

MECHANISMS FOR NONCATALYTIC AND CATALYTIC HYDROGEN TRANSFER PROCESSES UNDER COAL LIQUEFACTION CONDITIONS

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INTRODUCTION

Recent progress in the chemistry of coal liquefaction has enabled us to envisage that radical-induced monohydrogen transfer is one of the key processes in the hydrogenolysis of strong bonds bridging aromatic units in coal [1-4]. We have succeeded in verifying that radical mechanism operates in the noncatalytic and Fe-catalyzed hydrogenolyses of reporter molecules such as trans-stilbene [5] and 9-benzylphenanthrene [6].

This paper intended to discuss 1) hydrogen transfer mechanisms for hydrogenolyses of the above compounds, 2) selectivities of benzylic radicals toward addition to aromatic nucleus and hydrogen abstraction in hydroaromatic hydrocarbon solvents, 3) catalysis of Fe compounds in solvent-mediated hydrogen transfer processes, and 4) reactant dependent catalytic activities of Fe compounds such as Fe_2O_3 , $\alpha\text{-Fe}$, and Fe_{1-x}S .

EXPERIMENTAL

Materials

9-Benzylphenanthrene (9-BP) and di(1-naphthyl)methane (DNM) were synthesized according to the method described in the previous paper [4]. trans-Stilbene and the solvents were commercially purchased and purified if necessary by conventional methods. $\alpha\text{-Fe}$ was prepared by reducing Fe_2O_3 in hydrogen streams at 450°C for 20 h. Its BET surface area was $14.2 \text{ m}^2\text{g}^{-1}$ (Shimadzu 2200). Fe_{1-x}S was prepared by reacting $\alpha\text{-Fe}$ with a small excess of elemental sulfur in tetralin under nitrogen at 380°C for 30 min. Its BET surface area was $10.4 \text{ m}^2\text{g}^{-1}$. The above catalysts were identified by X-ray diffraction analysis (Rigaku Denki RU-200A). After preparation, they were immediately immersed in 1-methylnaphthalene (1-MN) or in tetralin in a dry box under nitrogen and kept until use.

Batch experiments

A reaction solution consisting of a model compound and a hydrocarbon solvent with or without an Fe catalyst was put into a 90 ml SUS 316, magnetically stirred autoclave, pressurized by hydrogen or nitrogen. It was heated up to a reaction temperature and was kept there for 30 min. After the reaction, the autoclave was cooled by an electric fan to room temperature.

Product analysis

Benzyl(1-methylnaphthalene (BMN), 1-benzyl naphthalene (1-BN), and octahydrobinaphthalenes were identified by GC-MS (JEOL JMS-

DX300, equipped with a glass column (4mm diameter, 1m length) of 5 % OV-1 on Chromosorb W). 6-Benzyl-1,2,3,4-tetrahydronaphthalene (BTHN) and 6-(1,2-diphenylethyl)-1,2,3,4-tetrahydronaphthalene (DETN) were isolated by column chromatography and vacuum distillation, and they were identified by MS, $^1\text{H-NMR}$ (Varian EM 360A (60 MHz)), and $^{13}\text{C-NMR}$ (JEOL JMN-GX-400 (400 MHz)).

The reaction products collected with tetrahydrofuran were analyzed quantitatively by GC (Shimadzu GC-4C, equipped with a stainless column (4 mm diameter, 4 m length) of 10 % OV-17 on Chromosorb W (DMCS)).

RESULTS AND DISCUSSION

Reaction products

The spectral data of the reaction products obtained in the hydrogenolyses of trans-stilbene and 9-BP are as follows.

BMN m/z: 232 (100, M^+), 217 (68), 115 (13).

1-BN m/z: 218 (100, M^+), 217 (55), 141 (17).

BTHN m/z: 222 (62, M^+), 131 (100), 91 (36). $^1\text{H-NMR}$ δ in CCl_4 (ppm) 1.69 (4H, m), 2.62 (4H, m), 3.77 (2H, s), 6.80 (3H, bs), 7.09 (5H, bs). $^{13}\text{C-NMR}$ δ in CDCl_3 (ppm) 23.24, 23.30, 29.01, 29.39, 41.59, 125.89, 126.06, 128.36, 128.85, 129.17, 129.48, 134.74, 137.06, 138.10, 141.44.

