

TASK II

Project II.8

DEUTERIUM TRACER STUDIES OF THE MECHANISM OF THERMAL AND CATALYTIC REACTION OF 1-[4-(2-PHENYLETHYL)BENZYL] NAPHTHALENE

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INTRODUCTION

In previous reports we have described the thermolysis of 1,2-diphenylethane (DPE) and 1,2,3,4-tetraphenylbutane under D_2 (1,2). We have also described the results with 2,3-diphenyl-2,3-dimethylbutane (3). The patterns of deuterium incorporation into the reaction products and recovered starting materials in these studies were interpreted in terms of a mechanism where benzylic radicals react with D_2 to produce D atoms. These atoms then reacted in pathways that are the reverse of the processes involved in their formation and also to add to unsaturated centers in the molecules.

This mechanism suggests that a role for a catalyst in promoting cleavage of Ar-R bonds during coal liquefaction and in studies of model compounds could be simply to facilitate hydrogenation of species which might otherwise trap H atoms. For example, a catalyst may function to insure hydrogenation of the stilbene produced during pyrolysis in the diphenylethane system. In this case, cleavage of the Ar-R bonds might be promoted because H atoms produced during the reaction would have no alternative except to add with the aromatic rings or to recombine to form hydrogen.

In order to mimic the coal liquefaction process, a more complicated organic compound 1-[4-(2-phenylethyl)benzyl] naphthalene (NMBB) has been proposed and studied in some detail (4). The experiments conducted by Farcasiu and Smith (4) utilized a sealed sample tube. The results showed that under thermal reaction

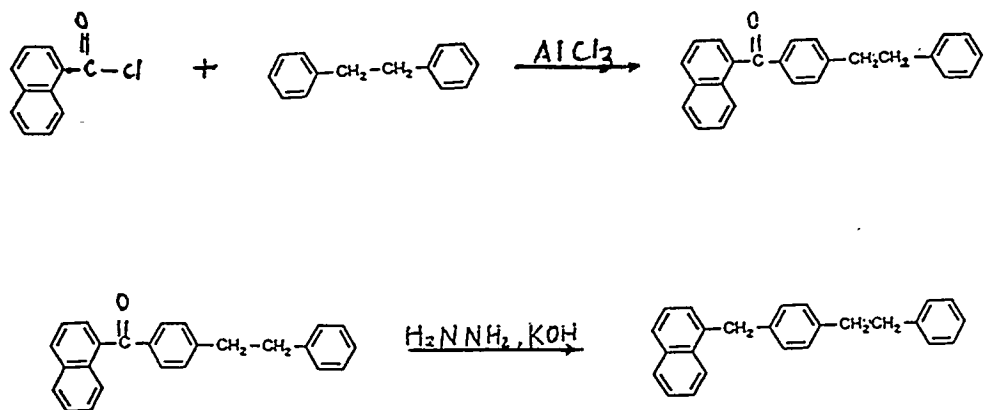
conditions, 56% of the products result from breaking the d-bond in the reactant (Figure 1); under catalytic conditions, about 80-90% of the products are a result of breaking the a-bond.

It is interesting to know what kind of behaviors this model compound will have under coal liquefaction condition; that is, in the presence of H_2 , solvent and catalyst. A conventional coal liquefaction catalyst (sulfided cobalt-molybdenum-alumina) as well as some other catalyst have been used in this study. To eliminate the uncertainty regarding the catalytic properties of the metal reactor, we have used a glass reactor as was described previously (1,5).

RESULTS AND DISCUSSION

Thermolysis of NMBB under D_2

NMBB was synthesized by the procedure outlined in Scheme 1. The synthetic procedure is given in detail in the Experimental Section.



Scheme 1: Synthesis of NMBB

NMBB underwent thermolytic reaction at $400^\circ C$ to give benzene 1, ethylbenzyl naphthalene 2, toluene 3, methylbenzyl naphthalene 4, ethylbenzene 5, enzyl naphthalene 6, bibenzyl 7, methyl naphthalene 8, methyl bibenzyl 9, and naphthalene 10. These products derived from bond breaking as indicated in Figure 1. Even at temperatures as low as $400^\circ C$, significant amounts of p-xylene (11) was produced. This probably is due to the secondary cleavage of 4. The formation of

ethylmethylbenzene **12** can be explained by a secondary reaction, the cleavage of **2**. Tetrahydro-NMBB **13** and naphthylmethylstilbene **14** are also present as major products. At 425°C and 450°C, the conversion was higher and the relative amount of each product changed, probably due to the secondary reactions. The product distribution for these runs are given in Table 1. Assuming a first order reaction for the thermolysis of NMBB under D₂, an Arrhenius plot yielded a straight line as indicated in Figure 2.

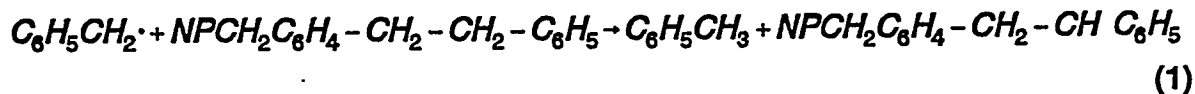
As can be seen from the data in Table 1, when N₂ was used rather than D₂, the conversion was similar, but the amount of **14** was increased. In addition, a significant amount of methylstilbene was produced in this run. This is understandable from our previous studies which showed that radicals formed from primary cleavage react with NMBB to produce **14**. This is because NMBB is the only hydrogen source when nitrogen is used.

For the thermolysis of DPE, the formation of ethylbenzene and benzene can be explained by a reaction of DPE with a hydrogen atom, produced by the reaction of a benzylic radical with H₂; in the absence of H₂ (in the presence of N₂), those products were not formed. In the case of NMBB, the products derived from breaking a, b, c, d, and e-bonds are formed in the presence of N₂, but the amounts of them are smaller than that in presence of D₂.

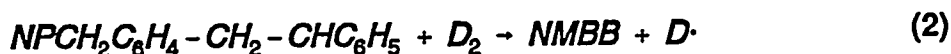
The data in Table 2 summarize the selectivity for bond breaking of NMBB. To make these calculations, we take the amount of **1** as representative of e-bond breaking, simply because this compound is not subject to secondary cleavage. The same argument applies for **3**, **5**, **7** and **10**. Secondary cleavage of **2** gives **10** and **12**, which are present even at 400°C. A similar reaction can also occur in the case of **4**, which generates **10** and **11**. These reactions make a calculation of a-bond breaking more difficult because **10** can result from a-bond breaking as well as other secondary reactions, and **9** can be subject to secondary reactions. Here, the average of **9** and **10** is considered to be representative of a-bond breaking. The amounts shown in Table 2 may not have sufficient quantitative accuracy of the cleavage of each bond; however, for a qualitative discussion, the trend is clear: under thermal conditions, $d \gg a > c = e = b$.

