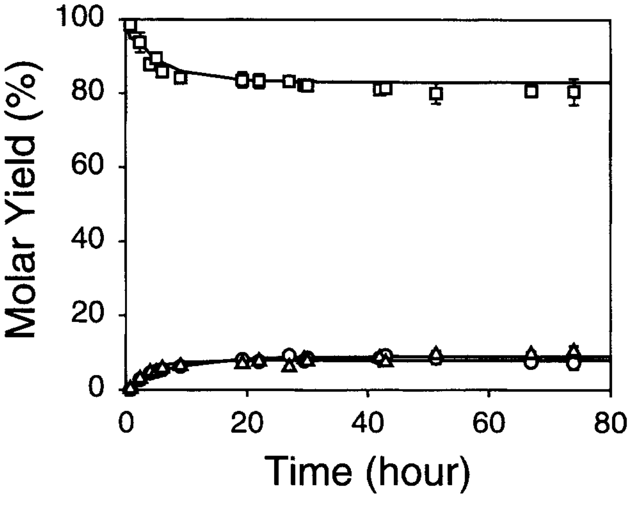

Figure 7. Mole fraction product yields as a function of time for the reaction of phenol with *tert*-butyl alcohol in water at 275°C and 172 bar.

(□) Phenol; (○) 2-*tert*-butylphenol; (△) 4-*tert*-butylphenol.

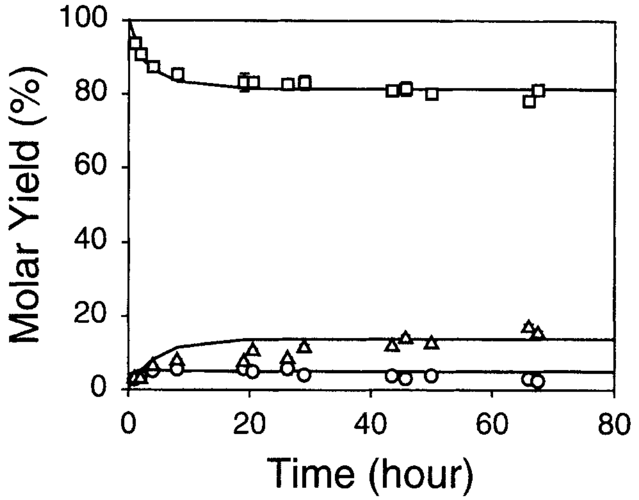

Figure 8. Mole fraction product yields as a function of time for the reaction of phenol with *tert*-butyl alcohol in water at 300°C and 172 bar.

(□) Phenol; (○) 2-*tert*-butylphenol; (△) 4-*tert*-butylphenol.

Table 1. Pseudo-First-Order Rate Constants for the Alkylation Reaction of Phenol with *tert*-Butyl Alcohol in Near-Critical Water

Temperature (°C)	$k_1 \times 10^5$ (s^{-1})	$k_{-1} \times 10^5$ (s^{-1})	$k_2 \times 10^5$ (s^{-1})	$k_{-2} \times 10^5$ (s^{-1})
250	0.19	1.1	0.17	1.4
275	0.61	6.4	0.36	3.3
300	2.1	35	0.92	5.4

which allowed further mechanistic analysis. The rate constants k_1, k_{-1}, k_2, and k_{-2} were obtained by an optimum fit of the predicted product yields to the experimental data using least-squares analysis. The rate constants are reported in Table 1 for each temperature studied in this investigation. The rate constants were also obtained using equilibrium constants from the long duration (> 60 h) equilibrium data and fitting two rate constants to the shorter duration data (details given in Chandler, 1997). The fit of the experimental data was superior when all four rate constants were fit simultaneously. The product yields of phenol, 2-*tert*-butylphenol, and 4-*tert*-butylphenol predicted with the optimum rate constants and the nonlinear regression model are shown in Figures 6 through 8 as continuous lines. Three different runs were performed at each reaction temperature, and the average standard deviation of the optimum rate constants was approximately 15%.