DETN m/z: 312 (2.3, M^+), 221 (100), 91 (17). $^1\text{H-NMR}$ δ in CCl_4 (ppm) 1.39-2.12 (4H, m), 2.32-3.04 (4H, m), 3.21 (2H, d, $J=7.6$ Hz), 4.05 (1H, dd, $J=7.6$ Hz), 6.56-7.48 (13H, m). $^{13}\text{C-NMR}$ δ in CDCl_3 (ppm) 23.22, 23.24, 28.96, 29.44, 42.18, 52.75, 127.91, 128.06, 128.12, 128.30, 128.34, 128.49, 128.64, 128.92, 129.12, 134.82, 136.85, 140.46, 141.62, 144.63.

The regiospecific formation of DETN and BTHN was described in the previous paper [5].

1,1',2,2',3,3',4,4'-Octahydrobinaphthalenes m/z: 262 (22, M^+), 131 (100), 130 (68), 91 (32). 1,2,3,4,5',6',7',8'-Octahydrobinaphthalenes m/z: 262 (50, M^+), 130 (100), 104 (84).

Hydrogen transfer mechanism for the hydrogenolysis of trans-stilbene

trans-Stilbene can be a pertinent probe in order to verify hydrogen transfer mechanism and to characterize hydrogen donating abilities of solvents and activities of catalysts because the degree of stilbene isomerization can be a measure for mechanism determination, and dibenzyl cannot be dehydrogenated to trans-stilbene at 380°C.

Figure 1 shows the plot of the cis-stilbene content against the stilbene conversion. A fairly good linear correlation suggests that the stilbene isomerization cannot be ascribed to thermochemical equilibration of trans- and cis-stilbenes, supporting radical mechanism. A possible intermediate could be 1,2-diphenylethyl radical because the step from 1,2-diphenylethyl cation to dibenzyl is unlikely. In fact, the adduct of this radical to tetralin (DETN) was obtained in the hydrogenolysis of trans-stilbene in the presence of $\alpha\text{-Fe}$. These findings may suggest that 1,2-diphenylethyl radical is an intermediate in the

hydrogenation of trans-stilbene. Since the acidity of α -Fe is negligible [7], 1,2-diphenylethyl radical stabilized on the surface of α -Fe could be trapped by tetralin solvent.

Selectivities of benzylic radicals toward addition and hydrogen abstraction

Table 1 summarizes some data on selectivities of benzylic radicals toward addition and hydrogen abstraction, which are relevant to radical-induced monohydrogen transfer from solvents. Dibenzyl added in the system of DNM and a solvent (Reaction 1) thermally decomposes to selectively give benzyl radicals. Their relative reactivity of addition to hydrogen abstraction is 0.015 in tetralin and 0.033 in 1-MN. These findings are the first example of ipso-substitution by benzyl radicals, i.e., alkyl-dealkylation [8].

This type of benzyl radical addition to the aromatic nucleus is promoted by α -Fe in the hydrogenolysis of 9-BP (Reaction 2), where only a low concentration of the benzyl radical is present.

As described above, addition of 1,2-diphenylethyl radical to tetralin can be observed only in the presence of α -Fe, and the relative ratios of addition to hydrogen abstraction are around 0.2 at initial hydrogen pressure of 1.0 to 6.0 MPa (Reaction 3). On the other hand, $Fe_{1-x}S$ promoted further hydrogenation to give dibenzyl in higher selectivities. When tetralin was used as solvent, trace amounts of octahydrobinaphthalenes were obtained only in the presence of α -Fe.

In a binary solvent system of 9,10-dihydrophenanthrene (DHP) and 1-MN, only dibenzyl was obtained from stilbenes with no formation of 1,2-diphenylethylphenanthrene or benzylphenanthrene. This fact can be ascribed to the rapid capping of 1,2-diphenylethyl radical by DHP, which is a superior hydrogen donor.

The chemical behavior of 1,2-diphenylethyl radical could be affected by hydrogen donating ability of solvent and stability of solvent adduct itself.

These data confirm that monohydrogen transfer predominates from hydroaromatic radicals such as tetralyl and hydrophenanthryl.

