Control of Reversible Reactions in Supercritical Water: I. Alkylations

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The reaction rates of alkylation of phenol and that of dealkylation of alkylphenol were evaluated in sub- and supercritical water. Dehydration of 2-propanol gave propene, and then alkylation with phenol, which produced 2-isopropylphenol. Then 2-propylphenol was formed by rearrangement of 2-isopropylphenol. The alkylation rate was higher than the dealkylation rate, as water density increased and temperature decreased at 613–713 K and 0.3–0.6 g/cm^3 of water density. At around 673 K, the order of magnitude of the alkylation and dealkylation rates reversed and become sensitive to the system temperature and density. These results demonstrate some of the specific features of supercritical water: the reaction rate of both forward and reverse reactions, such as alkylation and dealkylations, can be controlled through manipulation of temperature and density (pressure).
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Introduction

Phenolic chemicals such as phenol and the alkylphenols are important intermediates for the chemical industry and are produced at a rate of over 5 million tons per year. The main production route of alkylphenols is alkylation of phenol that has been produced from the cumene oxidation of benzene (Kroschwitz and Mary, 1991). For the development of sustainable processes, phenol needs to be considered in the chemical recycling of alkylphenolic materials, which can be made by controlling the alkylation rate and dealkylation rates by using phenolic resources.

Alkylation of phenol with the corresponding alkenes is usually carried out through Friedel-Crafts alkylation. Friedel-Crafts alkylation essentially requires strong acids such as $AlCl_3$ and H_2SO_4 (Olah, 1963) and organic solvent, which means the process requires extensive waste treatment. Further, the alky-

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lation of phenol occurs mainly at both the ortho and para positions, and it is difficult to control the regioselectivity because the hydroxy group strongly reactivates alkylation of its ortho and para positions.

Both high-temperature water and supercritical water (T_c = 647.3 K and P_c = 22.1 MPa) are expected to play an increasingly important role in the development of synthetic reaction routes that embrace the principles of green chemistry (Katritzky et al., 2001; Savage et al., 1995; Savage, 1999). Chandler et al. (1997, 1998) reported that alkylation of phenol with several alcohols occurred without catalyst in high-temperature water at 523 to 573 K, and found that ortho-substitution of the *tert*-butyl group was exothermic and para-substitution was endothermic. We reported that in supercritical water the alkylation of phenol with 2-propanol occurs without catalyst, and high ortho selectivity was obtained (Sato et al., 2001). These studies show that the alkylation process can be controlled without toxic catalysts or harsh chemicals.

The dealkylation of alkylphenols usually requires hydrogen, hydrogen donor solvents, or catalysts (Dorrestijn et al., 2000). On the other hand, dealkylation of alkylphenols proceeds without a hydrogen source and catalyst in supercritical water. Martino and Savage (1997) conducted the decomposition of cresols in supercritical water at 733 K. They found that ortho- and para-cresol yielded phenol as the main product and the conversion was almost 10% at about 10 s of the short reaction time. Adschiri et al. (1997) conducted the decomposition of bisphenol-A, namely, the dimer of phenol in supercritical water at 673 K, and found that phenol was obtained by hydrolysis. Tagaya et al. (1997) reported that bisphenol-F decomposed in supercritical water at 703 K while producing some polymerized products. In contrast, Katritzky et al. (1990a,b) reported that alkylphenols (ortho-, meta-, para-cresol, 4-ethylphenol, 4-propylphenol, 4-isopropylphenol, and 4-*tert*-butylphenol) are stable at 523 K in high-temperature water, which means that the high-temperature region might be suitable for promoting the dealkylation in high-temperature water.

Supercritical water has many favorable characteristics as a reaction solvent. Solvent properties of supercritical water, such as ion product (Marshall and Franck, 1981) and dielectric constant (Uematsu and Franck, 1980), can be changed greatly by small changes in pressure and temperature, which influences reaction rate and chemical equilibrium (Savage et al., 1995). Supercritical water has been considered as a solvent for decomposing organics through bond splitting, as reviewed by Savage et al. (1995). In general, cutting such bonds as those of ether (e.g., C—O bonds) are enhanced as water density increases (Klein et al., 1990). On the other hand, supercritical water is being examined as a solvent for noncatalytic organic syntheses, such as the Friedel-Crafts reaction (Sato et al., 2001), the Diels-Alder reaction (Korzenski and Kolis, 1997), and the Beckmann and Pinacol rearrangement reactions (Ikushima et al., 2000). In these reactions, bond formation also occurs in supercritical water. For example, the Friedel-Crafts reaction of phenol with 2-propanol yields alkylphenol through the formation of a carbon-carbon bond. The Diels-Alder reaction also proceeds through the formation of a carbon-carbon bond. Based on these findings, it is highly possible that forward and reverse reactions such as bond formation and bond splitting reactions can be manipulated in supercritical water.

