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著者 (英)	Tsunehisa Hirashita, Shuki Araki, Takao Tsuda, Shinya Kitagawa, Takayuki Umeyama, Mutsumi Aoki, Koichi Nakamura
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Reaction of hydroxybenzyl alcohols under hydrothermal conditions

Tsunehisa Hirashita,^{*a} Shuki Araki,^a Takao Tsuda,^{ab} Shinya Kitagawa,^a Takayuki Umeyama,^a Mutsumi Aoki^c and Koichi Nakamura^{cd}

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Under hydrothermal conditions, salicylic alcohol and *p*-hydroxybenzyl alcohol were transformed into phenol in high or moderate yields, whereas *m*-hydroxybenzyl alcohol and benzyl alcohol proved to be stable and remained almost intact.

Organic reactions in water have attracted considerable attention as a way of improving environmentally benign chemical processes, which obviate the need for harmful organic solvents.¹ One of the major obstacles is the poor solubility of organic compounds in ambient water. The properties of water can be tuned to overcome this difficulty by performing the reaction under hydrothermal conditions.² The dielectric constant of water decreases with increasing temperature close to the critical point, which makes it easier to solvate hydrophobic organic compounds in water. In addition, the ionic product of water increases with increasing temperature up to 10^{-11} in the range of 200–300 °C. Hence, the reaction under hydrothermal conditions provides a broad range of possibilities for chemical transformations that are not realized in ambient water.

Recently some researchers have focused their attention on woody biomass due to the growing concern of new energy and chemical resources.³ After cellulose, lignin is the second most abundant polymer on earth.⁴ In order to utilize lignin for any purpose, we must depolymerize lignin and convert it into low molecular weight compounds in an environmentally friendly way. The hydrothermal reaction seems to be a desirable procedure for this and reactions of lignin and related compounds have been documented.⁵ Hydroxybenzyl alcohols can be regarded as some of the model compounds of lignin. However, less attention has been paid to their reactions under hydrothermal conditions. The reactions of hydroxybenzyl alcohols in *organic* solvents at elevated temperature have been reported, where the benzylic cation is considered to be a reactive intermediate and benzyl ethers were mainly formed when alcohols were employed as a solvent.⁶

Here we describe the reaction behaviour of a series of hydroxybenzyl alcohols (Fig. 1), in which the location of the phenolic hydroxy and hydroxymethyl groups proved to be

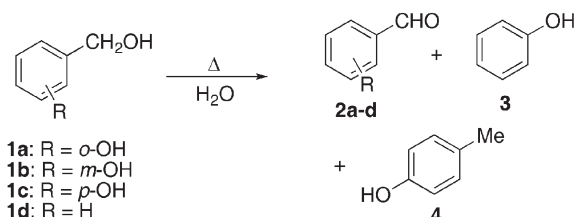


Fig. 1 Reaction of benzyl alcohols under hydrothermal conditions.

important for the level of conversion into phenol under hydrothermal conditions.

The present experiment was conducted with a laboratory made apparatus based on a commercially available HPLC system and a GC oven as shown in Fig. 2.⁷ The sample was dissolved in water containing a small amount of methanol (1%) and the aqueous solution (80 mM) was pumped to the reaction pressure and heated in the oven. The reaction period was regulated by the flow rate of pump A; pump B controlled the pressure by supplying distilled water.⁸ The length of the reactor line was 5 m (0.8 mm id) and the flow rate was adjusted to 0.2 mL min⁻¹ for all experiments. After cooling to room temperature, the products were immediately analyzed by LC and GC-MS. This system permits us to perform a rapid analysis under changing conditions; approximately only 20 min are required to complete a single experiment.

The hydrothermal reaction of salicylic alcohol (**1a**) did not proceed at 200 °C and 22.5 MPa and the starting alcohol was completely recovered (entry 1, Table 1). However, by elevating the temperature up to 300 °C, salicylic aldehyde (**2a**) and phenol (**3**) were obtained in 20% and 65% yields, respectively (entry 2). Under supercritical conditions, **1a** completely disappeared and **2a** and **3** were also obtained (entry 3). *m*-Hydroxybenzyl alcohol (**1b**) was more stable than **1a** under the hydrothermal conditions and the oxidation proceeded at 300 °C to give a small amount of *m*-hydroxybenzaldehyde (**2b**) (entry 4). Phenol (**3**) was not observed from **1b** under supercritical conditions (entry 5). The reaction of *p*-hydroxybenzyl alcohol (**1c**) at 300 °C afforded **3** together with trace amounts of *p*-hydroxybenzaldehyde (**2c**) and *p*-cresol (**4**) (entry 6). It should be noted that the formation of cresol from hydroxybenzyl alcohols was only observed in the case of **1c**. Benzyl alcohol (**1d**) was stable compared with hydroxybenzyl alcohols and small amounts of benzaldehyde (**2d**) were found at 300 °C and 390 °C, with the recovery of unreacted **1d** (entries 8 and 9).

