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Non-catalytic and selective alkylation of phenol with propan-2-ol in supercritical water

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Phenol can be alkylated with propan-2-ol without catalyst in supercritical water at 673 K with mainly *ortho* substituted alkylphenols being obtained and alkylation reaction rate increasing with increasing water density.

The Friedel–Crafts reaction is the most widely used in chemistry and industry for the alkylation of aromatics. This reaction is promoted by strong acid catalysts such as Lewis acids ($AlCl_3$ and BF_3) and mineral acids (HF, H_2SO_4),[1] and is frequently conducted in organic solvents, which requires considerable waste treatment. Because of increased awareness towards our environment, research has been directed towards alternative solvents and non-catalytic pathways.

The reactivity of the hydroxy group of phenol strongly activates the ring substituents, especially at the *ortho* and *para* positions. Thus, in the alkylation of phenol through the Friedel–Crafts reaction, it is difficult to alkylate only one position. If the alkylating agents are propan-1-ol or propan-2-ol, the condensation between alcohol and hydroxy group yields isopropyl phenoxy ether, in addition to the alkylation.[2] Solid catalysts have been used for *ortho*-selective alkylation of phenol.[3,4] Gray *et al.* reported that the etherification and alkylation of phenol could be controlled and the *ortho* alkylphenol obtained was over 3 times larger than that for *para* substituents in supercritical CO_2 with a solid catalyst.[4]

High temperature water can possibly provide an alternative pathway for formation of C–C bonds.[5,6] In the alkylation of phenol, Chandler *et al.*[7,8] studied non-catalytic alkylation of phenol with several alcohols in high temperature water at 523–573 K. They reported that alkylation of phenol with propan-2-ol occurred almost only at the *ortho* position of phenol. However, the reaction rate and alkylphenol yield obtained were low being about 20% after 120 hours reaction time.

Supercritical water (T_c = 647 K, P_c = 22.1 MPa) shows some unique properties and has been considered for the decomposition of organics.[5] It is completely miscible with many organics and can provide a homogeneous reaction field. Solvent properties such as density and relative permittivity can be varied by manipulating temperature and pressure. The reaction rate in supercritical water is expected to be much higher than that in sub-critical water due to not only the higher temperature but also to the homogeneous reaction environment[9] and the chemical effects caused by the relative permittivity.[10] In this study, we conducted non-catalytic alkylation of phenol with propan-2-ol in supercritical water at 673 K and water densities ranging from 0 to 0.5 g cm^{-3} and determined the reaction pathway. We show that high reaction rate, high alkylphenol yields and *ortho* selectivity are possible in high temperature dense water.

Reactions were conducted with 6 cm^3 stainless 316 tube bomb reactors. Phenol (99.0% purity, Wako Pure Chemical Industries, Ltd.) and propan-2-ol (99.5% purity, Wako Pure Chemical Industries, Ltd.) were loaded into the reactors and then a given amount of water was added. The air in the reactor was exchanged with argon gas by successive purgings and the reactor was sealed. The molar ratio of propan-2-ol to phenol was 1:5, which corresponded to a concentration of 0.33 mol L^{-1} for propan-2-ol and 1.65 mol L^{-1} for phenol. Water was loaded from 0 to 0.5 g cm^{-3} of water density corresponding to a range of concentration from 0 to 27.7 mol L^{-1}. The reactors were submerged into a sand bath controlled at 673 K. After 10–60 minutes, the reactors were quenched. Products were identified by GC-MS and by comparison of the GC retention time with standards. Quantitative analysis of products was conducted with GC-FID. For some cases, we conducted experiments for the analysis of gas products using a reactor that was connected to a valve. For these cases, the gas compositions were analyzed by GC-TCD. The product yield was defined on a propan-2-ol basis, as: yield (%) = (moles of carbon atom of the alkyl chain except benzene ring) / (moles of carbon atom in propan-2-ol loaded) × 100.