The major compounds from the thermolysis of NMBB in the presence of D_2 are toluene, **3**, methylbenzyl-naphthalene, **4** and unconverted NMBB. The deuterium incorporated into these compounds, summarized in Table 3, show that as the temperature increases from 400°C to 450°C, deuterium incorporation increases. However, the increase is much greater for NMBB than for toluene and **4**. A similar amount of deuterium was observed in DPE in each case. For the 450°C runs, the D/mol in DPE at 30 minutes is about 7 times greater than at 8 minutes, while it is only 3 times greater for toluene (5).

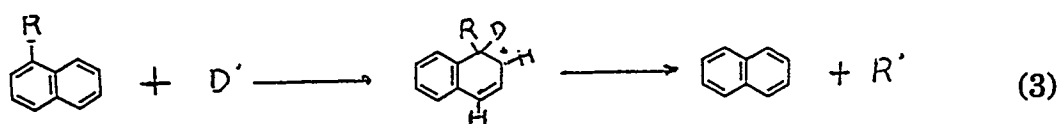
Considering the 20 kcal/mol difference in the H-H bond and C-H bond in BDE (6), the benzylic radical formed in the first step of this reaction is more likely to react with the H atom from NMBB (eq. 1) than with D_2 .



The NMBB radical thus formed can react with D_2 gas as shown in equation 2 to generate a D atom.



The active $D\cdot$ atom can then promote Ar-R bond cleavage as shown by equation 3.



Because the reverse of reaction (2) is energetically favorable, it seems likely that the NMBB radical will be formed again resulting in H/D exchange. The above mechanism can explain why under thermal conditions, NMBB exhibits more deuterium incorporation than toluene; it can also explain why the Ar-R bond is broken less frequently than the d-bond, simply because there is not enough D atoms present.

The Thermolysis of NMBB in the Presence of a Catalyst

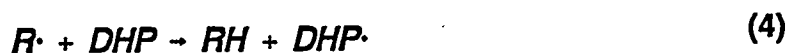
Thermolysis of NMBB was undertaken using several catalysts in the presence or absence of a solvent. The reaction conditions and the conversions are summarized in Table 4, the selectivity for the bonds broken are summarized in Table 5 and the deuterium incorporation data are given in Table 6. From the data in these tables, several conclusions are possible:

1. As expected, when 10% of a catalyst was added, the conversion was increased. Based on just the conversion data, a conventional coal liquefaction catalyst, sulfided Co-Mo-alumina, is the best one. Unsulfided Co-Mo-alumina has a high catalytic activity but it is not as active as the sulfided catalyst. A 30% Co catalyst (G-67) was mistakenly used in one run and this catalyst also increased the conversion. It is difficult to determine whether the graphized carbon increased the conversion, but based on the selectivity of the bonds broken, it appears to be a catalyst.

2. In the presence of a catalyst, bond-breaking is very different from the runs without a catalyst. Under thermal reaction conditions, about 60-80% of the NMBB is converted by breaking the d-bond. However, under catalytic conditions, about 80-90% of the NMBB is converted by breaking the a-bond in the case of the sulfided Co-Mo-alumina catalyst, and about 60-80% for the unsulfided Co-Mo-alumina. When the Co catalyst was used, about 60% of the a-bonds and 30% of the b-bonds were broken. For graphized carbon, the bonds broken were: a-bond, 40%; b-bond, 20%; and d-bond, 30%.

3. The cleavage pattern of NMBB in the presence of dihydrophenanthrene (DHP) different from the ones obtained for runs in the absence of solvent and in the runs with a catalyst. If we take the ratio [d-bond broken/a-bond broken] as a measure of the catalytic activity, the value obtained for runs with DHP present but no catalysts falls in the middle of the range of values (Table 7). From the data in Table 7, it may be concluded that in the presence of DHP, whether the reaction was run under D_2 (or H_2) or in a sealed tube, the cleavage of NMBB differs from that of the thermal condition with neat reactant. It is believed that the breaking of the a-

bond in the presence of DHP is because of the radical mechanism shown in equation 4.



The radicals formed in the initial step of the thermolysis of NMBB can abstract an H atom from the DHP, a good H atom donor, and the DHP radical is formed. The DHP radical can abstract an H atom from another molecule of DHP; also it can abstract an H atom from either the aromatic or aliphatic groups of the unconverted NMBB. If the H atom was abstracted from the naphthalene ring of NMBB, the radical that was formed certainly can promote a-bond breaking by β -bond scission.

4. The data in Table 4 show that there is no difference in either conversion or the selectivity of bond breaking when DHP or phenanthrene is used as the solvent. These preliminary results also indicate that there is very little, if any, difference between the results using DHP/phenanthrene as solvent and those with neat NMBB. In the thermolysis of NMBB the solvent is not as important as in the coal liquefaction process, in which the conversion of coal in the absence of solvent was much lower. This raises a concern as to whether the results from NMBB can be used as a model for coal conversion since their behavior towards solvent are so different. Coal remains, to great extent, a solid under normal liquefaction conditions; however, the melting point of NMBB is only about 65°C. In the case of coal, a solvent is needed in order to increase the dispersion of at least the "soluble" fragments, but in the case of NMBB, this solvent action is not necessary because at the thermolysis condition it is a liquid.

5. Many roles have been proposed for the solvent in coal liquefaction. The most important one is hydrogen transfer. It is believed that the mechanism for hydrogen transfer is through the route as indicated in equations 4 and 5:



The DHP radical reacts with H_2 to generate the $H\cdot$ atom and DHP. If this is indeed the case, when the reaction is run using D_2 , we should see less deuterium incorporation into the product in the presence of DHP. As can be seen from the data

in Table 8, this is not the case. The H/D ratios of the major products, naphthalene and tetralin, are the same as the ratio of NMBB reactant and D₂ gases when the experiment was run without solvent. In the run with solvent, the H/D ratios of naphthalene and tetralin are the same as the ratio of the NMBB reactant plus DHP and D₂ gas, even at 9 minutes. These results indicate that DHP is providing another source of hydrogen; however, deuterium incorporation into the products may by-pass DHP and directly add to the products.

When DHP or phenanthrene was used as the solvent, four compounds were found in the final mixture. These compounds were identified by GC/MS to be DHP, OHP (octahydrophenanthrene), THP (tetrahydrophenanthrene), and phenanthrene. The relative ratio of these compounds in each run (Table 8) depends on temperature and reaction time. However under the same reaction conditions, whether DHP or phenanthrene is the initial solvent, the same ratio of compounds are obtained (Figure 3).