The possibility of controlling reversible reactions such as alkylation and dealkylation with solvent properties may be one of the new characteristics of organic reactions in supercritical water. Recently, we found an exactly reversible reaction of alkylation and dealkylation in supercritical water (Sato et al., 2002a,b). We studied the alkylation of phenol with 2-propanol (Sato et al., 2002a) and the dealkylation of 2-isopropylphenol (Sato et al., 2002b), and reported that the dealkylation rate increased with increasing water density. The dependence of the alkylation rate on temperature and water density was not elucidated.

In this article, we conducted the alkylation of phenol with 2-propanol to study its reversibility in sub- and supercritical water. Experiments were performed over a wide range of temperatures (613 to 713 K) and water densities (0.3 to 0.6 g/cm^3). The alkylation rates were evaluated at each temperature and density from the experimental data and previously reported results of reverse reaction (Sato et al., 2002b). Alkylation rates and dealkylation rates are compared, and a relationship is developed to describe the dependence of temperature and water density on a reversible reaction.

Experimental

Phenol and 2-propanol had purities of >99.0% and 99.5%, respectively. The analytical reagents used were tetrahydrofuran (>97%) with 2,6-di-*tert*-butyl-4-methylphenol as an inhibitor and naphthalene. All chemicals were purchased from Wako Pure Chemical Industries.

Reactions were carried out in 6-cm^3 stainless steel batch reactors. The reactor consisted of SS 316 tubes (length = 105 mm, OD = 1/2 in., thickness = 2.1 mm) that had two SS 316 swagelok reducing unions. One port served as a K-type thermocouple entrance for measuring the inner reactor. In some cases, we used the reactor whose one port was connected to a high-pressure valve (Whitey, model SS-3NBF2) for gas analysis. The error in the volume of the reactor is estimated to be less than 5%. In general, we elected to minimize dead space in the experiments and used careful loadings to control density and temperature, with pressure being estimated. Measurement of pressure will cause some errors in pressure or in the reaction since dead space is introduced. The reactor was pretreated by introducing 3.0 g of 3.0 wt % hydrogen peroxide aqueous solution and heating this solution to 673 K for up to 10 h. The inner wall of the reactor was oxidized and became nonreactive. The reactor was loaded with 0.120 g of 2-propanol, 0.188 g of phenol, and 1.8–3.6 g of distilled water, corresponding to the water densities of 0.3–0.6 g/cm^3. The number of reactants loaded is shown in Table 1. The error in the loading of water was within 0.07 g. Phenol was introduced into the reactor by a pipet after the phenol was melted by heating, and thus the exact amount of phenol desired could not be loaded because a single drop of phenol can be relatively large. Air in the reactor was displaced with argon by successive purgings. After the reactor had been loaded, the reactor was submerged into a fluidized sand bath (Takabayashirika Co., model TK-3) that was controlled at the reaction temperature (613–713 K). Heatup time was measured to be within 3 min. After a given amount of time (10–720 min), including the heatup time, the reactor was removed from the sand bath, and the reaction was rapidly quenched in a water bath at 293 K. After being cooled, the reactor was opened and gas products were recovered to syringe

