

ENCLOSURE (B) 2

ON THE THERMAL CHANGE
OF AROMATIC COMPOUNDS IN THE PRESENCE
OF HIGH PRESSURE HYDROGEN

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by

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ENCLOSURE (B)2SUMMARY

Naphthalene, anthracene, phenol, a-naphthol and b-naphthol were heated at 450-500°C in the presence of a small amount of calcium chloride and hydrogen pressure of 70-80 atmospheres at 0°C. The chemical composition and physical properties of the reaction products were examined with the following results:

(1) Naphthalene: When naphthalene was heated at 500°C for 5 hours in the presence of calcium-chloride with hydrogen pressure of 80 atmospheres at 0°C, 60% of it was cracked, and the liquid reaction product consisted of benzene, and its homologues, and the gaseous reaction product consisted of methane (30 parts) and ethane (70 parts).

(2) Anthracene: This substance was cracked under the same conditions and was converted into 16% of gaseous hydrocarbons containing methane and ethane, and 74% of liquid hydrocarbons, containing 47% naphthalene and its derivatives, 27% benzene and its homologues, and 10% dianthracene.

(3) Phenol: At 500°C, phenol was decomposed into 30% benzene, 11% water and a small amount of di-phenyl, di-phenyl-ether and diphenol. The gaseous substances consisted of methane and ethane.

(4) Naphthol: When a-naphthol was heated at 450°C with a hydrogen pressure of 20 atmospheres at 0°C, most of it was liquefied. The products consisted of benzene homologues, naphthalene, tetralin, unreacted naphthol, and water.

b-Naphthol was cracked under the same conditions and its liquid product was very similar to that from a-naphthol.

I. INTRODUCTION

It is known that aromatic compounds are converted into lower aromatic compounds by cracking in the presence of hydrogen and a nickel catalyst. It was considered that further investigations along these lines would be of importance from the standpoint of developing a theory for production of gasoline from heavy oily substances, such as coal-tars or petroleum.

In earlier work on the cracking of aromatic compounds, the catalysts used were limited to reduced metals or metallic oxides. Calcium chloride was used in the present study, because it was known to be an excellent catalyst for catalytic cracking of petroleum oils.

Key research personnel working on project were: Chem. Eng. S. YAMAGUCHI and Chem. Eng. Assist. O. FUJII.

II. DETAILED DESCRIPTION

The naphthalene, anthracene, phenol, and a-, b-naphthol used in these experiments were proved to be fairly pure, on the basis of their physical constants, as shown in Table I(B)2.

In these experiments, a weighed sample was introduced into an autoclave, and

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after replacing the air by hydrogen, the pressure of the hydrogen was raised to the required value. The autoclave was electrically heated to the required temperature and was mechanically shaken during the reaction period. Changes of temperature and pressure during the reaction were recorded every ten minutes. After the reaction the apparatus was cooled, the volume of gas remaining was measured, and the chemical composition and physical properties of the reaction products were examined carefully.

A. Naphthalene

When naphthalene (100gm) was heated for 6 hours with 10% of calcium chloride at 500°C with initial hydrogen pressure of 71 atm. at 0°C, a fall of 11 atm. was observed (see Figure 1(B)2).

The gas in the autoclave was composed of 85.9% of H₂, 10.3% of C₂H₆, 4.6% of CH₄, and 0.2% of C_nH_{2n}.

The reaction product (67gm) in the autoclave consisted of liquid and solid substances, which were separated by filtration.

The solid amounted to 10gm and was found to be naphthalene, for, after purification by recrystallization from alcohol, it melted at 81°C, and the picrate at 151°C.

The liquid product (65gm) was distilled over metallic sodium at 759.5mm and separated into six fractions with the physical constants as shown in Table II(B)2.

Fractions 1 and 2, on the basis of their physical constants, appeared to be benzene and toluene respectively. The composition of the former was confirmed by converting it to nitrobenzene and then reducing it to aniline, and the latter by oxidation with potassium permanganate to benzoic acid (m.p. 121°C).

Fraction 3 and 4 were supposed, from their physical constants, to be a mixture of o-Xylene and ethyl benzene.

Fraction 5, consisting of naphthalene, Xylene, and ethyl benzene, was treated with picric acid in alcoholic solution to separate naphthalene.

The picrates, separated from volatile hydrocarbons by distillation under reduced pressure, amounted to 4.8gm, from which pure naphthalene was isolated with a yield of 1.2 gm.

The mixture of hydrocarbons separated from naphthalene weighed 3.6gm, and with its boiling point 124-145°C, refractive index $n_D^{25} = 1.4961$, and density $d_4^{25} = 0.8695$, the ratio of Xylene to ethyl benzene was estimated at 7:3.

