

## REACTIVITIES OF HYDROGENATED DI(1-NAPHTHYL)METHANES TOWARD THERMAL DECOMPOSITION AND HYDROCRACKING

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### INTRODUCTION

The decomposition mechanism of diarylmethanes has been extensively investigated [1-5], and it is generally accepted that the decomposition occurs via the ipso-addition of a hydrogen atom transferred from hydrogen donating solvent or gaseous hydrogen. It is noteworthy that the feasibility of the hydrogen transfer to the ipso-positions of diarylmethanes depends not only on the species of hydrogen donating solvent, hydrogen pressure and catalyst, but on aromatic ring sizes [4,5].

In the hydrogenolysis of di(1-naphthyl)methane(DNM) [5,6], hydrogenated di(1-naphthyl)methanes(H-DNMs) were formed in addition to naphthalene(Np) and 1-methylnaphthalene(1-MN). We previously reported that at low temperatures, the selectivities of H-DNMs were dependent upon the catalyst used to a large extent [7]. It is of significance to know how the reactivities of H-DNMs toward thermal decomposition or hydrocracking change with the degree of hydrogenation of H-DNMs.

### EXPERIMENTAL

#### Materials

DNM was synthesized according to the methods described in the previous paper [5] and 1,2-di(1-naphthyl)ethane(DNE) according to the method of Buu-Hoi [8]. H-DNMs were prepared by hydrogenating DNM with Ni-Mo-S/Al<sub>2</sub>O<sub>3</sub>, stabilized nickel or ultra fine metallic iron catalyst, respectively, as shown in Table 1. DNM and H-DNMs prepared were identified by GC-MS. Table 2 shows the structures of these compounds. The other substrates such as diphenylmethane (DPM) and 1,2-diphenylethane(DPE), and solvent dodecane were purchased commercially and further purified if necessary by conventional methods.

#### Thermal decomposition and hydrocracking of the substrates

7.5 mmol of a substrate, 30 ml of dodecane were put into a 90 ml stainless steel, magnetically stirred autoclave. After being pressurized by hydrogen or nitrogen to 10 MPa, the autoclave was heated to a reaction temperature and kept for a prescribed period of time. Then, the autoclave was immediately cooled to room temperature in an ice-water bath. Thermal decomposition was usually carried out under nitrogen at 400°C, and hydrocracking in the presence of 0.5 g of FeS<sub>2</sub> catalyst with 0.05 g of sulfur under hydrogen at 300°C.

The products were identified by GC-MS and quantified by GC.

## RESULTS AND DISCUSSION

### Reactivities of DNM and H-DNMs toward thermal decomposition

Figure 1(a) shows the reactivities of DNM and H-DNMs mixture (MIX) toward thermal decomposition under nitrogen in the temperature range 300-430°C. At 300°C, the thermal decomposition does not proceed for any substrate. Ditetralylmethanes (8H-DNM and 8H'-DNM) slightly decompose at 350°C. At above 400°C, 4H-DNM begins to decompose with concurrent increase in the DNM concentration, suggesting the occurrence of dehydrogenation of H-DNMs. Figure 1 (a) shows that the reactivities of H-DNMs toward thermal decomposition decrease in the order: 8H'-DNM > 8H-DNM > 4H-DNM. Although the thermal decomposition of DNM and 4H-DNM were promoted under hydrogen (Fig.2(b)), the order of the reactivities did not change.

8H-DNMs(1) was thermally decomposed. Figure 2 shows that in spite of low initial concentration of 8H'-DNM, the molar ratio of 8H'-DNM to 8H-DNMs decreases steadily as the reaction proceeds, indicating that 8H'-DNM decomposes faster than 8H-DNM. As the reaction proceeds, the selectivities of the dehydrogenated products such as 4H-DNM and DNM, and that of a hydrogenated product, 14H-DNM increased, while those of the decomposed products such as tetralin (THN) and 5-methyltetralin (5-MT) decreased. These facts suggest that the disproportionation reaction concurs. The time profile of the product distribution for the thermal decomposition of 8H-DNMs(2) is illustrated in Fig.3. These results given in Fig.3 show that 8H-DNM is as reactive as 14H-DNM, but much lower than 8H'-DNM in reactivity.