As shown in Table 1, the pseudo-first-order rate constants increased with increasing temperature. The effect of temperature on the forward and reverse rate constants for the alkylation of phenol to form 2-*tert*-butylphenol is depicted in Figure 10, and the effect of temperature on the forward and reverse rate constants for the alkylation of phenol to form 4-*tert*-butylphenol is depicted in Figure 11. The activation energies were calculated from the Arrhenius plots, and these values are also reported in Figures 10 and 11. The average standard deviation of the activation energies was approximately 20%. Based on the difference in activation energies, the heat of reaction of the forward reaction of phenol to form 2-*tert*-butylphenol was calculated to be − 13 kcal/mol and the heat of the forward reaction of phenol to form 4-*tert*-butylphenol was calculated to be + 4 kcal/mol. Because of the narrow temperature range and the complexity of the kinetic scheme, the numbers must be assumed to have a large uncertainty.

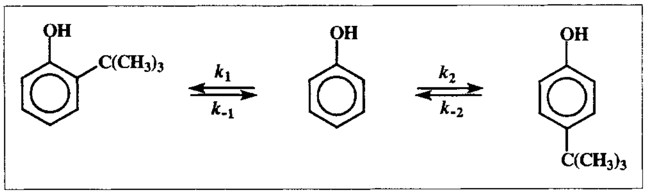

Figure 9. Model reaction network for the reversible alkylation reaction of phenol to form 2-*tert*-butylphenol and 4-*tert*-butylphenol in near-critical water.

The difference in the heats of reaction between the formation of the *ortho*-substituted product and the *para*-substituted product is large, and for comparison, the heats of reaction were calculated from heats of formation of the reactants and products available in the literature. The heats of formation of phenol, *tert*-butyl alcohol, and water were obtained from Lide (1995), and the heat of formation of 2-*tert*-butylphenol was obtained from Verevkin (1982). The calculated heat of reaction for the alkylation of phenol to form 2-*tert*-butylphenol was calculated to be − 5 kcal/mol. The heat of formation of the *para*-substituted product, 4-*tert*-butylphenol, was not found in the literature. However, Verevkin (1982) also reported the heat of formation of the

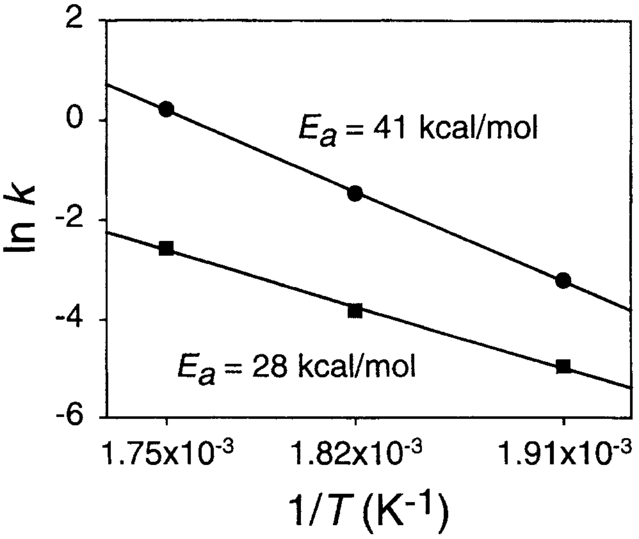

Figure 10. Arrhenius plot for the forward and reverse rate constants for the alkylation of phenol to form 2-*tert*-butylphenol in near-critical water.

(■) k_1; (●) k_{-1}.

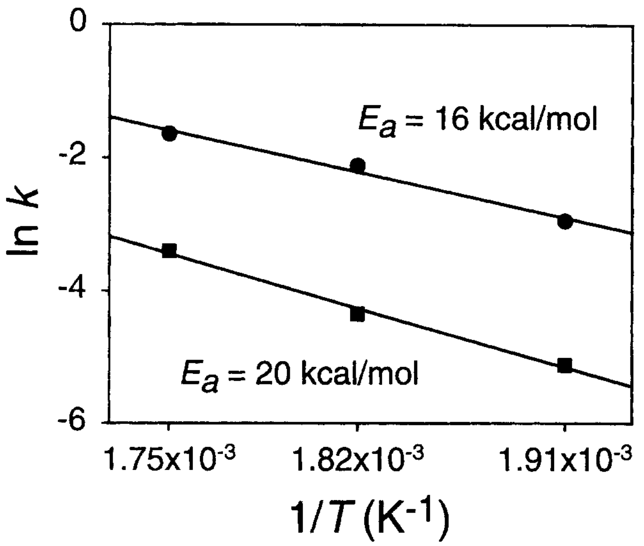

Figure 11. Arrhenius plot for the forward and reverse rate constants for the alkylation of phenol to form 4-*tert*-butylphenol in near-critical water.