Fraction 3 was composed of naphthalene as shown by the physical properties and also by the properties of the picrate.

B. Anthracene

Anthracene (100gm) was heated at 500°C for 6 hours with 10gm of calcium chloride and hydrogen pressure of 84 atm. at 0°C. The drop in pressure was 17.6 atm. at 0°C. (Refer to Figure 2(B)2).

The gaseous product was composed of 89.1% of H₂, 3.2% of CH₄, 7.6% of C₂H₆ and 0.1% of C_nH_{2n}. (Refer to Figure 2(B)2).

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From the reaction products, 10gm of solid and 74gm of liquid ($d_4^{25} = 0.984$, $n_D^{25} = 1.584$) were isolated.

The liquid reaction products (70gm) were fractionated at 758.8mm over metallic sodium as shown in Table III(B)2.

The fractions 1 and 2 were identified from their physical and chemical properties as benzene and toluene respectively.

The fractions 3 and 4 were also assumed to be mixtures of Xylene and ethyl benzene on the basis of their physical constants. Fractions 5 and 6, contained 14.9gm of crystals which had a m.p. of 78°C, and were confirmed to be naphthalene from the melting point and combustion analysis of the substance purified by crystallization from alcohol.

Found:	C, 93.62%;	H, 6.29%
Calc.		
for		
$C_{10}H_8$:	93.75%	6.25%

The liquid portion (7gm) remaining was supposed to contain alkyl-naphthalenes, and from it a-methyl naphthalene was isolated, by crystallization from hot alcoholic solution, in the form of a yellow crystalline picrate melting at 116-116.5°C in yield of 3.7gm.

Fractions 7 and 8, both were viscous liquids containing some solid substances, and were assumed to be mixtures of alkyl naphthalenes. The isolation of pure substances from the liquids by the formation of picrates was tried, but only red picrate melting at 161-172°C was isolated.

Lastly, there was a solid residue which was practically insoluble in alcohol, ether and benzene, and showed a melting point of 242-243°C. After purification by crystallization from ether solution.

These properties agreed with those of dianthracene prepared by Graebe and Lieberman, and by Ordendorff and Cameron.

Combustion analysis gave the following results:

Found:	C, 93.85%;	H, 5.41%
Calc.		
for		
$C_{14}H_{10}$:	94.38%	5.61%

C. Phenol

Phenol (100gm) was heated at 500°C for 5 hours with 10gm of calcium chloride and hydrogen pressure of 75 atm. at 0°C. The fall in pressure was 12 atm. at 0°C (Refer to Figure 3(B)2).

The gaseous product was composed of 91.4% of H_2 , 7.5% of C_2H_2n+2 , 0.4% of C_2H_2n , 0.7% of CO and 0.2% of CO_2 .

From the reaction products 77.5gm of liquid ($n_D^{25} = 1.532$, $d_4^{25} = 0.932$) and 10.7gm of water were isolated.

The liquid reaction product was subjected to fractional distillation

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as shown in Table IV(B)2.

Fractions 1, 2 and 3 were identified as benzene from their physical constants; and fractions 5 and 6 were assumed to be unreacted phenol and various kinds of di-phenols.

D. Naphthols

1. a-naphthol. When a-naphthol was heated at 450°C with 10% of calcium chloride and hydrogen pressure of 80 atm. at 0°C, a pressure drop of 19 atm. was observed. (Figure 4(B)2).

The compound was decomposed into 1-2% gas, 91% oily substance, and the balance, water.

The gas in the autoclave was composed of 97.8% of H_2 , 1.0% of C_nH_{2n+2} , 0.4% of C_nH_{2n} , 0.3% of CO and 0.4% of CO_2 .

The oily substance ($d_4^{25} = 1.021$, $n_D^{25} = 1.594$) was treated with 10% of NaOH solution and separated into acidic and neutral fractions. The former was found to be unreacted naphthol, for, after purification by recrystallization from alcohol, it melted at 97°C. The latter substance, 72gm ($n_D^{25} = 1.585$, $d_4^{25} = 1.016$), was distilled under atmospheric and reduced pressures and separated into six fractions with physical constants as shown in Table V(B)2.

Fraction 1 was believed, from its physical constants, to be a benzene derivative. The crystals in fractions 2 and 3 (m.p. 81°C and m.p. of its picrate is 151°C) were assumed to be naphthalene.

The liquid substance in fraction 2 (12gm) was treated with picric acid (9gm) in alcoholic solution in order to separate naphthalene. The picrate, separated from the volatile hydrocarbons by distillation under reduced pressure, amounted to 7.5gm, and with its boiling point 196-202°C, refractive index $n_D^{25} = 1.5363$, density $d_4^{25} = 0.9650$ and combustion analysis (C = 91.04%, H = 8.94%, Calc. for $C_{10}H_{12}$ being C = 90.91%, H = 9.09%), this was confirmed to be tetralin. The residual portion (4gm) of yellowish crystals separated from tetralin was presumed to be naphthalene.

