Phenolic Solvent-Assisted Hydrogenolysis of *trans*-Stilbene

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Phenolic solvents such as phenol, 3,4-xylenol, 2-naphthol, and 5,6,7,8-tetrahydro-2-naphthol greatly promote toluene formation in the hydrogenolysis of *trans*-stilbene, compared with hydroaromatic hydrocarbon solvents. Toluene is afforded in the thermal decomposition of the phenolic solvent adduct to *trans*-stilbene, not via bibenzyl.

It is well-known that mixed solvents composed of phenols and tetralin greatly promote coal liquefaction.[1-7)]

Considerable amounts of phenolic compounds are produced inherently in coal liquefaction[3)] and their ambident character is quite interesting as acid catalyst[4)] and polar media penetrating into the micropores of coal and dissolving polar and high molecular weight components of coal liquids formed during coal liquefaction.[3,6)]

Mechanisms for the action of phenols have already been investigated by some groups, using model compounds such as di-2-naphthyl ether,[4)] *p*-hydroxyphenyl phenyl ether,[8)] benzyl phenyl ether, and dibenzylamines.[9)] In these systems, however, unified interpretations have not been made on the source of donatable hydrogen and hydrogen transfer mechanism (homolytic[4,9)] or heterolytic[8)] cleavage of the O–H bond).

Quite recently, we have shown that phenolic solvents are greatly effective in the hydrogenolysis of *trans*-stilbene, compared with hydroaromatic hydrocarbon solvents.[10)] Since olefinic structures can be formed transiently during coal liquefaction, it is significant to clarify the reactivity of phenols toward aromatic olefins in their hydrogenolysis and solvent addition.

In this paper, we present that phenolic solvents can act as hydrogen-donor solvent under coal liquefaction conditions and that they promote hydrogenolysis of aromatic olefins such as *trans*-stilbene via solvent addition.

Experimental

Materials. The following substrates and solvents were commercially purchased and further purified if needed by the conventional method: *trans*-stilbene, bibenzyl, phenol, 3,4-xylenol, 2-naphthol, 5,6,7,8-tetrahydro-2-naphthol(THN), tetralin, 9,10-dihydroanthracene(DHA), and naphthalene.

Instrumental. The GC analyses were carried out on a Shimadzu GC-9A-TCD apparatus equipped with a stainless steel column of 5% OV 17 on Chromosorb W(DMCS). The ^{1}H NMR spectra of the products were obtained on a Varian EM 360A NMR Spectrometer (60 MHz), using Me_4Si as an internal standard.

Batch Experiments. 10 mmol of *trans*-stilbene or bibenzyl and a 10-fold molar excess of a solvent were put into a 90 ml SUS 316 magnetically stirred autoclave. After being pressurized up to 2.0 MPa, the autoclave was heated up to the prescribed temperature within 30 min and maintained at the temperature for 30 min. After the reaction, the autoclave was cooled by an electric fan to room temperature. The products were recovered with tetrahydrofuran and subjected to GC analysis using chlorobenzene as an internal standard.

Product Analyses. The yields of toluene, bibenzyl, *o*- and *p*-benzylphenols were analyzed by GC. (1,2-Diphenylethyl)-phenols[11)] were isolated by silica-gel column chromatography and identified by means of ^{1}H NMR and GC-MS. Their ^{1}H NMR and GC-MS data are as follows: δ=3.17 (d, 2H, J=7.2 Hz), 4.33 (t, 1H, J=7.2 Hz), 5.14 (s, 1H, exchangeable with D_2O), 6.62—7.06 (m, 14H). m/z=274 (2.5 (M^+)), 183 (100), 165 (46), 91 (17).

Results and Discussion

As Table 1 shows, phenolic solvents such as 3,4-xylenol, 2-naphthol, and THN show higher hydrogen-

Table 1. Solvent Effect on Hydrogenolysis of *trans*-Stilbene(t-ST)

Solvent	Conv. of t-ST/mol%	Yield of BB/mol%	Yield of TOL/mol%	Conv. of Solvent/mol%
DHA	100	97	6	
2-Naphthol	91	67	16	17
THN	84	59	25	12
3,4-Xylenol	91	54	26	22
Tetralin	33	27	1.1	5.4
Naphthalene	13	13	—	

t-ST 10 mmol; solvent 100 mmol; reaction temperature 400 °C; initial hydrogen pressure 2.0 MPa; reaction time 30 min. BB = Bibenzyl, TOL = toluene.