Fig. 1 shows the yield of main products for the alkylation of phenol with propan-2-ol in supercritical water at 0.5 g cm^{-3} of water density and 673 K. The main liquid products were 2-isopropylphenol, 2-propylphenol and 2,6-diisopropylphenol, and their maximal yields were 57.9, 6.9 and 5.9%, respectively. Other liquid products obtained were 2-isopropyl-6-propylphenol and 4-isopropylphenol, and their maximal yields were 1.7 and 2.4%, respectively. From 10 to 60 minutes reaction time, the gas product was almost all propylene, whose molar proportion to all gases was always above 90%. In particular, the proportion of propylene was above 95.9% before 30 minutes reaction time. After that, the proportion of hydrogen, methane and propane slightly increased up to 4.7, 1.5 and 3.4%, respectively. Propylene yields shown in Fig. 1 were obtained by the carbon balance and so include other gas products as well. The yield of propan-2-ol rapidly decreased and the conversion of propan-2-ol was above 90% at 20 minutes of reaction time. The yield of propylene was 52.1% at 10 minutes of reaction time and decreased with reaction time down to 25.8%. The yield of 2-isopropylphenol increased with time up to 57.9% and that of 2-propylphenol increased up to 6.9%. The yield of 2,6-diisopropylphenol increased up to 5.9% at 45 minutes and subsequently decreased to 5.2% at 60 minutes reaction time. After 45 minutes, the reaction appeared to be at equilibrium. In contrast, Chandler *et al.*[7] reported that the reaction did not reach equilibrium even after 120 hours of reaction time at 548 K.

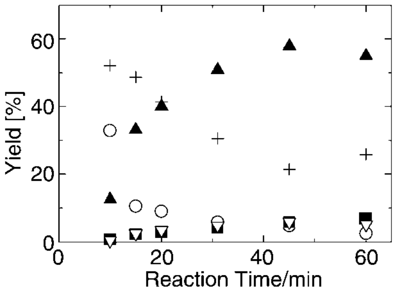

Fig. 1 Yield of (+) propylene, (▲) 2-isopropylphenol, (■) 2-propylphenol and (∇) 2,6-diisopropylphenol for reaction of phenol with propan-2-ol (○) at 0.5 g cm^{-3} of water density and 673 K.

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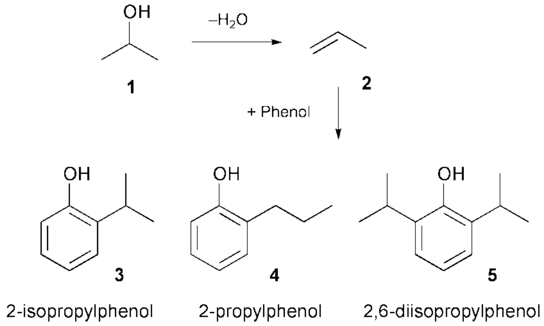
The dehydration of propan-2-ol yielded propylene at the early reaction times. Alkylphenols dissociate in its aqueous solution, as shown by Xiang *et al.*[11] who reported that β-naphthol dissociates even in supercritical water. For example, the dissociation constant of β-naphthol is 1.26×10^{-11} mol kg^{-1} at 673 K and 0.5 g cm^{-3} of water density. At room temperature and pressure, the dissociation constant of phenol (pK_a = 9.89) at 293 K and 0.1 MPa was similar to that of β-naphthol (pK_a = 9.51) at 298 K and 0.1 MPa.[12] Phenol probably dissociates in supercritical water. Antal *et al.*[13] reported that the acid-catalyzed dehydration of propan-2-ol yielded propylene in high temperature water at 593 K.