To clarify the different reactivities of 8H-DNM and 8H'-DNM, the thermal decomposition of DPM and DPE were separately carried out under the conditions similar to those for 8H-DNMs. As shown in Table 3, in comparison with ca. 6% of conversion for DPE, DPM does not decompose at all. The bond dissociation energies of some diaryl hydrocarbons listed in Table 4 indicate that the aliphatic C-C bonds in DPE and DNE are thermally cleaved much more readily than the C<sub>ar</sub>-C<sub>alk</sub> in DPM. By analogy of structural similarity between these compounds and octahydro-derivatives of DNM, the discrepancy in the reactivities of 8H-DNM and 8H'-DNM may be due to the different labilities of their breaking C-C bonds.

On the other hand, compared to 8H-DNM and 8H'-DNM, DPM and DPE are much less reactive, respectively. The difference should be attributed to the hydrogen donating effect of tetralyl groups in ditetralylmethanes. Table 3 indicates that DNM and DNE decompose more readily than DPM and DPE, respectively, but they are less reactive than 8H-DNM and 8H'-DNM, respectively. Because neither gaseous hydrogen nor hydrogen donating solvent was used, the hydrogen consumed in the thermal decomposition of DNM and DNE should result from dodecane used as a solvent. In decalin solvent, DNM does not decompose at all, but DNE decomposes much the same as in dodecane solvent. Two blank tests show that under the same reaction conditions (400°C, 10 MPa of N<sub>2</sub>, 1 h), ca. 1% of dodecane decomposes, but that decalin does not. These results indicate that the hydrogenolysis of DNM occurs in dodecane solvent. 20H-DNM derived from the complete hydrogenation of DNM shows even lower reactivity toward thermal decomposition than DNM. Compari-

son of the reactivities of the substrates listed in Table 3 suggests that the intramolecular hydrogen transfer plays a significant role in the cleavage of R-CH<sub>2</sub>-R', where the R and R' denote aromatic or hydroaromatic rings. It could be also said that the thermal decomposition of H-DNMs, except for 20H-DNM, includes hydrogenolysis primarily induced by the intramolecular hydrogen transfer. The reactivities of DNM and H-DNMs toward thermal decomposition decrease in the order: 8H'-DNM > 8H-DNM > 4H-DNM > DNM > 20H-DNM.

#### Reactivities of DNM and H-DNMs toward hydrocracking catalyzed by FeS<sub>2</sub>

The hydrocracking of a mixture of DNM and H-DNMs was carried out at 300°C in the presence of FeS<sub>2</sub> catalyst. Figure 4 shows that the reactivities of DNM and H-DNMs toward hydrocracking decrease in the order: DNM > 4H-DNM > 8H-DNM > 8H'-DNM, which is the reverse of that toward thermal decomposition (see above). The slight increase in the concentration of 8H'-DNM with the course of the reaction was observed, which may be due to the hydrogenation of DNM and 4H-DNM.

Fig. 5 shows the results of the hydrocracking of 8H-DNMs(1). In contrast to the relatively rapid hydrocracking of 8H-DNM, 8H'-DNM is hardly hydrocracked, partially because of its low concentration. Fig. 6 shows that in the hydrocracking of 8H-DNMs(2), the rate for the hydrocracking of 8H-DNM is above tenfold greater than that of 8H'-DNM. As is consistent with the low reactivity of 8H'-DNM toward hydrocracking, the yield of 1-methyltetralin(1-MT) is only small. As the hydrocracking of DNM and H-DNMs results principally from the ipso-addition of a hydrogen atom to an aromatic ring under the reaction conditions, the different reactivities of 8H-DNM and 8H'-DNM can be illustrated in Fig. 7. In the hydrocracking of 8H-DNM, the ipso-position of both tetralin rings can be attacked by H-atoms, and as an intermediate produced after the hydrocracking, tetralyl-5-methyl radical is much more stable than tetralyl-1-methyl radical. Hence, 8H-DNM is expected to decompose much more readily than 8H'-DNM after the ipso-addition of a hydrogen atom.