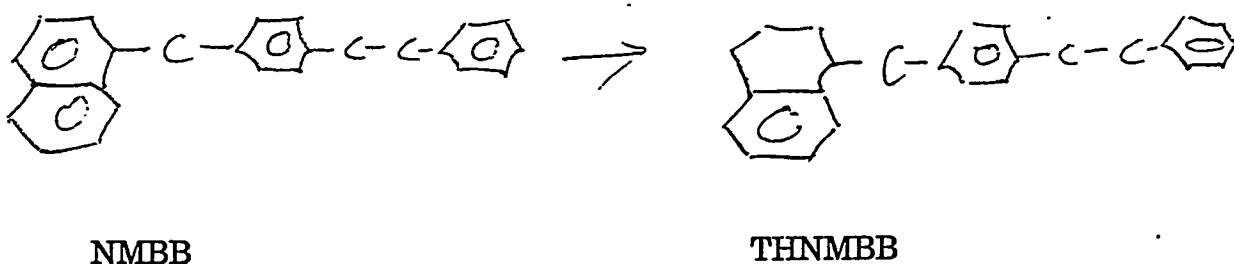
6. Under catalytic condition, deuterium was incorporated statistically into the products as well as unreacted NMBB. As can be seen from the data in Table 9, Figures 4 and 5, even at 9 minutes, the deuterium incorporation reached an equilibrium distributions. In comparing this result with the results from the thermal runs, we can see that there is a relationship between a-bond broken and deuterium incorporation. As more deuterium is incorporated into the products, the more a-bond breaking occurs during the thermolysis of NMBB. These results imply that the role of the catalyst in the thermolysis process is to activate the H-H bond rather than the Ar-R bond.

SUMMARY AND CONCLUSION

The mechanism for the reaction of NMBB with H₂ can be described as follows. The weaker d-bond is broken to generate the benzylic radical, this radical abstracts an H atom predominantly from unreacted NMBB as evidenced by the large amount of toluene-d₀ in the deuterium tracer studies. This radical may also react directly with D₂; this can explain why the small but significant amount of d₁ and d₀ toluene was also found in the products. The reaction of the benzylic radical with unreacted

NMBB produces the NMBB-radical. Just as in the DPE system, the NMBB-radical can react with D_2 to generate a D atom. The other products can be explained by the reaction of D atom with NMBB. Dehydrogenated NMBB and hydrogenated NMBB may also result from this kind of reaction. Evidence for the NMBB-radical reacting more readily with D_2 is provided by the GC/MS data in which the unreacted NMBB contain more deuterium than the toluene product does.

It is not surprising that the d-bond is broken during thermal conversions. However, under catalytic conditions the major products are produced by a-bond breaking. A hydrogenation catalyst operates in nearly, if not all, cases through a mechanism that involves homolytic dissociation of hydrogen. Thus, the catalyst becomes a source of hydrogen (or deuterium) atoms. In this case an adsorbed H (or D) atom can add to the most electron rich site, the naphthalene ring in NMBB, and thereby alter the reaction pathway from that of the thermal reaction. Thus, the rate limiting step in the thermal process is the breaking of the $-CH_2-CH_2-$ bond (the d-bond) whereas in the catalytic case the rate limiting step becomes that of bond breaking of a radical species which leads to breaking of the a-bond. Alternatively, it is possible that the catalyst functions first to hydrogenate NMBB as shown in equation 6:



The a-bond in the hydrogenated compound is expected to be broken much more readily than in NMBB.

Based on the d-bond breaking/a-bond breaking analysis, in the presence of DHP, the reaction should not be considered as a purely thermal reaction whether it is run under pressure, as in the present studies, or in sealed tube (4). In both of these cases, the cleavage pattern is significantly different from the purely thermal conditions conducted in this study using the neat compound.

The hydrogen transfer role of the solvent in coal liquefaction is elucidated to some extent by this study. The deuterium tracer data indicate that deuterium incorporation into the products and the unreacted NMBB may occur by a mechanism that by-passes the solvent.

EXPERIMENTAL SECTION

1. Preparation of naphthyl Bibenzyl Ketone

A 500 mL three-necked flask was fitted with a 250 mL addition funnel and a condenser protected by a drying tube connected to a NaOH trap. In it are placed 14.6 g (0.11 moles) of anhydrous aluminum chloride and 70 mL of dry carbon disulfide. The suspension was cooled to 10-15°C in an ice-water bath and 20.9 g (0.11 moles) of 1-naphthoyl chloride were added dropwise with stirring over a 30-minute period. After this addition was completed the reaction mixture was stirred for 15 minutes. A solution of 18.2 g (0.1 moles) of bibenzyl in 20 mL of dry carbon disulfide was added dropwise with stirring over a 1- hour period to the mixture, the temperature being maintained at 10-15°C.

After the addition was completed, the reaction mixture was refluxed for 1 hour and was then poured very cautiously with manual stirring onto a mixture of 200 g of crushed ice and 30 ml of 10% HCl in a 500 mL beaker. The mixture thus formed was extracted with carbon tetrachloride (3 X 50 mL). The combined organic extracts were washed with water (3 X 50 mL) and dried with MgSO₄.

The resulting solution was distilled and the residue was dissolved in 30 mL of CH₂Cl₂. The product was obtained by liquid chromatograph (silica gel: 250 g, 1 : 1 mixture of CH₂Cl₂ and hexane was used as the solvent system). The product was monitored by TLC (20% hexane in CH₂Cl₂; UV. R_f = 0.5). After the solvent was removed, 25 g of product was obtained. Yield: 74.4%.

H NMR 2.9 (m, CH₂), 7.2-8.1 9(m, aromatic).

M.P: 78-80°C (recrystallized from ethanol).

2. Preparation of 1-(4-(2-Phenylethyl)-Benzyl)-Naphthalene

A 500 mL three-necked flask was fitted with a condenser and a thermometer. In it are placed 34 g (0.1 moles) of 1-naphthyl bibenzyl ketone, 212 ml of ethylene

glycol and 43 mL of anhydrous hydrazine. The mixture was heated slowly with stirring to 80°C, it became a clear solution and then immediately the solution became milky, an indication of formation of the hydrazone. Then 15 g of potassium hydroxide was added slowly through the condenser and the mixture was refluxed overnight (140-160°C). After the ketone was no longer observed on the TLC plate, water and excess hydrazine were removed by a take-off condenser until the temperature rose to the boiling point of ethylene glycol (196-198°C). Refluxing was continued for at least 4 hours. (TLC was used to follow the formation of the product).