Catalysis of Fe compounds in solvent-mediated hydrogenolysis of trans-stilbene

Table 2 shows the effects of Fe catalysts and hydrogen pressure on the hydrogenation of trans-stilbene in 1-MN. Comparison of Runs 1 and 3 shows that catalytic hydrogen transfer from 1-MN to trans-stilbene is negligible, and only about 2 % of 1-MN is consumed in these cases. Direct hydrogenation of trans-stilbene by molecular hydrogen is rather slow in the absence of α -Fe in 1-MN (see Runs 2 and 4). $Fe_{1-x}S$ showed a comparable catalytic activity, but it was more effective as hydrogenation catalyst than α -Fe. The differences in the trans-stilbene conversions and in the dibenzyl yields between Runs 1, 4, and 5 give the baseline increments caused by the α -Fe-catalyzed hydrogenation of trans-

stilbene, and comparison of Runs 1, 7, and 8 gives the corresponding increments for the $Fe_{1-x}S$ -catalyzed reactions.

Comparison of Runs 9, 11, and 14 (Table 3) clearly shows that intermolecular hydrogen transfer from tetralin to trans-stilbene is greatly promoted by α -Fe and $Fe_{1-x}S$. Dibenzyl yield increments at 6.0 MPa of hydrogen in the presence of α -Fe and $Fe_{1-x}S$ were 45 and 63%, respectively. The expected increment caused by catalytic incorporation of molecular hydrogen is not more than 25% for α -Fe (compare Runs 2 and 5) and 26% for $Fe_{1-x}S$ (compare Runs 2 and 8). Thus, in the system of H_2 -tetralin-Fe catalyst, trans-stilbene could be hydrogenated predominantly on the catalytic cycle.

Ogawa and coworkers have shown that the catalytic activity of $Fe_{1-x}S$ highly depends on H_2S pressure in the hydrocracking of diphenylmethane without solvent at 450°C [9]. At low pressures of H_2S , $Fe_{1-x}S$ is converted to FeS which is less active than $Fe_{1-x}S$. However, our results clearly show that both of α -Fe and $Fe_{1-x}S$ promote tetralin-mediated hydrogen transfer from gaseous hydrogen. Since dry coal liquefaction is not so feasible, catalyzed solvent-mediated hydrogen transfer could be a key reaction in coal liquefaction.

Reactant dependent catalytic activities of Fe compounds

As Table 4 shows, the catalytic activities of Fe compounds in the hydrogenolysis of 9-BP decreased in the order: α -Fe > $Fe_{1-x}S$ > Fe_2O_3 . The apparent catalytic activity of Fe_2O_3 can be ascribed to that of α -Fe partly produced in the deoxygenative reduction of Fe_2O_3 during the course of the reaction. The above order is different from that for the hydrogenolysis of trans-stilbene at 380°C. Almost the same product distributions with α -Fe and $Fe_{1-x}S$, and negligible surface area changes of both the catalysts suggest the catalyst dependent adsorption behavior of 9-BP, i.e., 9-BP is selectively adsorbed at its 9,10-position on α -Fe, while 9-BP is competitively adsorbed at its 1,2-, 3,4-, 5,6-, 7,8-, 9,10- positions on $Fe_{1-x}S$ [10]. For radical A in Scheme 1, a benzyl radical release is energetically more favorable than that of a hydrogen atom, promoting the hydrogenolysis of 9-BP. On the other hand, reversible hydrogen atom elimination predominates over subsequent hydrogenation for radicals $B \sim F$, which decreases the apparent conversion of 9-BP.

These data suggest that the regioselectivity of 9-BP adsorption is lost on $Fe_{1-x}S$ compared to α -Fe, and that radicals $B \sim F$ are competitively formed against radical A.

The lack of such catalyst dependence of trans-stilbene hydrogenolysis can be ascribed to the stronger adsorbing ability of the olefinic moiety in trans-stilbene.

Figure 2 shows the relationship between the 9-BP conversion and the yield of naphthalene derived from tetralin. A good linear correlation suggests that the bimolecular hydrogen transfer from tetralin to 9-BP is promoted by α -Fe and $Fe_{1-x}S$.

CONCLUSION

We have shown that in the noncatalytic and Fe-catalyzed hydrogenolyses of trans-stilbene and 9-benzylphenanthrene, radical mechanism operates, and that bimolecular hydrogen transfer from solvents is promoted by α -Fe and $Fe_{1-x}S$ without overhydrogenation of aromatic nuclei.