Table 5 shows the different reactivities of DPM and DPE, and those of DNM and DNE. DNE is mainly hydrogenated rather than decomposed. In general, hydrogen donating solvent scarcely shows its donating ability at a temperature as low as 300°C, especially in the presence of both gaseous hydrogen and an active catalyst [12-14]. Thus, the difference in the hydrocracking reactivities between 8H-DNM and DPM, and those between 8H'-DNM and DPE should be primarily due to the ring size effect. Under the same reaction conditions, 20H-DNM does not decompose at all. The order of the hydrocracking reactivities decreases: DNM > 4H-DNM > 8H-DNM > 8H'-DNM > 20H-DNM. The results may be explained on the basis of the hydrogen-accepting ability and adsorption ability [13,14] on the surface of catalyst used. They decrease in the order: naphthalene > tetralin > decalin. Because the hydrocracking proceeds mainly on the surface of FeS<sub>2</sub> catalyst via the attack (involving ipso-addition) on the substrates by H-atoms dissociated, the synergistic effect can be expected in the hydrocracking of DNM and H-DNMs.

Whitehurst et al. [15] have proposed that coal reactivity in liquefaction reactions is affected by its chemical structure. Takegami et al. [16] and Maekawa et al. [17] suggested that coal liquefaction proceeds through cleavage of ether and methylene bridges connecting relatively small structure units, such as polycyclic aromatic and hydroaromatic rings. According to our results, therefore, the severe hydrogenation of aromatic moieties in coal structure is likely to decrease the reactivity of the coal hydrogenated in the catalyzed hydroliquefaction, but the partial hydrogenation of aromatic moieties in coal structure forms precursors which are labile to thermal decomposition.

#### CONCLUSION

1. Mono- and di-tetrahydromethanes, which are afforded in the partial hydrogenation of DNM, are more reactive than DNM toward thermal decomposition. This fact suggests that the intramolecular hydrogen donation plays a significant role in the thermal decomposition of hydrogenated dinaphthylmethanes.
2. In hydrocracking with  $\text{FeS}_2$ , di(1-naphthyl)methane decomposes rapidly, and the more fully it is hydrogenated, the more slowly its hydro-derivatives decompose.

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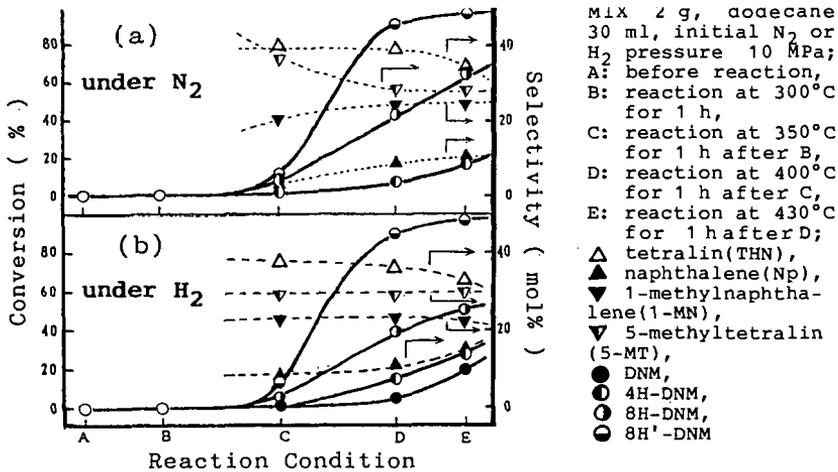


Fig. 1. Thermal decomposition of DNM and H-DNMs mixture (MIX)