After the above mixture was cooled to room temperature, 100 mL of water was added. The mixture was acidified with 10% HCl to pH = 2, and then extracted with CH₂Cl₂ (4 X 100 mL). The combined organic layer was washed with water (3 X 50 mL) and dried over MgSO₄. After the solvent was removed, recrystallization from ethanol gave 28g of product. Yield: 87%.

M.P. 65-67°C (66-67°C).

Purity: > 99% (GC)

3. General Reaction Procedure

The reactions were conducted in a glass liner contained in a stainless steel reactor; the glass liner was sized to occupy most of the stainless steel value (Figure 6). Glass beads were added to the glass tube filled out one end with a capillary tube, and then the end of the tube with the larger diameter sealed off. A known amount of the solid reactant was added to the reactor through the capillary tube. The tube was placed in the stainless steel holder, using stainless steel wool to insulate the glass reactor from breaking while being shaken. The stainless steel reactor was connected to a glass handling system and pressurized with sufficient hydrogen to provide a pressure of about 2000 psig at reaction temperature. The reactor was placed in a preheated sand-bath. The reactor attained reaction temperature in 2 minutes or less. At the end of a run the reactor was removed from the hot sand-bath and transferred to a cold sand-bath where it cooled to below 100°C in 1 to 2 minutes.

Carbon disulfide was added through the capillary and the products removed for analysis using a long syringe needle. Little or no material is lost from the interior

of the glass bulb. Control experiments in which a hydrogenation catalyst was added showed that complete saturation of an aromatic compound could be effected under the appropriate reaction conditions, showing that the amount of gas and its mixing during the reaction was adequate.

Gas chromatographic analysis were carried out on a Hewlett Packard Model 5880A gas chromatograph equipped with an DB-5 60-m column. GC/MS analysis was accomplished using a Hewlett Packard GC/MS model 5890 instrument operated using 70 eV impact voltage.

Identification of reaction products was accomplished by GC/MS analysis and, when possible, by GC comparison with an authentic chemical sample. Reported product yields and overall conversion of NMBB are based on GC measurements using the appropriate response factor. GC/MS analysis provided deuterium data that was corrected for M+1 and M+2 peaks; where required, M-1, M-2, M-3 and M-4 peaks were also taken into consideration.

ACKNOWLEDGMENT

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REFERENCES

1. R. D. Guthrie, B. Shi, R. Sharipov and B. H. Davis, *Prepr., Div. Fuel Chem., Am. Chem. Soc.*, **38**, 526 (1993).
2. V. Rajagopal, R. D. Guthrie, B. Shi and B. H. Davis, *Prepr., Div. Fuel Chem., Am. Chem. Soc.*, in press.
3. S. Ramakrishnan, R. D. Guthrie, B. Shi and B. H. Davis, *Prepr., Div. Fuel Chem., Am. Chem. Soc.*, in press.
4. a. M. Farcasiau and C. Smith, *Energy & Fuels*, **5**, 83 (1991); b. M. Farcasiau and C. Smith, *Prepr. Div. Fuel Chem., Am. Chem. Soc.*, **35**, 404 (1990); c. M. Farcasiau, C. Smith, V. Pradhan and I. Wender, *Fuel Proc. Tech.*, **29**, 199 (1991).
5. R. D. Guthrie, B. Shi, S. Rajagopal, R. Ramakrishnan, R. Sharipov and B. H. Davis, *Prepr. Div. Fuel Chem., Am. Chem. Soc.*, in press.
6. S. W. Beuson, *J. Chem. Ed.*, **42**, 502 (1965).

FIGURE LEGEND

- Figure 1. Products of bond cleavage reactions of NMBB.
- Figure 2. Arrhenius plot for the thermolysis of NMBB under D_2 .
- Figure 3. Hydrogenation/dehydrogenation product distribution of DHP/phenanthrene in the thermolysis of NMBB (Top: starting from DHP; bottom: starting from phenanthrene).
- Figure 4. Deuterium incorporation into tetralin in the thermolysis of NMBB under D_2 at 400°C, 30 min. over Co-Mo-S. (-●-, without DHP; -□-, in the presence of DHP).
- Figure 5. Deuterium incorporation into naphthalene in the thermolysis of NMBB under D_2 at 400°C, 30 min. over Co-Mo-S (-●-, without DHP; -□-, in the presence of DHP).
- Figure 6. Glass reaction vessel for thermolysis under D_2 .

Table 1

Product Distribution in the Thermolysis of NMBB

<u>Compound</u>	<u>mol%</u>			
	<u>400°C/D₂</u>	<u>425°C/D₂</u>	<u>450°C/D₂</u>	<u>425°C/N₂</u>
1	0.3	0.5	0.8	0.2
2	0	0.2	0.5	0.1
3	1.7	13.8	28.6	9.2
4	1.4	5.8	15.7	6.4
5	0.1	0.4	0.9	0.1
6	0.3	0.7	2.3	1.3
7	0.3	0.3	0.6	0.3
8	0.3	1.2	2.0	0.7
9	0.8	2.4	4.9	2.0
10	0	2.0	4.6	0.5
11	0.4	0	0	0
12	1.0	0	0.1	0
13	1.5	1.7	2.7	1.1
14	0.5	2.2	3.4	4.9
NMBB	91.4	68.3	28.9	72.7
conversion	7.3	20.6	59.7	22.0

Table 2

Selectivity of Bond Breaking in Thermolysis of NMBB at 60 min

<u>Bond Broken</u>	<u>D₂/400°C</u>	<u>D₂/425°C</u>	<u>D₂/450°C</u>	<u>N₂/425°C</u>
a	19	13	13	11
b	9	2	2	3
c	5	3	5	6
d	57	79	78	79
e	10	3	2	2

Table 3

Deuterium Incorporation into the Major Compounds
in the Thermolysis of NMBB under D₂