At the high temperature (390 °C), low total yields were obtained (entries 3, 5, and 7). We found unidentified resinous materials between the cooling loop and the sample collecting loop, indicating some side reactions took place to cause the erosion of the mass balance.

^aDepartment of Materials Science and Engineering, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso, Showa, Nagoya 466-8555, Japan. E-mail: hirasita@nitech.ac.jp; Fax: +81 52-735-5206; Tel: +81 52-735-5206

^bPico-Device Co., Ltd., Incubation Center, Nagoya Institute of Technology, Gokiso, Showa, Nagoya 466-8555, Japan

^cDepartment of Computer Science and Engineering, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso, Showa, Nagoya 466-8555, Japan

^dKaela R&D Co., Inc., Incubation Center, Nagoya Institute of Technology, Gokiso, Showa, Nagoya 466-8555, Japan

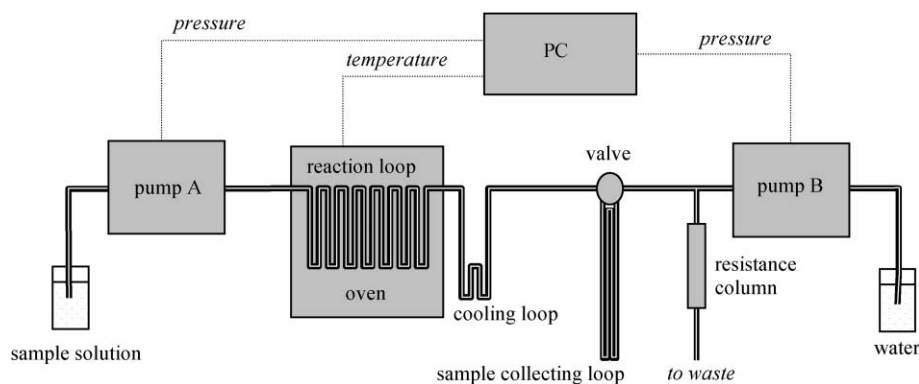
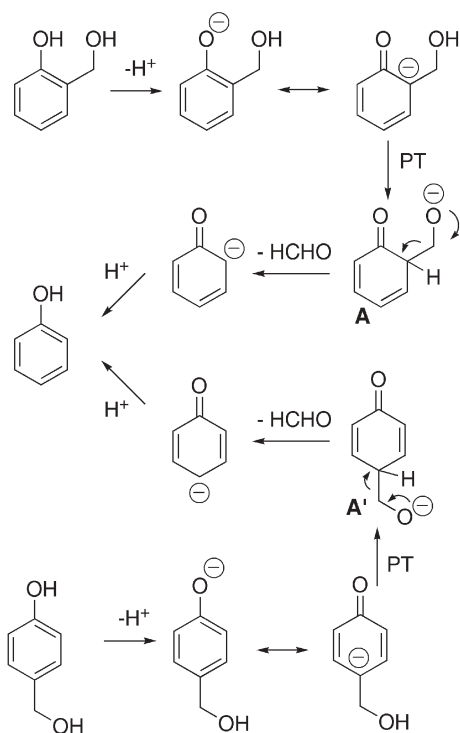


Fig. 2 Apparatus for hydrothermal reactions.

Table 1 Results of hydrothermal treatment of a series of benzyl alcohols

Entry	1	$T/^\circ\text{C}$	P/MPa	Yield and recovery (%)			
				2	3	4	1
1	1a	200	22.5	<1	<1	0	>99
2	1a	300	22.5	20	65	0	17
3	1a	390	23.5	7	63	0	0
4	1b	300	22.5	2	0	0	98
5	1b	390	23.5	39	0	0	32
6	1c	300	22.5	<1	34	3	56
7	1c	390	23.5	1	21	24	11
8	1d	300	22.5	<1	0	0	86
9	1d	390	23.5	8	0	0	85

A most plausible mechanism to form phenol is depicted in Scheme 1. The formation of phenol may be attributed to a facile dissociation of the phenolic proton under the hydrothermal conditions. The resulting phenoxide liberates formaldehyde via



Scheme 1 Plausible reaction pathway to form phenol.

proton transfer leading to phenol. The distinctive reaction behaviour observed in 1a and 1c reveals the crucial contribution of the intermediates A and A' which can be easily transformed into phenol by release of formaldehyde. The highest conversion was achieved with the reaction of 1a in which the *o*-hydroxymethyl group is considered to promote a dissociation of the phenolic hydroxy proton under the hydrothermal conditions.⁹

The present results provide informative examples for depolymerization of lignin and related compounds under hydrothermal conditions. Further studies for transformation of organic compounds using this system are currently in progress.

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