Table 1. Concentration of Products at 0.3–0.6 g/cm^3 Water Density and 613–713 K

T (K) [Nominal Water Density (g/cm^3)]	Reaction Time (min)	Initial Value (g)			Concentration (mol/L)					Carbon Balance of Phenol Structure
		2-Propanol	Phenol	Water	2-Propanol	Propene	Phenol	IPP	PP	
613 (0.6)	60	0.120	0.193	3.61	0.205 ± 0.044	0.122 ± 0.040	0.320 ± 0.049	0.002 ± 0.034	0.000 ± 0.033	0.926
	180	0.120	0.195	3.61	0.143 ± 0.045	0.173 ± 0.046	0.315 ± 0.053	0.012 ± 0.038	0.000 ± 0.038	0.923
	360	0.120	0.197	3.60	0.084 ± 0.041	0.204 ± 0.047	0.299 ± 0.052	0.035 ± 0.038	0.002 ± 0.037	0.937
	540	0.120	0.186	3.61	0.070 ± 0.024	0.191 ± 0.030	0.246 ± 0.033	0.051 ± 0.023	0.003 ± 0.020	0.949
	720	0.120	0.200	3.61	0.059 ± 0.043	0.178 ± 0.049	0.265 ± 0.053	0.066 ± 0.043	0.004 ± 0.040	0.942
633 (0.5)	60	0.120	0.195	3.00	0.207 ± 0.040	0.121 ± 0.035	0.372 ± 0.048	0.002 ± 0.029	0.000 ± 0.029	1.052
	120	0.120	0.186	3.00	0.182 ± 0.024	0.143 ± 0.022	0.308 ± 0.030	0.004 ± 0.015	0.000 ± 0.015	0.967
	180	0.121	0.185	3.01	0.167 ± 0.024	0.156 ± 0.024	0.318 ± 0.032	0.009 ± 0.017	0.000 ± 0.016	1.033
	240	0.120	0.201	3.01	0.137 ± 0.039	0.166 ± 0.040	0.361 ± 0.050	0.023 ± 0.033	0.001 ± 0.032	1.028
	360	0.120	0.199	3.01	0.112 ± 0.035	0.175 ± 0.038	0.339 ± 0.046	0.034 ± 0.031	0.003 ± 0.029	1.030
653 (0.4)	180	0.120	0.197	2.40	0.253 ± 0.057	0.073 ± 0.048	0.328 ± 0.060	0.003 ± 0.044	0.000 ± 0.044	0.915
	360	0.120	0.191	2.40	0.244 ± 0.036	0.072 ± 0.028	0.307 ± 0.039	0.011 ± 0.025	0.002 ± 0.024	0.943
653 (0.5)	20	0.120	0.190	3.00	0.281 ± 0.031	0.048 ± 0.019	0.350 ± 0.034	0.001 ± 0.017	0.000 ± 0.017	1.040
	60	0.120	0.187	3.00	0.147 ± 0.025	0.171 ± 0.026	0.330 ± 0.034	0.011 ± 0.018	0.001 ± 0.017	1.047
	180	0.120	0.191	3.00	0.085 ± 0.020	0.178 ± 0.025	0.290 ± 0.030	0.049 ± 0.018	0.006 ± 0.016	1.031
673 (0.3)	120	0.127	0.190	1.81	0.356 ± 0.039	0.000 ± 0.021	0.318 ± 0.037	0.002 ± 0.021	0.000 ± 0.021	1.005
	360	0.120	0.196	1.82	0.321 ± 0.040	0.000 ± 0.024	0.360 ± 0.042	0.006 ± 0.025	0.003 ± 0.024	1.030
673 (0.4)	30	0.126	0.194	2.47	0.324 ± 0.034	0.019 ± 0.019	0.330 ± 0.035	0.002 ± 0.018	0.001 ± 0.018	0.995
	45	0.126	0.201	2.41	0.294 ± 0.047	0.036 ± 0.035	0.372 ± 0.051	0.006 ± 0.033	0.001 ± 0.033	1.030
	60	0.123	0.189	2.43	0.266 ± 0.032	0.058 ± 0.022	0.330 ± 0.035	0.010 ± 0.019	0.001 ± 0.019	1.040
	180	0.122	0.183	2.41	0.223 ± 0.029	0.091 ± 0.023	0.289 ± 0.033	0.012 ± 0.019	0.003 ± 0.018	0.972
	360	0.120	0.203	2.42	0.141 ± 0.038	0.124 ± 0.037	0.278 ± 0.045	0.045 ± 0.033	0.024 ± 0.032	0.987
673 (0.5)	15	0.122	0.193	3.00	0.243 ± 0.044	0.086 ± 0.036	0.360 ± 0.050	0.005 ± 0.032	0.000 ± 0.032	1.069
	30	0.117	0.185	3.01	0.212 ± 0.027	0.102 ± 0.022	0.312 ± 0.032	0.007 ± 0.017	0.001 ± 0.017	0.974
	45	0.118	0.184	3.00	0.132 ± 0.026	0.169 ± 0.028	0.287 ± 0.034	0.019 ± 0.021	0.002 ± 0.020	0.962
	60	0.124	0.195	3.05	0.152 ± 0.029	0.149 ± 0.029	0.318 ± 0.037	0.030 ± 0.023	0.004 ± 0.022	1.028
	90	0.120	0.186	3.00	0.094 ± 0.017	0.185 ± 0.021	0.268 ± 0.026	0.037 ± 0.014	0.006 ± 0.012	0.974
693 (0.3)	30	0.122	0.185	1.80	0.294 ± 0.042	0.027 ± 0.029	0.294 ± 0.042	0.000 ± 0.027	0.000 ± 0.027	0.935
	60	0.121	0.203	1.80	0.262 ± 0.057	0.059 ± 0.046	0.357 ± 0.061	0.002 ± 0.043	0.000 ± 0.043	0.946
	120	0.122	0.203	1.81	0.234 ± 0.058	0.083 ± 0.050	0.351 ± 0.063	0.005 ± 0.046	0.001 ± 0.046	0.940
	180	0.122	0.193	1.82	0.231 ± 0.059	0.075 ± 0.052	0.289 ± 0.062	0.007 ± 0.048	0.003 ± 0.048	0.935
693 (0.4)	10	0.120	0.193	2.39	0.269 ± 0.034	0.061 ± 0.023	0.336 ± 0.037	0.000 ± 0.020	0.000 ± 0.020	0.966
	20	0.120	0.185	2.40	0.263 ± 0.041	0.066 ± 0.031	0.297 ± 0.042	0.001 ± 0.028	0.000 ± 0.028	0.933
	30	0.121	0.189	2.41	0.234 ± 0.015	0.094 ± 0.008	0.326 ± 0.020	0.004 ± 0.004	0.001 ± 0.004	0.997
	45	0.120	0.195	2.40	0.205 ± 0.028	0.113 ± 0.024	0.350 ± 0.035	0.009 ± 0.018	0.002 ± 0.018	1.017
	60	0.121	0.199	2.41	0.178 ± 0.037	0.138 ± 0.035	0.359 ± 0.046	0.013 ± 0.028	0.003 ± 0.028	1.035
693 (0.5)	15	0.121	0.199	3.04	0.055 ± 0.042	0.242 ± 0.052	0.317 ± 0.055	0.023 ± 0.041	0.001 ± 0.040	0.938
	20	0.121	0.199	3.04	0.061 ± 0.046	0.224 ± 0.054	0.300 ± 0.058	0.031 ± 0.045	0.004 ± 0.043	0.927
	30	0.121	0.192	3.02	0.020 ± 0.035	0.235 ± 0.046	0.250 ± 0.047	0.047 ± 0.037	0.010 ± 0.035	0.915
	45	0.120	0.183	3.02	0.027 ± 0.047	0.224 ± 0.057	0.213 ± 0.056	0.045 ± 0.048	0.014 ± 0.046	0.890
	60	0.120	0.194	3.01	0.013 ± 0.037	0.211 ± 0.047	0.232 ± 0.048	0.053 ± 0.039	0.027 ± 0.038	0.922
713 (0.3)	30	0.122	0.195	1.82	0.283 ± 0.064	0.033 ± 0.052	0.307 ± 0.066	0.002 ± 0.050	0.000 ± 0.050	0.885
	60	0.122	0.192	1.82	0.207 ± 0.053	0.103 ± 0.048	0.295 ± 0.058	0.004 ± 0.043	0.003 ± 0.043	0.892
	90	0.120	0.189	1.81	0.165 ± 0.047	0.126 ± 0.045	0.276 ± 0.053	0.009 ± 0.039	0.009 ± 0.039	0.885
	120	0.120	0.192	1.80	0.197 ± 0.041	0.118 ± 0.038	0.309 ± 0.047	0.004 ± 0.032	0.005 ± 0.032	0.925