	<u>Toluene</u>			<u>MBN^a</u>			<u>NMBB</u>		
	<u>400°C</u>	<u>425°C</u>	<u>450°C</u>	<u>400°C</u>	<u>425°C</u>	<u>450°C</u>	<u>400°C</u>	<u>425°C</u>	<u>450°C</u>
d ₀	89.9	78.8	78.2	75.6	63.8	52.0	95.4	81.1	55.7
d ₁	8.5	20.4	19.4	24.3	34.2	39.7	4.1	16.5	32.5
d ₂		0.8	2.2		1.3	6.3		2.0	9.5
d ₃			0.2			1.8		0.4	1.9
d ₄									0.3
D/mol	0.13	0.22	0.24	0.25	0.39	0.59	0.05	0.22	0.59

a. MBN: methylbenzyl-naphthalene

Table 4

Thermolysis of NMBB^a in the Presence of Solvent/Catalyst

<u>Temp.(°C)</u>	<u>Time (min.)</u>	<u>Catalyst</u>	<u>Gas (800 psi)</u>	<u>Solvent</u>	<u>Conversion mol.%</u>
425	60	/	N ₂	DHP	31.9
400	15	Co-Mo-S	D ₂	/	99.7
400	30	Co-Mo-S	D ₂	/	99.9
400	60	Co-Mo-S	D ₂	/	100
400	9	Co-Mo-S	D ₂	DHP	42.9
400	30	Co-Mo-S	D ₂	DHP	84.0
400	60	Co-Mo-S	D ₂	DHP	96.0
400 ^a	60	Co-Mo-S	D ₂	DHP	98.4
400	60	Co-Mo-S	D ₂	Phen.	98.4
425	60	Co-Mo-S	D ₂	DHP	99.1
425	60	Co-Mo-S	D ₂	Phen.	99.7
425	60	Co-Mo	D ₂	/	90.0
425	60	Co-Mo	N ₂	DHP	34.7
425	60	Co-Mo	D ₂	DHP	44.2
425	60	Co-Mo	D ₂	Phen.	95.2
425	48	G-67	N ₂	DHP	87.7
425	60	Graph. Carbon	N ₂	DHP	30.5

a. In this run 600 mg of NMBB and 60 mg of Co-Mo-S were charged.

Table 5

Selectivity of Bond Broken in the Thermolysis of NMBB
in the Presence of Solvent/Catalyst

<u>Reaction Condition</u>	<u>a</u>	<u>b</u>	<u>c</u>	<u>d</u>	<u>e</u>
425°C/N ₂ /DHP/60 min	2	34	3	28	34
400°C/Co-Mo-S/D ₂ /15 min	88	11	0.4	1	0.1
400°C/Co-Mo-S/D ₂ /30 min	85	12	1	2	0.3
400°C/Co-Mo-S/D ₂ /60 min	83	13	1	0	0
400°C/Co-Mo-S/D ₂ /DHP/9 min	93	7	0.1	1	0
400°C/Co-Mo-S/D ₂ /DHP/30 min	91	7	0.3	2	0.2
400°C/Co-Mo-S/D ₂ /DHP/60 min	90	6	0.4	3	0.3
400°C/Co-Mo-S/D ₂ /DHP/60 min ^a	90	7	1	2	0.3
400°C/Co-Mo-S/D ₂ /Phen/60 min	90	9	0.2	1	0
425°C/Co-Mo-S/D ₂ /Phen/60 min	82	10	1	7	1
425°C/Co-Mo-S/D ₂ /DHP/60 min	84	7	1	8	1
425°C/Co-Mo/D ₂ /60 min	75	11	2	11	1
425°C/Co-Mo/D ₂ /DHP/60 min	66	7	2	23	2
425°C/Co-Mo/N ₂ /DHP/60 min	63	6	2	28	2
425°C/G-67/N ₂ /DHP/48 min	58	35	0.3	7	0.3
425°C/G-67/N ₂ /Grap. c/48 min	43	23	2	30	2

a. In this run 600 mg of NMBB and 60 mg of Co-Mo-S were charged.

Table 6

Deuterium Incorporation in the Major Components in the Thermolysis of NMBB under Catalytic Conditions

<u>Reaction</u>	<u>Conv.</u>	<u>D/molecule</u>									
		<u>mol%</u>	<u>Toluene</u>	<u>EB</u>	<u>p-xylene</u>	<u>Tetralin</u>	<u>NP</u>	<u>MNP</u>	<u>DPE</u>	<u>MBB</u>	<u>NMBB</u>
Co-Mo-S/400°C 15 min	99.7	3.5	5.7	4.1	8.2	6.1	6.5	6.3	7.3	/	
Co-Mo-S/400°C 30 min	99.9	4.2	6.2	4.9	8.3	6.3	7.0	7.5	8.8	/	
Co-Mo-S/400°C 60 min	100	4.5	6.5	5.2	8.1	6.2	6.8	8.2	9.5	/	
Co-Mo-S/400°C DHP/9 min	42.9	0.5	/	/	3.6	2.2	2.3	1.2	1.3	2.4	
Co-Mo-S/400°C DHP/30 min	84.0	0.9	1.3	1.2	4.0	2.5	2.7	1.7	1.9	3.8	
Co-Mo-S/400°C DHP/60 min	96.0	1.1	1.5	1.5	3.7	2.6	2.9	2.3	2.4	4.6	
Co-Mo-S/400°C DHP/60 min ^a	98.4	1.2	1.7	1.6	3.5	2.6	2.8	2.4	2.4	5.0	
Co-Mo-S/400°C Phen/60 min	98.4	1.8	/	/	4.3	3.4	3.7	3.5	4.0	/	
Co-Mo-S/425°C Phen/60 min	99.7	2.3	3.0	2.7	4.5	3.6	3.9	4.3	4.3	/	
Co-Mo-S/425°C DHP/60 min	99.1	1.4	2.0	1.8	3.6	2.8	3.1	2.7	3.4	5.6	
Co-Mo/425°C Phen/60 min	95.2	1.6	2.2	2.0	4.0	3.0	3.4	3.1	3.5	6.2	
Co-Mo/425°C DHP/60 min	90.0	1.5	1.4	1.4	3.2	2.6	2.1	2.7	2.9	4.7	
Co-Mo/425°C 60 min	90.0	4.1	5.0	4.7	7.1	5.8	6.2	7.1	8.8	/	

a. In this run 600 mg of NMBB and 60 mg of Co-Mo-S was charged.

Table 7

Comparison in Selectivity of Bond Broken

<u>Reaction Condition</u>	<u>d-bond broken/a-bond broken</u>
425°C/D ₂ /60 min	6.12
425°C/N ₂ /60 min	7.15
425°C/N ₂ /60 min/DHP	1.02
419°C/60 min/sealed tube/DHP ^a	1.4
425°C/N ₂ /60 min/DHP/graph.c.	0.71
425°C/D ₂ /60 min/DHP/Co-Mo	0.36
425°C/D ₂ /60 min/DHP/Co-Mo-S	0.09
425°C/D ₂ /60 min/Phen./Co-Mo-S	0.08
419°C/60 min/sealed tube/black pearl 2000/DHP ^a	0.06

a. Data from reference 4.