REFERENCES

1. Y. Kamiya, S. Futamura, T. Mizuki, M. Kajioka, and K. Koshi, *Fuel Proc. Technol.*, **14**, 79 (1986).
2. Y. Kamiya, E. Ogata, K. Goto, and T. Nomi, *Fuel*, **65**, 586 (1986).
3. D. F. McMillen, R. Malhotra, S.-J. Chang, W. C. Ogier, S. E. Nigenda, and R. H. Fleming, *Fuel*, **66**, 1611 (1987).
4. S. Futamura, S. Koyanagi, and Y. Kamiya, *Fuel*, **67**, 1436 (1988).
5. S. Futamura, K. Fujimoto, and Y. Kamiya, *Bull. Chem. Soc. Jpn.*, **63**, 2564 (1990).
6. S. Futamura, S. Koyanagi, and Y. Kamiya, *J. Fuel Soc. Jpn.*, in press.
7. K. Tanabe and H. Hattori, *Sekiyu Gakkaishi*, **29**, 280 (1986).
8. M. Tiecco and L. Testaferri in 'Reactive Intermediates', Vol. 3 (Ed. R. A. Abramovitch), Plenum Press, New York, 1983, p. 88.
9. T. Ogawa, V. I. Stenberg, and P. A. Montano, *Fuel*, **63**, 1660 (1984).
10. M. Minabe and K. Nakada, *Bull. Chem. Soc. Jpn.*, **58**, 1962 (1985).

Table 1 Selectivities of Benzylic Radicals toward Addition and Hydrogen Abstraction.

Reaction	Solvent	Catalyst	Radical	Addition/H abstraction
1	Tetralin	None	Benzyl	0.015 [b]
1	1-MN	None	Benzyl	0.033 [b]
2	Tetralin	Fe_2O_3	Benzyl	~ 0
2	Tetralin	α -Fe	Benzyl	0.057 [c]
2	Tetralin	$Fe_{1-x}S$	Benzyl	~ 0
2	1-MN	Fe_2O_3	Benzyl	~ 0
2	1-MN	α -Fe	Benzyl	0.14 [d]
2	1-MN	$Fe_{1-x}S$	Benzyl	~ 0
3	Tetralin	None	[a]	~ 0
3	Tetralin	α -Fe	[a]	0.21 [e]
3	Tetralin	$Fe_{1-x}S$	[a]	~ 0

Reaction 1: hydrogenolysis of DNM in the presence of dibenzyl (0.5-1.0 mol equiv.) under hydrogen (2.0 MPa) at 460°C.

Reaction 2: hydrogenolysis of 9-BP in the presence of Fe catalyst (0.5 mol equiv.) under hydrogen (6.0 MPa) at 450°C.

Reaction 3: hydrogenolysis of trans-stilbene in the presence of Fe catalyst under hydrogen (1.0 MPa) at 380°C.

a: 1,2-Diphenylethyl. b: [1-BN]/[toluene]; c: [BTHN]/[toluene]; d: [BMN]/[toluene]; e: ([DETN] + [BTHN])/[dibenzyl].

Table 2 Fe-Catalyzed Hydrogenolysis of trans-Stilbene in 1-MN.

Run	Gas phase (MPa)	Cat.	t-ST conv. (mol%)	Products (Selectivity/mol%)
				c-ST Dibenzyl Toluene
1	N ₂ (1.0)	None	6.9	43 44 tr.
2	H ₂ (1.0)	None	10	38 50
3	N ₂ (1.0)	α-Fe	7.4	53 36 3.6
4	H ₂ (1.0)	α-Fe	26	13 62 3.8
5	H ₂ (6.0)	α-Fe	44	6.6 68 3.0
6	N ₂ (1.0)	Fe _{1-x} S	7.9	48 37 3.8
7	H ₂ (1.0)	Fe _{1-x} S	21	18 71 3.3
8	H ₂ (6.0)	Fe _{1-x} S	40	7.7 78 2.9

trans-Stilbene 3 g (16.7 mmol), 1-MN 15 g (106 mmol), Fe catalyst 3.75 mmol of Fe, reaction temperature 380°C, reaction time 30 min.

c- and t-ST = cis- and trans-Stilbenes. tr.=trace.

Table 3 Fe-Catalyzed Hydrogenolysis of trans-Stilbene in Tetralin.

Run	Gas phase (MPa)	Cat.	t-ST conv. (mol%)	Products (Selectivity/mol%)
				c-ST Dibenzyl Toluene BTHN DETN
9	N ₂ (1.0)	None	24	18 39
10	H ₂ (1.0)	None	27	15 41
11	N ₂ (1.0)	α-Fe	41	8.3 51 5.6
12	H ₂ (1.0)	α-Fe	64	4.2 59 6.1 3.9 5.5
13	H ₂ (6.0)	α-Fe	95	— 71 9.5 7.8 6.4
14	N ₂ (1.0)	Fe _{1-x} S	51	6.7 69
15	H ₂ (1.0)	Fe _{1-x} S	61	4.6 70 2.1
16	H ₂ (6.0)	Fe _{1-x} S	91	— 81 1.6

trans-Stilbene 3 g (16.7 mmol), tetralin 15 ml (110 mmol), Fe catalyst 3.75 mmol of Fe, reaction temperature 380°C, reaction time 30 min.

c- and t-ST = cis- and trans-Stilbenes.