through the sampling loops attached to two GC-TCD (Shimadzu, model GC-8A), which have a molecular sieve 5A and Porapak Q column. The composition of gas products was analyzed with these GCs. After that, the reactor was washed with THF and analyzed with a GC-FID (Hewlett-Packard, model 6890) equipped with an HP-5 column, and a GC-MS (Japan Electron Optics Laboratory, model Automass 20) equipped with an HP-5 MS column. The concentration of products was determined by GC-FID with naphthalene as the internal standard.

Results and Discussion

Table 1 provides a summary of the experimental results. The main products obtained were 2-propanol, phenol, 2-isopropylphenol (IPP), and 2-propylphenol (PP). The 2,6-diisopropylphenol, 2-isopropyl-6-propylphenol, 2,6-dipropylphenol, 4-isopropylphenol, and 1-propanol were detected as minor products and the maximal concentrations were 0.010, 0.004, 0.001, 0.001, and 0.017, respectively. The carbon balance of phenol structure (= mols of phenol and alkylphenols/mols of phenol loaded) is shown in Table 1. The carbon balance of phenol structure for each run was above 0.89 up to 1.07 due to various errors including the analyses. The final error was determined from the sum of (1) the ideal concentration of reactant loaded (0.33 mol/L) × (the error in loading + the error in balance of phenol structure) and (2) the experimental concentration × the maximum possible error in the reactor volume (5%).

We analyzed the gas products at 673 K, 0.5 g/cm^3 of water density, and 30 min of reaction time. The propene composition was 97.9%, that of carbon dioxide was 1.1%, and those of either methane or hydrogen were 0.5%. These main products were the same as those reported previously for the alkylation reaction at 673 K (Sato, 2002a). The quantitative evaluation of gas produced required a valve to be attached to the reactor and an accurate measurement of the gas volume. The gas volume recovered was generally lower than 10 cm^3 at STP, and partial

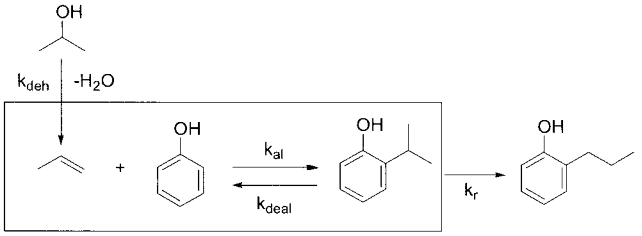

Figure 1. Reaction of phenol with 2-propanol in sub- and supercritical water.