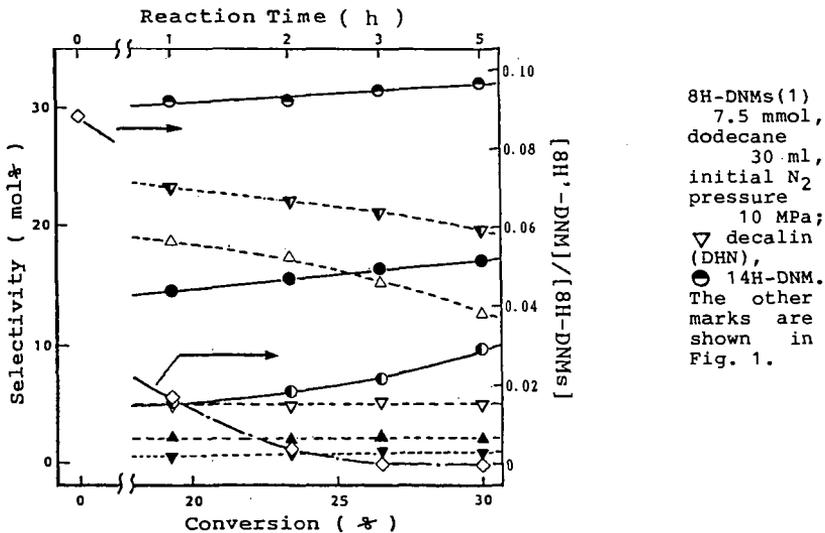


Fig. 2. Thermal decomposition of 8H-DNMs(1) at 400°C

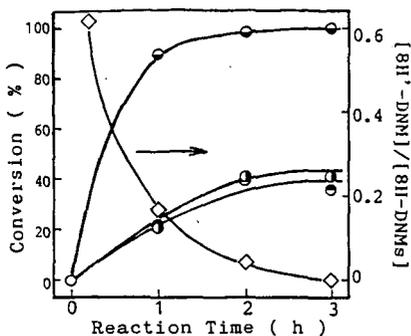


Fig. 3. Thermal decomposition of 8H-DNMs(2) at 400°C

8H-DNMs(2) 7.5 mmol, dodecane 30 ml, initial N<sub>2</sub> pressure 10 MPa. The marks are shown in Figs. 1 and 2.

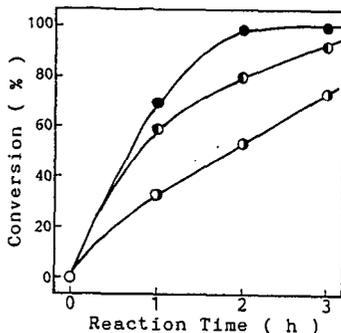


Fig. 4. Hydrocracking of MIX with FeS<sub>2</sub> catalyst at 300°C

MIX 2 g, dodecane 30 ml, FeS<sub>2</sub> 0.5 g, sulfur 0.05 g, initial H<sub>2</sub> pressure 10MPa. The marks are shown in Fig. 1.

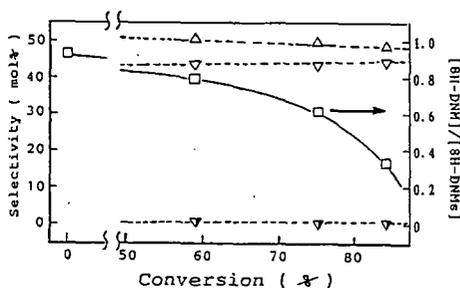


Fig. 5. Hydrocracking of 8H-DNMs(1) with FeS<sub>2</sub> catalyst at 300°C

8H-DNMs(1) 7.5 mmol, dodecane 30 ml, FeS<sub>2</sub> 0.5 g, sulfur 0.05 g, initial H<sub>2</sub> pressure 10 MPa, ▼ 1-methyltetralin (1-MT). The other marks are shown in Figs. 1 and 2.