The crystals separated from fractions 4 and 5 by recrystallization (m.p. 181.5-182°C) were found to be b,b-dinaphthyl, for, its picrate melted at 184.2-184.6°C and combustion analysis was:

Actual:	C, 94.09%	H, 6.00%
Calc. for $C_{20}H_{14}$:	94.50%	5.50%

The solution from which b,b-naphthyl had been separated was assumed to be a mixture of di-naphthyl, di-naphthyl-ether and di-tetra-hydro-naphthyl-ether from its distillation (125-130°C at 2mm) and combustion analysis, C=88.1%, H=7.1% and 0.4.8%.

2. b-Naphthol. The cracking of b-naphthol was performed under the same conditions and the compounds was decomposed into 2.5% gaseous hydrocarbons ($H_2 = 94.0\%$, $C_nH_{2n+2} = 4.2\%$, $CO = 1.4\%$) and the balance, liquid hydrocarbons, (Refer to Figure 3(B)2).

The latter was examined similarly to the a-naphthol case, and analytical results are as follows:

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III. CONCLUSIONS

By comparison of these results with previous work, it is evident that the thermal conversion of aromatic compounds in the presence of high pressure hydrogen was accelerated by the presence of calcium chloride, and the rate of conversion into lower hydrocarbons was about the same as when metallic or metallic oxide catalysts are used.

Table I(B)2
PHYSICAL CONSTANTS OF COMPOUNDS USED

	B.P. (°C)	M.P. (°C)
Naphthalene	214-218 (761mm)	81
Anthracene		216
Phenol	179-180 (764mm)	41
α -naphthol		97.5
β -naphthol		106

Table II(B)2
PHYSICAL CONSTANTS OF FRACTIONS

Fraction	B.P. (°C)	Yield (gm)	n_D^{25}	d_4^{25}	Remarks
1	75-90	4.5	1.497	0.869	Benzene
2	90-120	13.1	1.496	0.867	Toluene
3	120-140	10.1	1.495	0.865	Ethyl-Benzene
4	140-155	3.0	1.499	0.871	O-Xylene
5	155-200	4.8	1.531	0.916	
6	200-220	26.5		Solid	

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Table III(B)2
FRACTIONATION OF REACTION PRODUCTS

Fraction	B.P. (°C)	Yield (gm)	n_D^{25}	d_4^{25}	Remarks
1	75-90	6.0	1.490	0.858	Benzene
2	90-120	13.5	1.495	0.862	Toluene
3	120-140	1.5	1.497	0.866	Ethyl-Benzene
4	140-200	3.2	1.528	0.895	o-Xylene
5	200-220	8.7	Liquid with naphthalene crystals		
6	220-240	13.5			
7	240-270	13.5			
8	270-325	5.0	Resin with crystals		
9	Residue	5.1			

Table IV(B)2
FRACTIONATION OF PHENOL REACTION PRODUCT

Fraction	B.P. (°C)	Yield (gm)	n_D^{25}	d_4^{25}
1	70-79.5	10.8	1.484	0.852
2	79.5-80	19.5	1.494	0.869
3	80-81	1.0	1.496	0.870
4	81-175			
5	175-188	41.0	Crystals	
6	(120-154) at 2mm	2.1	Resinous matter	
7	Residue	3.1		

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Table V(B)2
FRACTIONATION OF a-NAPHTHOL REACTION PRODUCT

Fraction	B.P. (°C)	Yield (gm)	n _D ²⁵	d ₄ ²⁵
1	180-200	2.1	1.5306	0.9305
2	200-220	50.0	1.5607	0.9821
3	(120) at 2.5mm	0.5	Crystal	
4	(120-200) at 2.5mm	6.5		
5	(200-240) at 2.5mm	7.5		
6	Residue	5.4		

Table VI(B)2
FRACTIONATION OF b-NAPHTHOL REACTION PRODUCT

Acidic Substance: 19.5% (mostly unreacted β-naphthol)					
Fraction	B.P. (75Emm) (°C)		Yield (gm)		
1	270-277		2.5		
2	277-280		14.5		
3	280		2.5		
Neutral substance: 69.5% of b-naphthol					
Fraction	B.P. (°C)	Yield (gm)	n _D ²⁵	d ₄ ²⁵	Remarks
1	132-190	0.5	1.5260		Benzene-derivative
2	190-208	27.5	1.5517	0.9721	Naphthalene 28 + Tetralin 72
3	208-215	15.3			
4	(60-120) 2.5mm	3.6			White crystal Naphthalene
5	(120-200) 2.5mm	5.4			Resin with Crystals Crystal, β,β-Dinaphthyl
6	(200-240) 2.5mm	13.8			Resinous matter*
7	Residue	3.4			

* Mixture of β,β-Dinaphthyl, tetra-hydro-dinaphthyl ether and dinaphthyl ether.