Table 4 Additive Effect of Fe Catalysts on the Hydrogenolysis of 9-BP in Tetralin (Tet).

Catalyst	Conv. of 9-BP	Selectivities of			
		Tol	BTHN	Phen	DHP
None	4%	100%	nd.	80%	3%
Fe ₂ O ₃	20	90	tr.	83	10
α -Fe	72	87	5%	92	8
Fe _{1-x} S	39	87	tr.	82	10

9-BP 7.5 mmol, Tet 75 mmol, Fe catalyst 3.75 mmol of Fe, initial hydrogen pressure 6.0 MPa, 450°C, 30 min.

Tol=Toluene, Phen=Phenanthrene.

Nd. and tr. denote 'not detected' and 'traces', respectively.

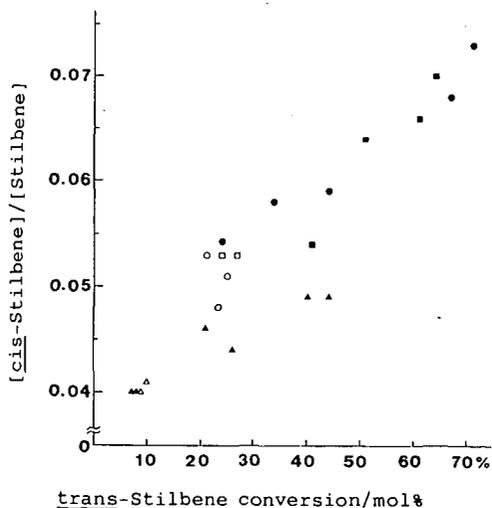


Fig. 1 Correlation of the trans-Stilbene Conversion and the cis-Stilbene Content in the Hydrogenolysis of trans-Stilbene at 380°C. ● DHP-1-MN, Fe cat. ○ DHP-1-MN, no cat. ■ Tetralin, Fe cat. □ Tetralin, no cat. ▲ 1-MN, Fe cat. △ 1-MN, no cat.

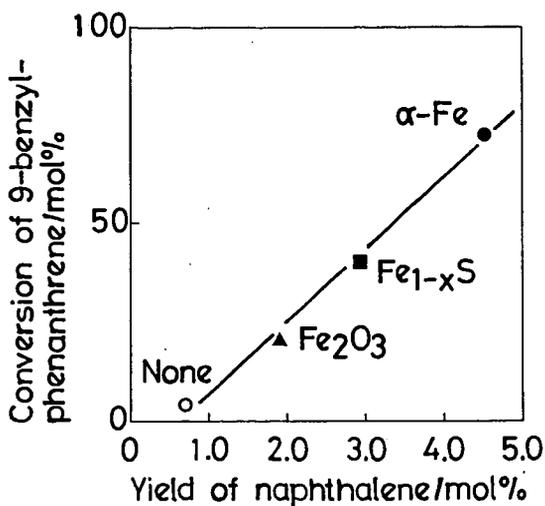
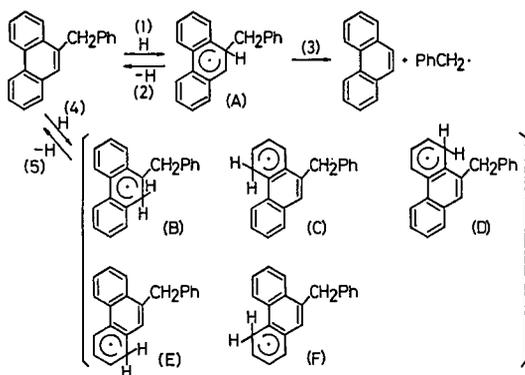


Fig. 2 Relationship between the 9-BP Conversion and the Naphthalene Yield in the Hydrogenolysis of 9-BP in Tetralin. 9-BP 7.5 mmol, tetralin 75 mmol, initial hydrogen pressure 6.0 MPa, 450°C, 30 min.



Scheme 1 Mechanism for the Hydrogenolysis of 9-BP.