Table 2. Solvent Effect on Molar Ratio [Toluene(TOL)]/[Bibenzyl(BB)] in the Hydrogenolyses of *trans*-Stilbene(t-ST) and BB

Solvent	[TOL]/[BB] from t-ST=A	[TOL]/[BB] from BB=B	Ratio A/B
Phenol	1.38	0.04	34.5
2-Naphthol	0.24	0.008	30
THN	0.43	0.01	43
Tetralin	0.02	0.01	2.0

Substrate 10 mmol; solvent 100 mmol; reaction temperature 400 °C; initial hydrogen pressure 2.0 MPa; reaction time 30 min.

Table 3. Activation Energies(Ea) and Frequency Factors for the Hydrogenolysis of *trans*-Stilbene

Solvent	Ea/kcal mol^{-1} a)	A factor/mol^{-1} s^{-1}
2-Naphthol	32.6	6×10^7
THN	31.1	9×10^6
Tetralin	29.4	8×10^5

a) 1 cal = 4.184 J.

donatabilities than tetralin in the hydrogenolysis of *trans*-stilbene at 400 °C. It is noteworthy that toluene formation is greatly promoted by these solvents, contrasting with hydroaromatic hydrocarbon solvents.

Table 2 shows a solvent effect on molar ratio of toluene/bibenzyl in the hydrogenolyses of *trans*-stilbene and bibenzyl. If toluene is afforded exclusively via the thermal cracking of bibenzyl, ratio A/B in Table 2 is expected to fall around unity. In fact, this ratio is given as 2 for tetralin as solvent. On the other hand, 30- to 40-fold increase in ratio A/B is observed for the phenolic solvents. These facts suggest that in the phenolic solvents, toluene could be given in the common mechanism other than the thermal cracking of bibenzyl.

A good linearity was observed in the first-order plot for *trans*-stilbene conversion in the temperature range of 380—435 °C. Figure 1 shows the plot of ln k_{obsd} versus $1/T$ depicted on the basis of the above data. As Table 3 shows, almost no difference is observed in the activation energies for 2-naphthol, THN, and tetralin as solvent.

On the other hand, 10 to 100 times larger values of frequency factor are obtained for the phenolic solvents compared with tetralin. Such difference still has to be unravelled, but it may indicate that some ionic interaction between phenols as weak acids and *trans*-stilbene as π-base is effective in formation of the encounter complex.

Thus, hydrogenolysis of *trans*-stilbene in phenol was carried out in order to understand the reaction profile. As Fig. 2 shows, 71% of *trans*-stilbene was converted in this reaction, and bibenzyl, toluene, benzylphenol, and (1,2-diphenylethyl)phenol(DPEP) were afforded in 27, 19, 24, and 19% selectivities, respectively. Neither benzene nor ethylbenzene was obtained in this reaction. According to GC analysis, benzylphenol was a 2.7 : 1.0 mixture of *o*- and *p*-forms. Phenol adduct to *trans*-stilbene, DPEP is considered to be formed in the coupling of 1,2-diphenylethyl radical and phenoxyl radical or in the addition of 1,2-diphenylethyl radical to phenol followed by loss of a hydrogen atom. Since 1,2-diphenylethyl radical is detected by ESR[12] and is known to be produced in the pyrolysis of bibenzyl,[13] it can be also produced in the monohydrogen transfer from phenol to *trans*-stilbene.

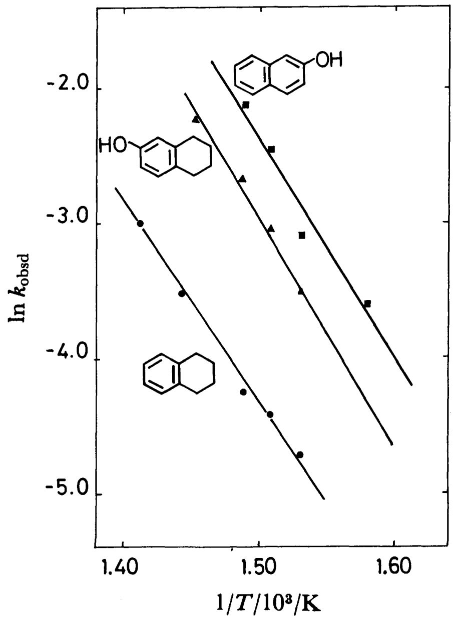


Fig. 1. The plot of ln k_{obsd} versus $1/T$ for *trans*-stilbene conversion.

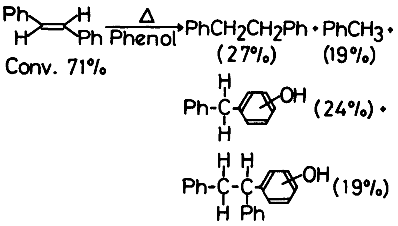
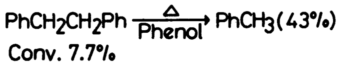


Fig. 2. Hydrogenolysis of *trans*-stilbene in phenol. Parentheses denote selectivities.