condensation sometimes occurred in the valve, which leads to a higher experimental error. We evaluated the quantity of propene from the carbon balance because direct quantitative evaluation of the propene was inaccurate due to the amounts. The carbon balance was derived from 2-propanol loaded as [propene] = $[\text{2-propanol}]_0 - \Sigma$([product] $\times$ carbon atom in product except benzene ring/3). For 673 K and 0.3 g/cm^3 of water density, the concentration of propene was estimated to be zero due to low reactivity, although the calculated concentrations were negative. Based on the product distribution, the reaction pathway determined is shown in Figure 1. The 2-propanol was dehydrated to propene, and it followed that the alkylation of phenol with propene yielded IPP. If the hydration of propene to 2-propanol should occur, however, this reaction could be neglected, because the reverse reaction, namely, dehydration of 2-propanol, was dominant in the reaction time of this study. Alkylation proceeds through a phenol-catalyzed mechanism in supercritical water (Sato et al., 2002a). In the phenol-catalyzed mechanism, the alkylation of phenol and propene can form PP as well as IPP. The direct formation of PP, although possible, is unlikely, and evidence for the direct rearrangement from IPP to PP is clear (Sato et al., 2002b). In this article, alkylation was considered to proceed through the formation of IPP based on earlier works (Sato et al., 2001, 2002a). IPP was converted through both rearrangement to PP and dealkylation to phenol and propene. The rate constant for the spontaneous rearrangement of IPP to PP has been reported to be from 613 to 713 K in water, and the rearrangement rate is not influenced by water density (Sato et al., 2002b). However, the mechanism of rearrangement has not been reported. Judging from these results, the effect of the ionic properties of water was small and the rearrangement reaction possibly proceeded via a free-radical mechanism.

Product distribution changed greatly with water density. At 673 K and 0.3 g/cm^3 water density, the concentration of IPP and PP were below 0.006 mol/L for 360 min of reaction time, which means that there were no significant reactions at this water density. In the range from 0.4 to 0.5 g/cm^3 water density, the concentration of 2-propanol clearly decreased with increasing water density, while the concentration of propene, IPP, and PP increased by comparison at the same reaction time. For example, the concentration of propene increased from 0.058 mol/L to 0.149 mol/L, and that of IPP increased from 0.010 mol/L to 0.030 mol/L by changing water density from 0.4 g/cm^3 to 0.5 g/cm^3 at 60 min. The same trends were observed at 653 and 693 K. In supercritical water, both dehydration and alkylation were promoted with increasing water density. The concentration of hydronium ion generally governs the alkylation rate; however, the reaction rate of alkylation was not proportional to proton concentration (Sato et al., 2002a). The phenol-catalyzed reaction became significant for the alkylation in supercritical water. The increase in water density probably promoted local dissociation of hydroxy groups and stabilized the intermediate as reported by Sato et al. (2002a). The experiments were also conducted in the subcritical region at 613 and 633 K. The subcritical experiments could possibly have two phases present. For this reason, we used the total water density of the batch reactor based on the initial amount of water in Table 1. For the subcritical experiments, more propene might separate into the lower-density gas phase, and there could possibly be mass-transfer limitations between the liquid and gas phases that would suppress the reaction. However, we could not discern these effects from our data. In the subcritical region, both propene and IPP were produced, whereas PP was very low below 0.004, which means that the dehydration and alkylation occurred and rearrangement from IPP to PP was relatively slow.

We determined the alkylation rate constant (k_{al}) and dehydration rate (k_{deh}) by considering the reaction pathways shown in Figure 1. The rates are given below as follows:

$$d[\text{2-propanol}]/dt = -k_{deh}[\text{2-propanol}] \qquad (1)$$

$$d[\text{propene}]/dt = k_{deh}[\text{2-propanol}] + k_{\text{deal}}[\text{IPP}] - k_{al}[\text{propene}][\text{phenol}] \qquad (2)$$

$$d[\text{phenol}]/dt = -k_{al}[\text{propene}][\text{phenol}] + k_{\text{deal}}[\text{IPP}] \qquad (3)$$

$$d[\text{IPP}]/dt = k_{al}[\text{propene}][\text{phenol}] - k_{\text{deal}}[\text{IPP}] - k_r[\text{IPP}] \qquad (4)$$

$$d[\text{PP}]/dt = k_r[\text{IPP}] \qquad (5)$$

where units of k_{deh}, k_{deal}, and k_r are s^{-1} and units of k_{al} are mol $\cdot$ L^{-1} $\cdot$ s^{-1}.

We fit the models to the experimental data of 2-propanol, propene, and IPP at each temperature and water density. The first-order rate constant of dealkylation (k_{deal}) and rearrangement (k_r) have been reported at 613–713 K and 0–0.6 g/cm^3 of water density (Sato et al., 2002b), so we used these values. Dehydration and alkylation were assumed to be first order in 2-propanol, propene, and phenol as described earlier. Hence, the fitting parameters were k_{deh} and k_{al}. These two rate constants were obtained by an optimum fit of the predicted product concentrations to the experimental data using least-square analysis. We did not evaluate the rate constant at 673 K and 0.3 g/cm^3 of water density because of the low propene concentration.