(■) k_2; (●) k_{-2}.

meta-substituted product, and the difference in the heats of formation of the *ortho*- and *meta*-substituted phenols was less than 0.3 kcal/mol. Based on this difference, the heat of formation of 4-*tert*-butylphenol should also be similar to the heat of formation reported for 2-*tert*-butylphenol. Therefore, the calculated heats of reaction do not clarify the large difference found in the experimental heats of reaction. However, the calculated heats of reaction are for a gas-phase reaction at 25°C. The reactions reported in this investigation are in highly nonideal aqueous solutions at high temperatures and this would affect the heats of reaction considerably; however, it seems unlikely that solution effects alone could account for a difference as large as that reported here.

The rate of formation of 2-*tert*-butylphenol was faster than the rate of formation of 4-*tert*-butylphenol at all reaction temperatures. Further, the calculation of activation energies and heats of reaction revealed that the formation of 2-*tert*-butylphenol from phenol was exothermic, and, thus, the equilibrium concentration of 2-*tert*-butylphenol actually decreased with increasing temperature. Conversely, the formation of 4-*tert*-butylphenol from phenol was found to be endothermic and the equilibrium concentration of 4-*tert*-butylphenol increased with increasing temperature.

The alkylation reactions studied in this work provide an important example of how reactions in near-critical water could be tuned with reaction conditions, such as temperature, to produce specific reaction products. If the desired products are sterically hindered phenols for use as antioxidants, the *ortho*-substituted product would often be the desired product, and lower reaction temperatures would improve the product yields. However, the unique properties of near-critical water that allow organic synthesis are also a strong function of temperature. As the temperature is decreased, the solubilizing properties change and reactants and products could drop out of solution. Furthermore, the ionization constant decreases as the temperature is decreased which would hinder the ability of water to act as an effective acid catalyst. Therefore, the reaction temperatures used for the production of sterically hindered phenols would require optimization to balance the effects of temperature on the exothermic reaction and on the solvent properties of near-critical water.

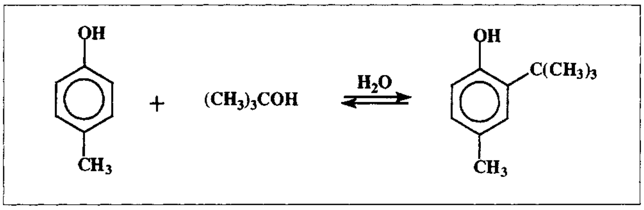

Figure 12. Reaction of *p*-cresol with *tert*-butyl alcohol in near-critical water.

Alkylation reactions of p-cresol

The reaction of *p*-cresol with *tert*-butyl alcohol (Figure 12) was also carried out at 250, 275, and 300°C, and the mole fraction product yields are shown as a function of time for each temperature in Figures 13 through 15. The alkylation of *p*-cresol with *tert*-butyl alcohol produced only one reaction product 2-*tert*-butyl-4-methylphenol, and the product produced phenol when subjected to near-critical water at 275°C indicating that the reaction was reversible. The disubstituted product, 2,6-di-*tert*-butyl-4-methylphenol, was not identified as a reaction product at any of the reaction temperatures.

Because only one reaction product was produced by the alkylation reaction of *p*-cresol with *tert*-butyl alcohol in the temperature range studied in this investigation, the model reaction network involved only one reversible first-order reaction. Also, the *tert*-butyl alcohol was present in large excess