Considering these experimental findings, the reaction pathway shown in Scheme 1 was developed. The dehydration of propan-2-ol (**1**) probably yields propylene (**2**), following alkylation of phenol with propylene to 2-isopropylphenol (**3**), 2-propylphenol (**4**) and 2,6-diisopropylphenol (**5**). It is probable that phenol acts as an acid catalyst and promotes the dehydration of propan-2-ol at supercritical conditions.



Scheme 1

The alkylation of phenol with propylene yielded 2-isopropylphenol, 2-propylphenol and 2,6-diisopropylphenol and this reaction was the rate-determining step. Phenoxyether was not produced, probably because hydrolysis of ethers occurs readily in supercritical water.[5] Phenol was alkylated almost solely at the *ortho* position of the hydroxy group even in the homogeneous system as obtained in high temperature water by Chandler *et al.*[7] The hydroxy group of phenol and several water molecules can construct a ring structure formed by hydrogen-bonds[14] and the distance between hydroxy oxygen and hydrogen increases with increasing the number of water molecules in a ring structure.[15] In supercritical carbon dioxide, specific solvation around the hydroxy group of phenol can occur.[16] Taking these results into account, water molecules probably locate around the hydroxy group of phenol at supercritical conditions and construct a ring structure with the hydroxy group of phenol. Then, the dissociation of the hydroxy group is promoted locally around it. This makes the reaction field limited only around the hydroxy group, which results in mainly the *ortho* position being alkylated.

The data reported above were measured at 0.5 g cm^{-3} of water density. At these conditions, the phase in the reactor was probably homogeneous and phenol was dissociated to a certain extent as discussed previously. In order to determine the effect of phase behavior and the dissociation of phenol, we conducted the experiment at various water densities from 0 g cm^{-3} (in Ar atmosphere) to 0.5 g cm^{-3} and at reaction times of 60 minutes. The sum of the yield of alkylphenol was less than 2.4% below 0.3 g cm^{-3} of water density. Table 1 shows the yield of propan-2-ol (**1**), 2-isopropylphenol (**3**), 2-propylphenol (**4**) and 2,6-diisopropylphenol (**5**) at 673 K and more than 0.3 g cm^{-3} of water density. The yields of all alkylphenols increased with increasing water density at more than 0.4 g cm^{-3} of water density, compared with the yield of propan-2-ol. This result clearly shows that alkylation was accelerated with increasing water density. We consider that phase behavior and the concentration of protons can affect the reaction. At low water density, the reactants were separated into two phases. Phenol would probably be mainly distributed in the liquid phase while the propan-2-ol would be distributed in the gas phase. With increasing water density, the phase in the reactor probably became homogeneous. In addition, the dissociation constant of β-naphthol increases with increasing water density in supercritical water.[11] This trend seems to be applicable to the dissociation of phenol. If the dissociation constant of phenol increased with increasing water density, the concentration of protons also increased. Then, dehydration and alkylation was promoted with increasing water density, because the proton catalyzed both reactions.

Table 1 Yield of propan-2-ol and alkylphenols with water density for 60 minutes of reaction time at 673 K, $[\text{propan-2-ol}]_0$ = 0.33 mol L^{-1}, $[\text{phenol}]_0$ = 1.65 mol L^{-1}

Water density/ g cm^{-3}	Yield (%)			
	1	**3**	**4**	**5**
0.3	75.9	3.1	0.3	0
0.4	58.5	18.0	2.2	0.6
0.42	13.7	45.5	5.8	3.7
0.46	4.5	55.1	7.1	5.1
0.48	3.6	58.8	7.5	5.4
0.5	2.6	55.0	6.9	5.1

In summary, phenol was alkylated with propan-2-ol without catalyst in supercritical water at 673 K. The alkylphenols obtained were mainly *ortho* substituted compounds and the maximum yield of 2-isopropylphenol was 58.8%. The sum of *ortho* alkylphenols yield was 71.7%. Further, alkylation was enhanced with increasing water density. Our results show that supercritical water can provide a unique reaction field for the alkylation, which is non-catalytic and highly selective.

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