Figure 2 shows the experimental and predicted concentrations at 673 K and 0.5 g/cm^3. The magnitude of error was determined as described previously. The decrease in 2-propanol, and increase in propene, IPP, and PP with reaction time could be predicted, which means that this model can describe the reaction pathway of this system. Although our objective was to determine the rate constants at various conditions, it is possible to measure the chemical equilibrium constant if long

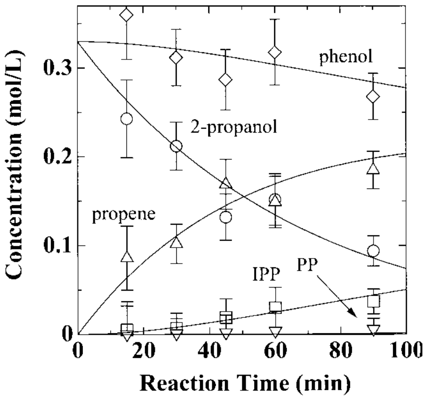

Figure 2. Product concentration vs. time for the reaction of phenol with 2-propanol in supercritical water at 673 K and 0.5 g/cm^3 water density.

reaction times are used along with appropriate experimental methods. In this work, we chose to study the variation of the reaction rate constants. Figure 3 shows a parity plot of the calculations for all conditions. The concentrations of 2-propanol and propene covered a wide range of concentrations. Phenol was at the high concentration range, and both IPP and PP were at the low concentration ranges. The model predicted the experimental values well. The standard deviation between the experimental data and calculated results was 0.019 mol/L, corresponding to 5.76% of the initial concentration of 2-propanol and phenol.

Figures 4 and 5 show an Arrhenius plot of k_{deh} and k_{al}. Plots of the rate constants from 0.3 g/cm^3 to 0.5 g/cm^3 water density increased with the increasing temperature and followed the Arrhenius relationship, and the rate constants for 0.4 and 0.5 g/cm^3 of water density were evaluated at more than three temperatures. The error bars show the maximal error about the sum of the error for loading, carbon balance of phenol structure, and reactor volume in each condition. We calculated the rate constant at 0.4 and 0.5 g/cm^3 of water density, as shown in Table 2. The dealkylation rate was calculated from the previous study (Sato et al., 2002b). For dehydration, the magnitude of the activation energy decreased with increasing water density. The activation energy of alkylation was almost constant, the same as in the case of dealkylation.

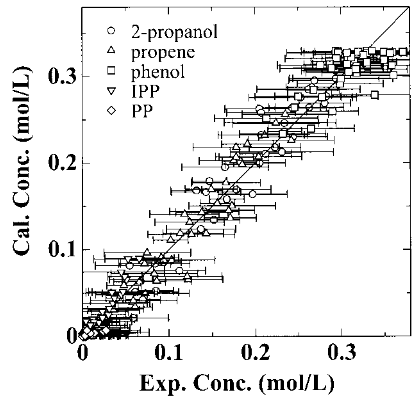

Figure 3. Parity plot of calculated and experimental concentrations.

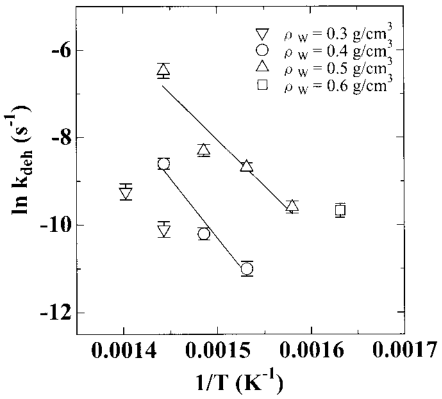

Figure 4. Arrhenius plot for reaction of dehydration at a water density of 0.3 to 0.6 g/cm^3.

The rate constant of dehydration (k_{deh}) increased with increasing water density at each temperature. For example, k_{deh} at 0.5 g/cm^3 of water density was 6.5 times larger than that at 0.4 g/cm^3 of water density at 673 K. Dehydration of 2-propanol occurs through both proton catalyzed and phenol-catalyzed mechanisms in high-temperature water (Antal et al., 1998; Sato et al., 2002a). Dehydration proceeds through the E1 or E2 mechanisms in proton-catalyzed mechanisms, and the phenol protonates 2-propanol and extracts a hydrogen atom from 2-propanol in the phenol-catalyzed mechanism. The increase of proton concentration can be one of the factors facilitating the reaction. For example, in sub- and supercritical water, phenol dissociates and the dissociation constant of phenol increases with increasing water density (Sue et al., 2002a), which leads to the increase in proton concentration. At 673 K, the dissociation constant of phenol increases from 10^{-12} mol/kg to 10^{-11} mol/kg as the water density increases from 0.36 g/cm^3 to 0.47 g/cm^3, which corresponds to proton concentrations of 3.4×10^{-7} and 1.3×10^{-6}, respectively, calculated by the same method as used by Sato et al. (2002a). In proton-catalyzed and phenol-catalyzed mechanisms, an increase in water density promotes the reaction by the increase of the proton concentra-