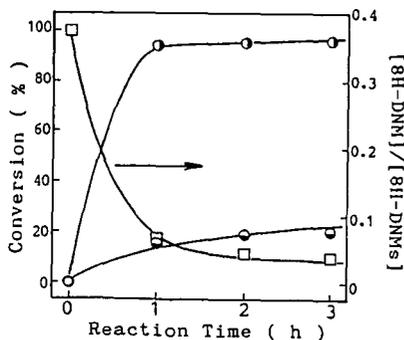


Fig. 6. Hydrocracking of 8H-DNMs(2) with FeS<sub>2</sub> catalyst at 300°C

8H-DNMs(2) 7.5 mmol, dodecane 30 ml, FeS<sub>2</sub> 0.5 g, sulfur 0.05 g, initial H<sub>2</sub> pressure 10 MPa. The marks are shown in Fig. 1.



Table 3 Thermal decomposition of H-DNMs and diarylalkanes at 400°C for 1 h

Substrate	Conv. (%)	Selectivity ( mol% )							
		DHN	THN	Np	5-MT	1-MN	1-EN	Tol	Others
DNM	8.3 <sup>a</sup>	0	0	50	0	50	-	-	0
DNE	46.8	0	0	0.7	1.3	86.9	0.6	-	10.5
8H-DNMs(1)	19.3 <sup>b</sup>	5.1	18.6	2.2	23.1	0.6	-	-	50.4
	84.7 <sup>c</sup>								
8H-DNMs(2)	22.6 <sup>b</sup>	3.0	28.9	4.2	45.5	4.1	-	-	14.3
	89.5 <sup>c</sup>								
20H-DNM	~ 4	>90	-	-	-	-	-	-	-
DPM	0	-	-	-	-	-	-	0	-
DPE	6.0	-	-	-	-	-	-	15.9	84.10

substrate(s) 7.5 mmol, dodecane 30 ml, initial N<sub>2</sub> pressure 10 MPa; Tol: toluene, 1-EN: 1-ethylnaphthalene, <sup>a</sup> in decalin at 400°C, DNM does not decompose; <sup>b</sup> conversion of 8H-DNM; <sup>c</sup> conversion of 8H'-DNM; Others: including hydro- and dehydro-derivatives for DNE, 8H-DNMs(1), 8H-DNMs(2), and other alkylbenzenes for DPE.

Table 4 Bond dissociation energies(BDE) of some hydrocarbons

Bond	BDE(kcal/mol)	Reference
Ph-Ph	100	9
PhCH <sub>2</sub> -Ph	84,89	9, 1
PhCH <sub>2</sub> CH <sub>2</sub> -Ph	97	10
PhCH <sub>2</sub> -CH <sub>2</sub> Ph	56,62	9, 1
NpCH <sub>2</sub> -CH <sub>2</sub> Np	50,55	9, 11

Np denotes naphthyl group.

Table 5 Hydrocracking of H-DNMs and diarylalkanes at 300°C for 1

Substrate	Conv. (%)	Selectivity ( mol% )								
		THN	Np	5-MT	1-MN	1-EN	H-DNMs	H-DNEs	Bz	Tol
DNM	87.4	2.3	48.1	1.8	42.3	-	2.9	-	-	-
DNE	49.1	tr.	0.9	1.4	1.2	0.2	-	86.1	-	-
8H-DNMs(1)	59.1 <sup>a</sup>	50.2	0.5	48.0	0	-	0.2	-	-	-
20H-DNM	0	0	0	0	0	-	-	-	-	-
DPM	6.1	-	-	-	-	-	-	-	28.0	35.0
DPE	0	-	-	-	-	-	-	-	0	0

substrate(s) 7.5 mmol, dodecane 30 ml, FeS<sub>2</sub> 0.5 g, sulfur 0.05 g, initial H<sub>2</sub> pressure 10 MPa; Bz: benzene; H-DNMs: hydro-derivatives of DNE. The other abbreviations are defined in Figs 1, 2 and Table 3. <sup>a</sup> conversion of 8H-DNM. In the case of DNE, 8H-DNMs(1) and DPM, some unidentified products were obtained.