Table 8

The H/D Ratio in the Major Products
in the Thermolysis of NMBB under D₂ (800 PSI)

<u>Reaction Condition</u>	<u>Conversion</u>	<u>H/D Tetralin</u>	<u>NP</u>	<u>MNP</u>	<u>H/D_{calculated}</u>
Co-Mo-S/400°C 15 min	99.7	0.46	0.31	0.54	0.4
Co-Mo-S/400°C 30 min	99.9	0.44	0.27	0.44	0.4
Co-Mo-S/400°C 60 min	100	0.48	0.30	0.47	0.4
Co-Mo-S/400°C DHP/9 min	42.9	2.30	2.69	3.29	2.0
Co-Mo-S/400°C DHP/30 min	84.0	2.03	2.21	2.66	2.0
Co-Mo-S/400°C DHP/60 min	96.0	2.25	2.08	2.51	2.0
Co-Mo-S/400°C DHP/60 min ^a	98.4	2.47	2.03	2.54	2.4
Co-Mo-S/425°C DHP/60 min	99.1	2.32	1.87	2.28	2.0
Co-Mo-S/400°C phen/60 min	98.4	1.77	1.32	1.74	1.7
Co-Mo-S/425°C phen/60 min	99.1	1.66	1.24	1.54	1.7
Co-Mo/425°C DHP/60 min	44.2	2.74	2.14	3.80	2.0
Co-Mo/425°C 60 min	90.0	0.69	0.38	0.61	0.4
Co-Mo/425°C phen/60 min	95.2	1.99	1.64	1.93	1.7

a: In this run 600 mg of NMBB and 60 mg of Co-Mo-S were charged.

Table 9

The Relative Amount of Hydrogenation/Dehydrogenation Products
of 9,10-Dihydrophenanthrene/Phenanthrene in the Thermolysis of NMBB

<u>Condition</u>	<u>mol%</u>			
	<u>DHP</u>	<u>OHP</u>	<u>THP</u>	<u>Phen.</u>
425°C/D ₂ /60 min DHP/Co-Mo-S	21.3	16.8	22.2	39.7
400°C/D ₂ /60 min Phen./Co-Mo-S	28.2	14.4	17.9	39.5
400°C/D ₂ /60 min DHP/Co-Mo-S a	26.1	18.8	18.9	36.0
400°C/D ₂ /60 min DHP/Co-Mo-S	28.7	12.6	17.3	41.4
400°C/D ₂ /30 min DHP/Co-Mo-S	32.5	5.2	11.6	50.6
400°C/D ₂ /9 min DHP/Co-Mo-S	63.1	4.0	0.3	32.7
425°C/D ₂ /60 min DHP/Co-Mo	48.6	1.1	7.9	45.4
425°C/D ₂ /60 min Phen/Co-Mo-S	18.7	19.6	24.0	37.7
425°C/D ₂ /60 min Phen/Co-Mo	23.0	5.7	18.3	52.9
425°C/N ₂ /60 min DHP	84.3	1.0	1.0	13.7
425°C/N ₂ /60 min DHP/graph.c	82.7	0.8	1.0	15.5
425°C/N ₂ /60 min DHP/Co-Mo	43.1	0.8	3.0	53.2

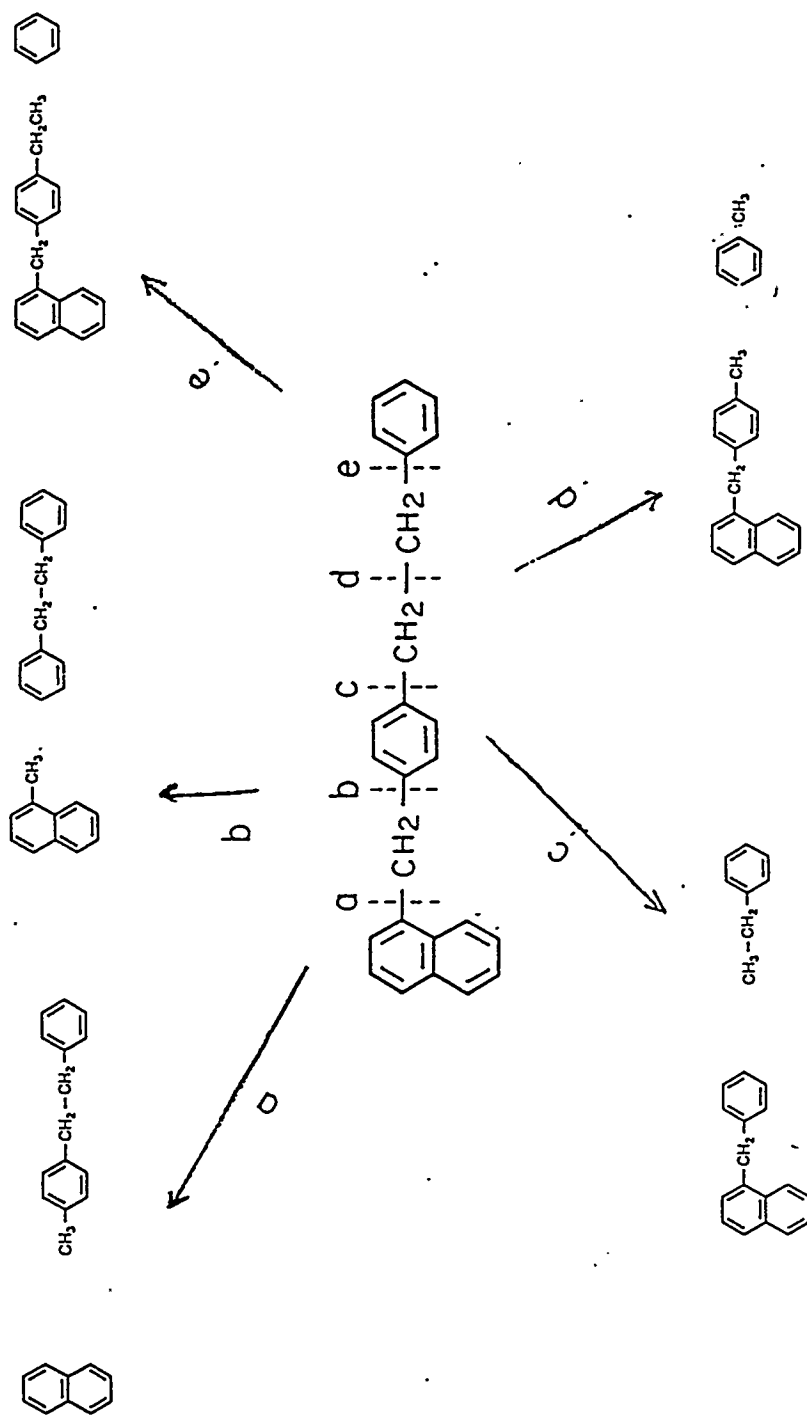


Figure 1. Products of bond cleavage reactions of NMBB.