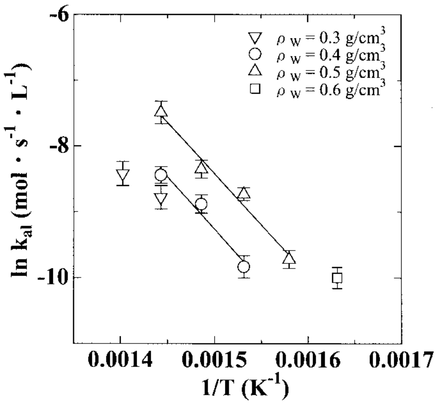

Figure 5. Arrhenius plot for reaction rate constant of alkylation at a water density of 0.3 to 0.6 g/cm^3.

Table 2. Rate Constant for Dehydration, Alkylation, and Dealkylation at 0.4 and 0.5 g/cm^3 Water Density

Water Density (g/cm^3)	k_{deh} (s^{-1})*	k_{al} (s^{-1} · mol · L^{-1})*	k_{deal} (s^{-1})*
0.4	$10^{13.2}\exp(-2.25 \times 10^5/RT)$	$10^{6.26}\exp(-1.31 \times 10^5/RT)$	$10^{11.2}\exp(-2.00 \times 10^5/RT)$
0.5	$10^{10.3}\exp(-1.77 \times 10^5/RT)$	$10^{6.45}\exp(-1.29 \times 10^5/RT)$	$10^{11.3}\exp(-2.01 \times 10^5/RT)$

* R: (J · mol^{-1} · K^{-1}).

tion and the support of the intermediates through electrostatic effects (Sato et al., 2002a), respectively.

The alkylation rate constant (k_{al}) increased with increasing water density at each temperature as well as that of dehydration. At 673 K, the alkylation rate constant at 0.5 g/cm^3 water density was 1.7 times larger than that of 0.4 g/cm^3 water density. The alkylation of phenol with propene probably proceeded through the direct reaction of propene and phenol with local dissociation of the hydroxy group. The increased water density probably promoted local dissociation of the hydroxy groups and stabilized the polar transition state of the reaction through the increase in the dielectric constant, as noted by Sato et al. (2002a).

On the other hand, dealkylation also increased at the higher water densities. The dealkylation rate constant increased only 1.2 times with the increase in water density from 0.4 g/cm^3 to 0.5 g/cm^3 at 673 K (Sato et al., 2002b). The magnitude of the change in the alkylation rate constant with increasing water density (1.7 times) was larger than that for the dealkylation (1.2 times). This is probably due to the stability of the system of propene and phenol, the transition state, and IPP in terms of the dielectric environment of the solvent. In other words, if the stabilization of the transition state were higher than that of the reactant, the reaction should be more rapid at the higher density conditions. By considering these assumptions, the small change in the dealkylation rate is evidence that the stabilization of the transition state and IPP are roughly the same, and, further, that the increase in the alkylation rate with water density shows that the stabilization of the reactant (phenol + propene) was less than that of the transition state.

In the case of equilibrium, the heat of reaction provides the useful information for the dependence of equilibrium on temperature. Based on the activation energy of alkylation and dealkylation, the heat of alkylation was evaluated at each water density. Table 3 summarizes the heat of formation for the alkylation of phenol. The heat of formation was −69 and −72 kJ/mol and 0.4 and 0.5 g/cm^3 of water density, respectively. In this system, the heat of formation was almost constant, regardless of water density, whereas the heat capacity of the solute can change greatly with temperature in supercritical water, which probably affects the heat of formation (Sue et al., 2002b; Sedlbauer et al., 2000; Kiselev and Rainwater, 1998).

We calculated the heats of reaction of propene + phenol to IPP from values of propene and phenol in the literature (Society of Chemical Engineers, Japan, 1999) and estimated the values of IPP (Benson, 1976). The calculation was based on a gas phase, and the calculated value was −10 kJ/mol for the heat of alkylation at 673 K. Chandler et al. (1998) reported heats of reaction for the reaction of alcohol and phenol to form alkylphenol in near-critical water. For the alkylation of phenol with *tert*-butylalcohol to 2-*tert*-butylphenol or 4-*tert*-butylphenol, the heats of formation were −54 and 20.9 kJ/mol, respectively, as shown in Table 3. The experimental heats of reaction were on the same order as those of the calculated values and those values found in the literature. Although the heats obtained from experiment contain some error, the alkylation of phenol with propene was exothermic regardless of phase, which means that the low-temperature region should be favorable for alkylation. Further, ortho-alkylation is exothermic and para-alkylation is endothermic in high-temperature water (Chandler et al., 1998). The heat of formation for ortho-alkylation in this study was approximately the same as the values for ortho-alkylation in the literature. Ortho-alkylation was exothermic in high-temperature water, including the supercritical region.