1,2-Diphenyl-1-phenoxyethane(DPPE), one of the solvent adducts was not obtained in this reaction. Thermal instability of benzyl phenyl ether at 340 °C[14] suggests that all of DPPE decompose thermally at 400 °C.

The larger value for ratio toluene/bibenzyl from *trans*-stilbene in phenol (1.38) in Table 2 may reflect less steric hindrance of phenol or phenoxyl radical toward the approach of 1,2-diphenylethyl radical.



$$PhCH_2CH_2Ph \xrightarrow[Phenol]{\Delta} PhCH_3(43\%)$$

Conv. 7.7%

Fig. 3. Hydrogenolysis of bibenzyl in phenol. Parenthesis denotes selectivity.

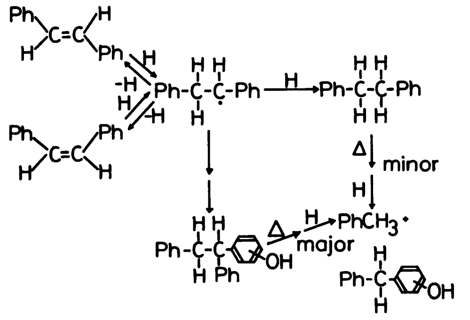


Fig. 4. Possible mechanism for the hydrogenolysis of *trans*-stilbene in phenol.

In these systems, isomerization of stilbene from trans to cis is observed during the course of the reaction. Although no *cis*-stilbene can be detected, using DHA as solvent, about 5% of stilbene is recovered as a cis-form in the phenolic solvents at 380 °C. This value is a little larger than that obtained in the isomerization of *trans*-stilbene to *cis*-stilbene in naphthalene. Such solvent effect on the distribution of the stilbene isomers also supports the homolytic monohydrogen transfer mechanism from phenolic solvents to *trans*-stilbene, and the concerted mechanism can be precluded.

Under these reaction conditions, only 7.7% of bibenzyl was converted to give toluene in 43% selectivity. No benzylphenol was detected by GC in this reaction(see Fig. 3). Therefore, it is unlikely that toluene and benzylphenol were derived from the benzyl radical produced in the thermal cracking of bibenzyl under the reaction conditions. 68% of DPEP decomposed to afford benzylphenol and toluene in 66 and 61% selectivities, respectively, under the same conditions. Since the carbon to carbon single bond in DPEP is more labile than that of bibenzyl, toluene and benzylphenol could be produced in the thermal cracking of DPEP as Fig. 4 shows.

Proton transfer from phenol to *trans*-stilbene is another possibility,[5] but bibenzyl formation from 1,2-diphenylethyl cation cannot be explained by this mechanism.

Here remains the question as to the transferable hydrogen in the phenolic solvents. Comparison of the hydrogen donatabilities of 2-naphthol and naphthalene in Table 1 suggests the involvement of phenolic hydrogens in the hydrogen-transfer process. Thus, hydrogenation of *trans*-stilbene was carried out using a 7:3 mixture of 2-NpOD and 2-NpOH. GC-MS analysis shows that deuterated bibenzyls are formed as shown in Fig. 5. According to GC analysis, the conversion of 2-naphthol(2-NpOD+2-NpOH) was lower than that of 2-NpOH by 10%. ^{1}H NMR spectroscopy showed that scrambling between phenolic hydrogens and aromatic ring hydrogens was negligible under the reaction conditions. All these facts suggest that phenolic hydrogens are really used in the hydrogenolysis of *trans*-stilbene.

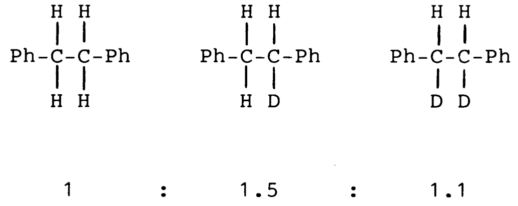


Fig. 5. Deuterium distribution in bibenzyl.

In conclusion, it has been shown that hydrogenolysis of *trans*-stilbene is promoted by the phenolic solvents such as phenol, 3,4-xylenol, 2-naphthol, and 5,6,7,8-tetrahydro-2-naphthol via the phenolic solvent adduct to *trans*-stilbene. Hydrogen-transfer from these phenolic solvents is considered to proceed by radical mechanism.

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