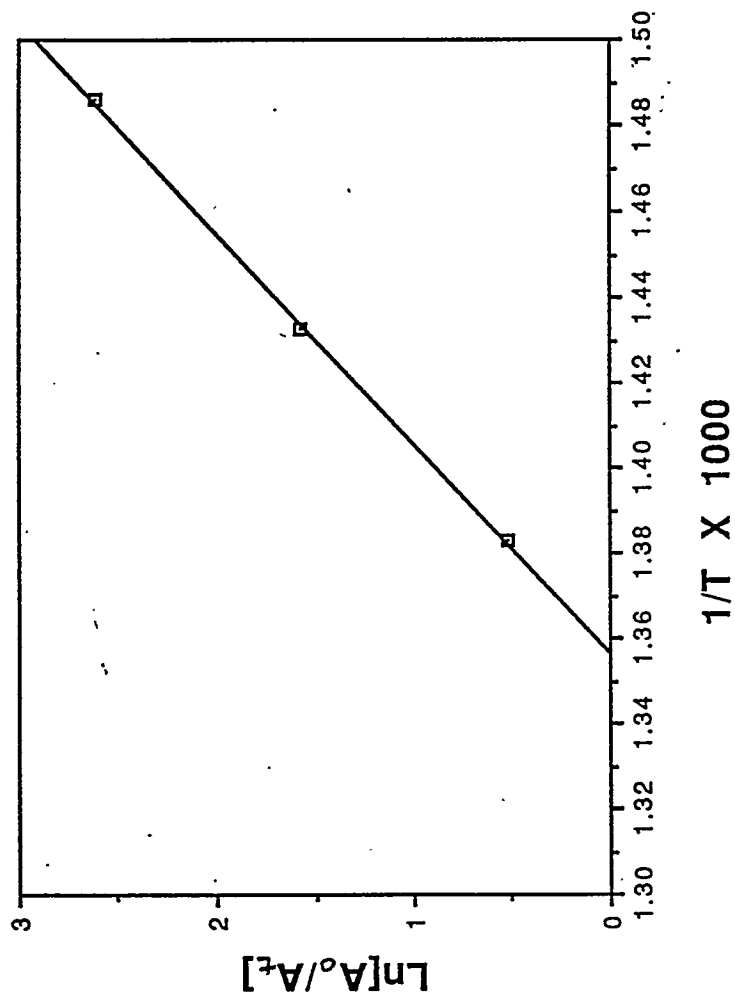
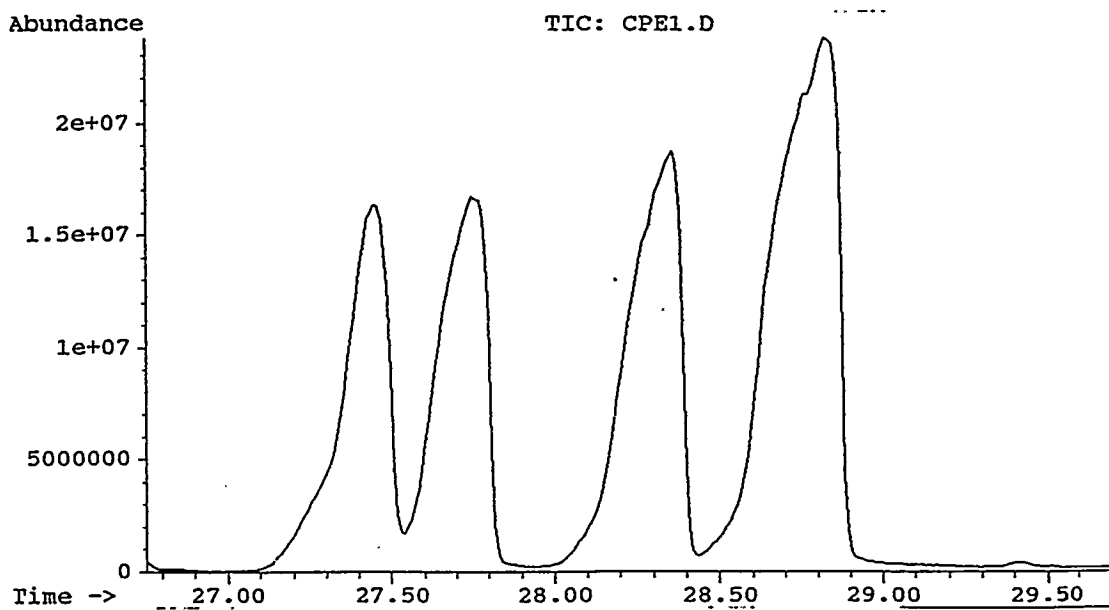
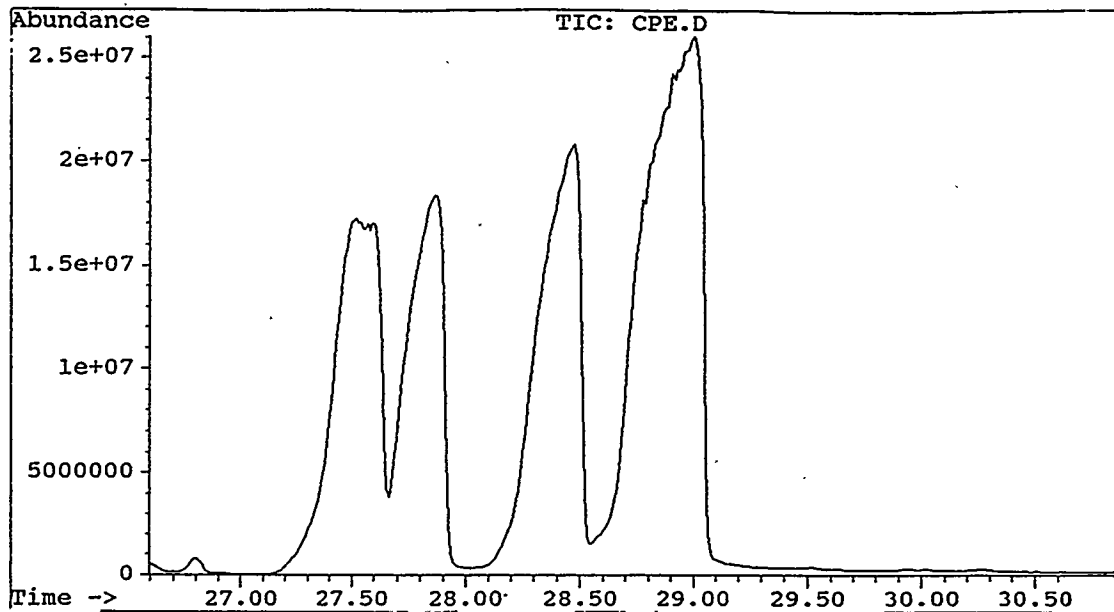


Figure 2. Arrhenius plot for the thermolysis of NMBB under D_2 .