Next, we evaluated the contribution of each reaction rate as compared with the initial reaction rate, as described below

$$\text{Alkylation rate: } r_{al} = k_{al}[\text{propene}]_0[\text{phenol}]_0 \tag{6}$$

$$\text{Dealkylation rate: } r_{\mathrm{deal}} = k_{\mathrm{deal}}[\text{IPP}]_0, \tag{7}$$

where [propene]$_0$, [phenol]$_0$, and [IPP]$_0$ are the initial concentrations of each compound. Here, the initial concentrations were set equal to the experimentally ideal values of 0.33 mol/L.

Figure 6 shows the initial reaction rates of alkylation (r_{al}) and dealkylation (r_{deal}). The alkylation rate was evaluated from the data obtained in this study and shown by a plot. The dealkylation rate was taken from the literature (Sato et al., 2002b), and is shown by the lines and the solid square. At 0.5 g/cm^3 of water density, the alkylation rate seemed to be governed by temperature, regardless of whether conditions were in the subcritical (under 647 K) or supercritical region (above 647

Table 3. Heat of Formation for Alkylation of Phenol

	Propene + Phenol = IPP			Phenol + *tert*-Butylalcohol = 2-*tert*-Butylphenol	Phenol + *tert*-Butylalcohol = 4-*tert*-Butylphenol
Water density/pressure	0.4 g/cm^3*	0.5 g/cm^3**	0 g/cm^3 (gas phase)†	172 bar††	172 bar††
Heat of formation (kJ/mol)	−69	−72	−10	−54	20.9

* 653–693 K in water.
** 633–693 K in water.
† Calculated at 673 K.
†† 523–573 K in water, by Chandler et al. (1998).

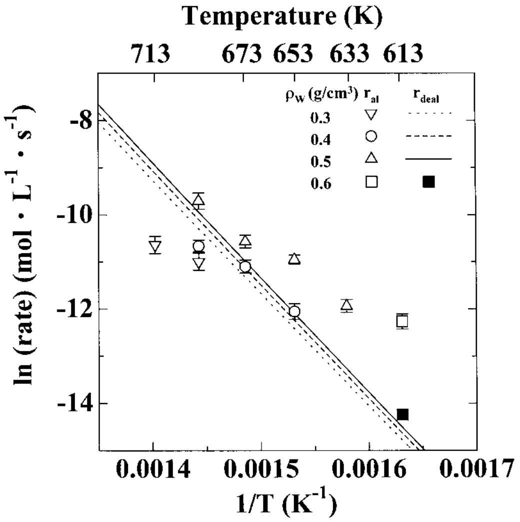

Figure 6. Reaction rate for alkylation and dealkylation at 613–713 K and a water density of 0 to 0.6 g/cm^3.

K). At a given temperature, both the alkylation and dealkylation rates increased with increasing water density; however, the magnitude of the increase was different. The rate of dealkylation changed with water density over a very narrow range, as shown in Figure 6. On the other hand, the alkylation rate changed with water density more than the dealkylation rate. In other words, the water density had a much greater effect on the alkylation rate than it did on the dealkylation rate. Moreover, the order of the magnitude of the alkylation rate and dealkylation rates reversed between 673 K and 693 K at 0.4 g/cm^3 of water density, giving an alkylation rate at higher temperatures that is lower than the dealkylation rate. This dependence of the alkylation and dealkylation rates on temperature and water density shows that the reversible reaction could be shifted to the alkylation or dealkylation side by manipulating temperature and water density (reaction pressure).

Alkylation can be considered as a *formation* reaction and dealkylation as a *decomposition* reaction. In this case, the decomposition can be promoted by setting the conditions at low water densities and high temperatures. For a *formation* reaction, the increase in water density by increasing pressure in the supercritical region and at some appropriate temperature probably makes the reaction rate higher than that in the subcritical region and can prevent the effect of decomposition as a reverse reaction. We believe that analysis of various reversible reactions can help develop applications for controlling the forward and reverse reactions by temperature and water density in supercritical water and that this feature is a new characteristic of supercritical water as a reaction solvent.

Conclusions

Alkylation of phenol with 2-propanol was conducted at 613–713 K and 0.3–0.6 g/cm^3 of initial water density in sub- and supercritical water. In the reactions, both dehydration and alkylation rate constants increased with increasing water density. Alkylation rates were compared with dealkylation rates. In the high-temperature and low-water-density region, the dealkylation rate was greater than the alkylation rate. The alkylation rate became predominant in the low-temperature and high-water-density region. The reaction rate reversed at around 673 K. Based on these results, the forward and reverse reaction of alkylation and dealkylation could be controlled by manipulating both the temperature and pressure of water, especially in its supercritical region.

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