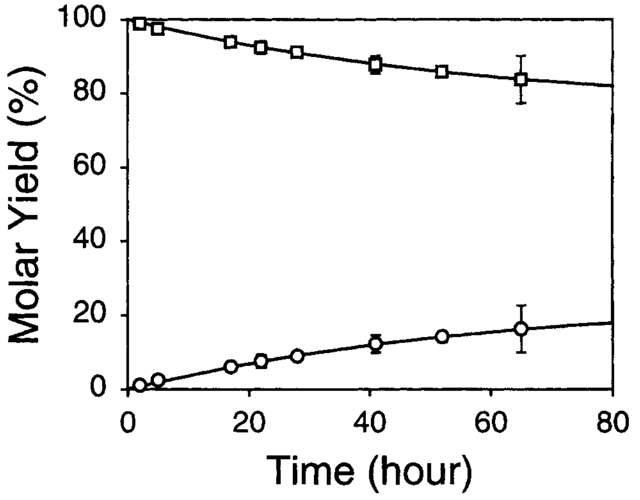

Figure 13. Mole fraction product yields as a function of time for the reaction of *p*-cresol with *tert*-butyl alcohol in water at 250°C and 172 bar.

(□) *p*-cresol; (○) 2-*tert*-butyl-4-methylphenol.

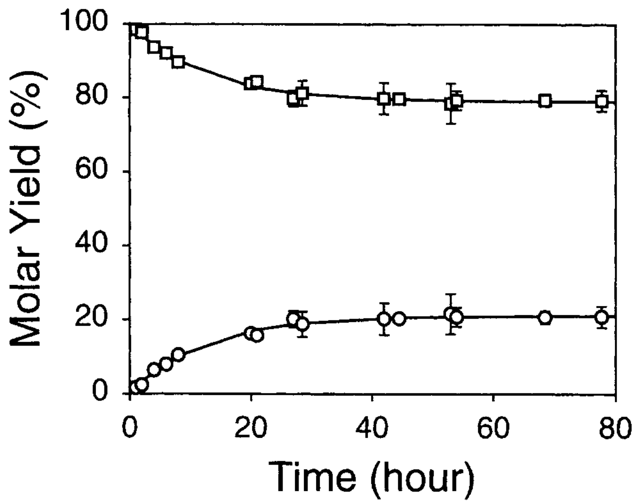

Figure 14. Mole fraction product yields as a function of time for the reaction of *p*-cresol with *tert*-butyl alcohol in water at 275°C and 172 bar.

(□) *p*-cresol; (○) 2-*tert*-butyl-4-methylphenol.

and the reaction kinetics were assumed to be pseudo-first-order in *p*-cresol. Kinetic analysis was used to summarize the experimental data in terms of two pseudo-first-order rate constants, k_1 and k_{-1}, where k_1 was defined as the rate constant of the forward reaction and k_{-1} was defined as the rate constant of the reverse reaction. Again, least-squares analysis was used to obtain the rate constants by optimizing the predicted product yields from the model to the experimentally measured product yields, and the optimum pseudo-first-order rate constants are reported in Table 2 for each temperature studied in this investigation. The product yields of *p*-cresol and 2-*tert*-butyl-4-methylphenol predicted with the optimum rate constants are shown as continuous lines in Figures 13 through 15. Three experimental runs were performed at 275°C, and the standard deviations of the rate constants were less than 3%. The product yields reported at 250 and 300°C were obtained from only one experimental run at each temperature.

Table 2. Pseudo-First-Order Rate Constants for the Alkylation Reaction of *p*-Cresol with *tert*-Butyl Alcohol in Near-Critical Water

Temperature (°C)	$k_1 \times 10^5$ (s^{-1})	$k_{-1} \times 10^5$ (s^{-1})
250	0.11	0.35
275	0.48	1.8
300	1.3	6.3

As shown in Table 2, the pseudo-first-order rate constants increased with increasing temperature and the effect of temperature on the forward and reverse rate constants is depicted in Figure 16. The activation energies were calculated from the Arrhenius plots and are reported in Figure 16. The standard deviations of the activation energies were approximately 5%. Based on the activation energies, the heat of the forward reaction of *p*-cresol to form 2-*tert*-butyl-4-methylphenol was calculated to be −6 kcal/mol. The heat of reaction was calculated from heats of formation for the reactants and products available in the literature. The heats of formation of *p*-cresol, *tert*-butyl alcohol, and water were obtained from Lide (1995), and the heat of formation of the product was obtained from Verevkin et al. (1984). The heat of reaction was calculated to be −3 kcal/mol. Again, this heat of reaction is for a gas-phase reaction at 25°C.