Figure 3. Hydrogenation/dehydrogenation product distribution of DHP/phenanthrene in the thermolysis of NMBB (Top: starting from DHP; bottom: starting from phenanthrene).



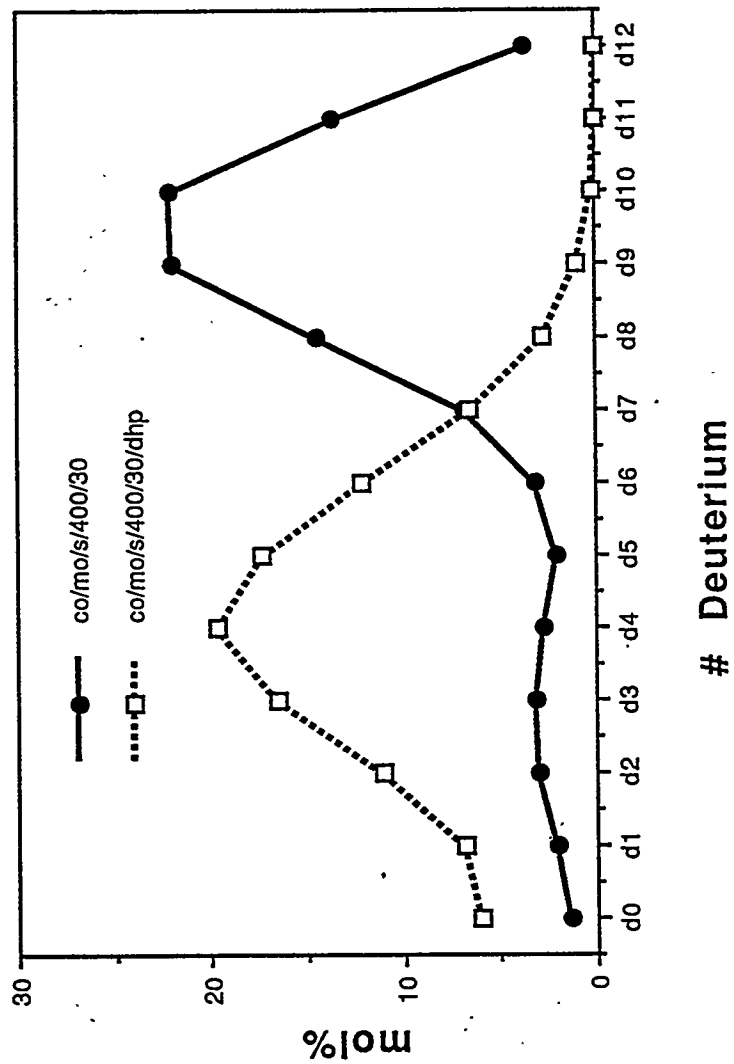


Figure 4. Deuterium incorporation into tetralin in the thermolysis of NMBB under D_2 at 400°C, 30 min. over Co-Mo-S. (- - -, without DHP; - - -, in the presence of DHP).

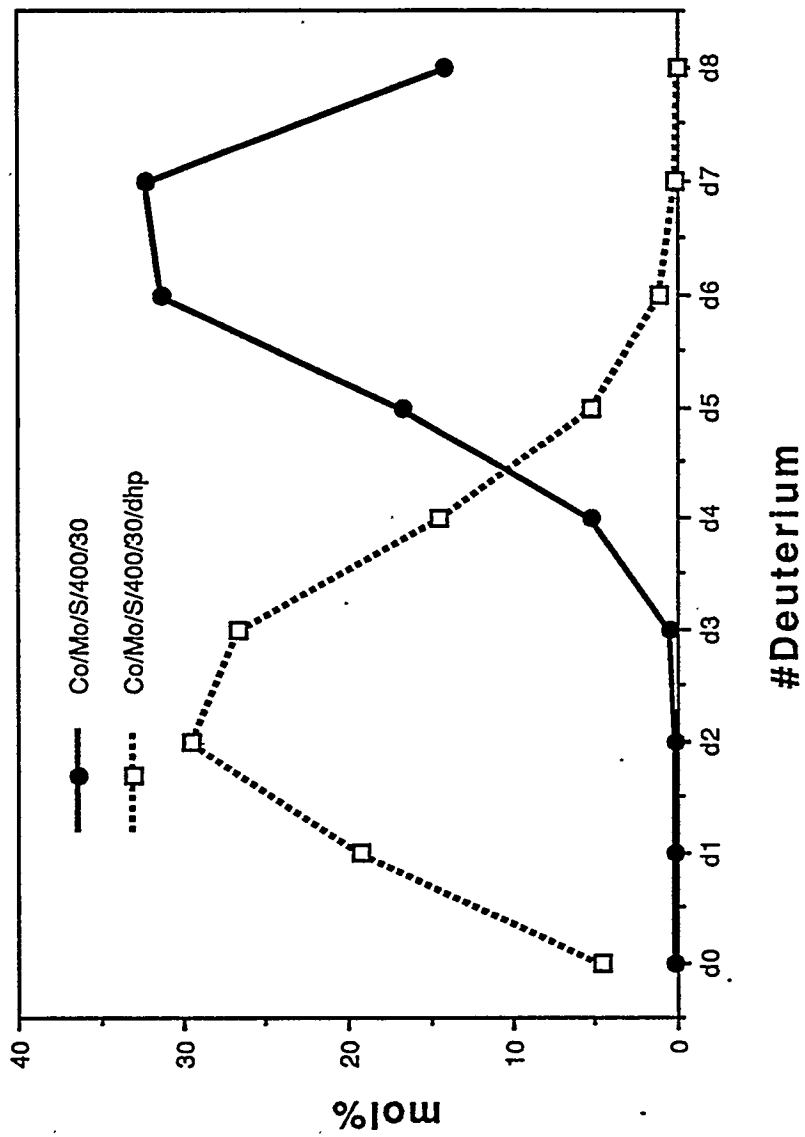


Figure 5. Deuterium incorporation into naphthalene in the thermolysis of NMBB under D₂ at 400°C, 30 min. over Co-Mo-S (- - -, without DHP; - - -, in the presence of DHP).

Figure 6. Glass reaction vessel for thermolysis under D_2 .