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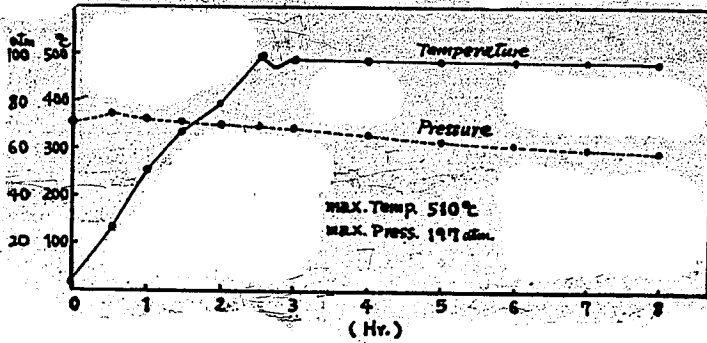


Figure 1(B)2
NAPHTHALENE

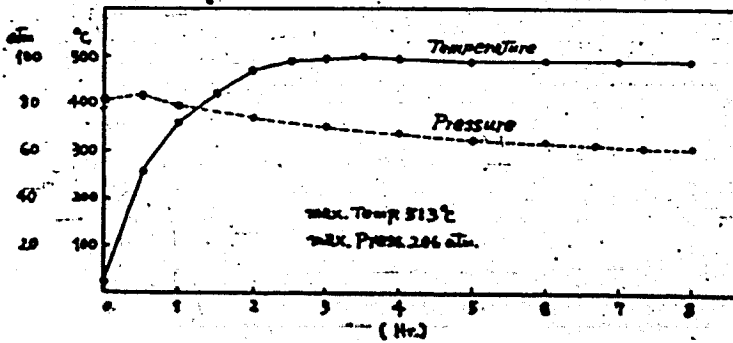


Figure 2(B)2
ANTHRACENE

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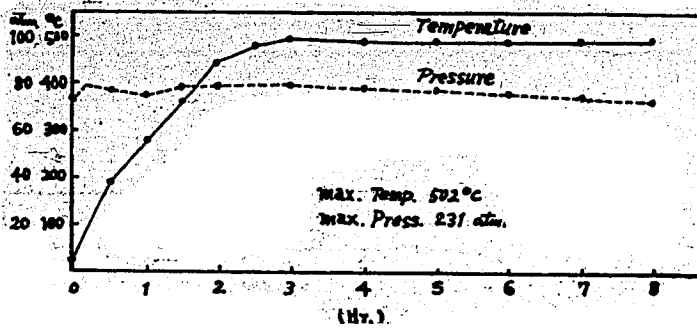


Figure 3(B)2
PHENOL

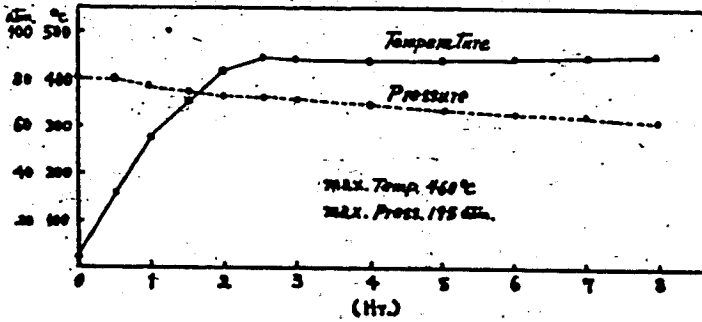


Figure 4(B)2
a-NAPHTHOL

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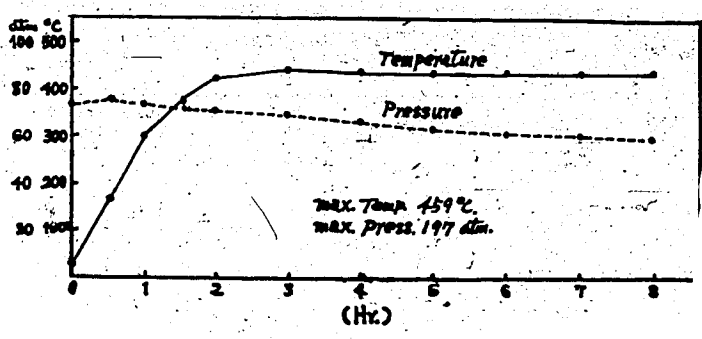


Figure 5(B)2
b-NAPHTHOL