The rate of formation of the *ortho*-substituted product for the alkylation reaction of *p*-cresol was slower than the for-

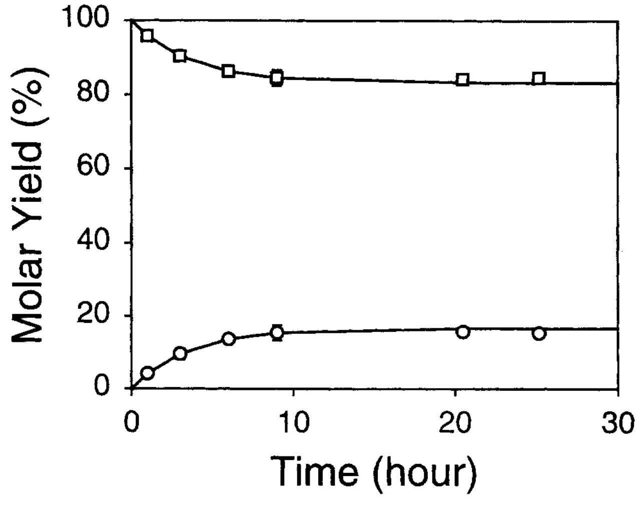

Figure 15. Mole fraction product yields as a function of time for the reaction of *p*-cresol with *tert*-butyl alcohol in water at 300°C and 172 bar.

(□) *p*-cresol; (○) 2-*tert*-butyl-4-methylphenol.

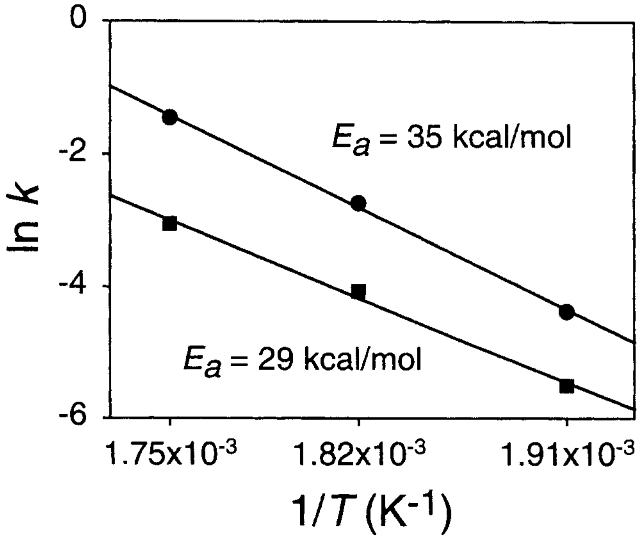

Figure 16. Arrhenius plot for the forward and reverse rate constants for the alkylation of *p*-cresol to form 2-*tert*-butyl-4-methylphenol in near-critical water.

(■) k_1; (●) k_{-1}.

mation of the *ortho*-substituted product for the alkylation reaction of phenol. However, because the *para* position of *p*-cresol was not available for reaction, only the desired *ortho*-substituted product was formed, and if near-critical water were used for the industrial production of sterically hindered phenols, separation of isomers would not be required. Further, the equilibrium concentration of 2-*tert*-4-methylphenol was more than double that of 2-*tert*-butylphenol at each temperature studied in this investigation. The disubstituted product, 2,6-di-*tert*-4-methylphenol or BHT, was not observed at any of the reaction temperatures studied. However, based on the kinetic results determined in this investigation, reaction temperatures could be predicted to optimize the production of the disubstituted product.

Conclusions

The use of near-critical water as a solvent for organic reactions would provide many advantages over conventional processing with environmentally undesirable organic solvents and catalysts, but an understanding of the kinetic properties will be required to tune successfully reaction conditions to optimize commercial processes. In this investigation, kinetic analyses were performed for the alkylation reactions of phenol and *p*-cresol with *tert*-butyl alcohol in near-critical water. A new experimental reaction apparatus was designed, constructed, and successfully operated to allow pressure control and sampling of the reaction system, which provided reaction kinetics as well as product distribution information as a function of temperature. In both alkylation reactions, the formation of the *ortho*-substituted products were found to be exothermic, whereas in the alkylation reaction of phenol, the formation of the *para*-substituted product was found to be endothermic. Based on these results, it is evident that the product distribution of the alkylation reactions could be tuned with temperature to produce specific products.

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