ENCLOSURE (B) 14

STUDIES ON THE HYDROGENATION OF MIXTURES OF AROMATIC COMPOUNDS

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by

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ENCLOSURE (B)14

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)14

SUMMARY

The object of these studies was to investigate the catalytic hydrogenation of mixtures of aromatic compounds to obtain a better understanding of coal tar hydrogenation reactions. The following results were obtained:

(1) High pressure hydrogenation of anthracene over a nickel catalyst was accelerated by mixing with benzene, whereas, conversion of the latter was retarded.

(2) The effect of cyclo-hexane on the hydrogenation of anthracene was similar to that of benzene.

I. INTRODUCTION

These studies on the hydrogenation of mixtures of aromatic compounds, especially benzene and anthracene, which are two important components of coal tar, were made from January, 1940 to June, 1941.

II. DETAILED DESCRIPTION

A. Feed Stocks

1. Anthracene. An extra-pure commercial anthracene was treated with acid clay and recrystallized with alcohol and benzene. The melting point of the final product was 214-216°C.

2. Benzene. A fraction of an extra-pure commercial benzene, boiling at 79.5°C, was washed with 80% concentrated sulphuric acid and 10% concentrated caustic soda solution. The fraction of this refined distillate boiling from 80°C. to 80.3°C. was further washed with a solution of mercuric oxide and sulphuric acid, then with 10% caustic soda solution and distilled water, dried with calcium chloride, redistilled and dehydrated over metallic sodium. Properties were as follows:

Boiling point	80.2°C.
Density (20/4)	0.8793
Refractive index (n^{20}_{D})..........	1.4986

3. Cyclo-hexane. The product of refined benzene, hydrogenated at 200°C. over a nickel catalyst, was washed with 98% concentrated sulphuric acid, 10% concentrated caustic soda solution, and distilled water, dried with calcium chloride, redistilled and dehydrated over metallic sodium. Properties were as follows:

Boiling point	80.5°C.
Density (20/4).............	0.7780
Refractive index (n^{20}_{D}).....	1.4230

4. Hydrogen. Hydrogen gas was produced by electrolysis of water with a purity over 99.5%.

5. <u>Catalyst.</u> An extra-pure metallic nickel was dissolved in concentrated nitric acid and, after filtering off impurities, this solution was diluted and neutralized with ammonia. The precipitated nickel hydroxide was washed with distilled water, dried and powdered This catalyst was oxydized and reduced at 280-290°C. before using.

B. <u>Apparatus.</u> A shaking type autoclave was used with the following characteristics:

Inner volume	625 c.c.
Material	Ni-Cr-steel.
Heating	Outside, electric.
Frequency of vibration	60-70/min.

C. <u>Experimental Procedure</u>

The autoclave, including the sample and catalyst, was pressured with hydrogen to the 100 atmospheres, and heated to the required temperature at a rate of 2°C/min.

After holding at the reaction temperature for one hour, heating was stopped, but the shaking was continued until the temperature fell below 200°C. After cooling for one day, the pressure and the temperature were measured and the gas was released. The liquid product was separated by distillation into a benzene-cyclohexane cut and an anthracene-hydroanthracene cut. The benzene yield was determined by the density and the refractive index of the first cut.

The latter cut was analyzed by recrystallization with alcohol and each compound was determined by appearance, melting point, properties of picrate and ultimate analysis.

D. <u>Hydrogenation of Benzene</u>

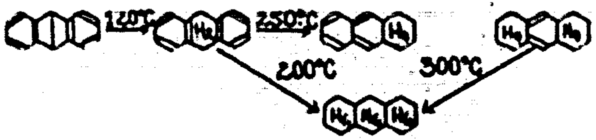
It is well known, that the reduction of benzene to cyclohexane in the presence of reduced nickel catalyst starts at 70°C. and is accelerated by increased temperature, up to 300°C. Over 300°C., cyclohexane is dehydrogenated again to benzene.

The author hydrogenated benzene at several temperatures under high pressure hydrogen in the presence of reduced nickel catalyst and obtained the yields summarized in Table I(B)14.

The content of saturated hydrocarbons in the produced gas was 2.5%. The change of reaction velocity with temperature, as indicated by change of pressure with time, dp/dt, was as shown in Table II(B)14. (Also refer to Figures 1(B)14 through 3(B)14.)

E. <u>Hydrogenation of Anthracene</u>

Dr. YOKOTA reported, that by hydrogenation of anthracene, the dihydrocompound was produced first, and this compound changed, on one hand, directly to the perhydro-compound and, on the other hand, the tetrahydrocompound, octahydro-compound, and finally to the perhydro-compound:



The author hydrogenated anthracene in the presence of reduced nickel catalyst under high pressure and the results are summarized in Table III(B)14.

At 180-200°C a small amount of tetrahydro-compound was produced. Above 217°C, the melting temperature of this compound, the hydrogenation was accelerated and the tetrahydro-compound was hydrogenated to octa- or perhydro-compounds.

The maximum rates of pressure change were as shown in Table IV(B)14. (Also refer to Figures 2(B)14 and 3(B)14.)

F. Hydrogenation of a Mixture of Benzene and Anthracene

1. Hydrogenation of a mixture of 1 part benzene and 1 part anthracene.

At a temperature of 140°C, the reaction of a mixture of 1 part benzene and 1 part anthracene began at 170°C after 35 minutes, and dp/dt reached the maximum value of 1 kg/min after 1 hour (refer to Figure 1(B)14).

After this, only a slow reaction occurred. This showed, that for the first hour, only the hydrogenation of benzene took place and after one hour, anthracene was converted.

At a reaction temperature of 200°C, the maximum value of dp/dt, 0.7 kg/min, was reached after one hour. Afterwards, a slow reaction took place and the value of dp/dt was 0.3 kg/min after 1 hr. 45 min., and 0.6 kg/min after 2 hrs. 20 min. (refer to Figure 2(B)14). This indicated, that after 1 hr. 45 min., the hydrogenation of anthracene began.

At a reaction temperature of 260°C, the maximum point dp/dt at 1 hour was due to the hydrogenation of benzene and the maximum of 3.6 kg/min at 1 hr. 45 min. was due to hydrogenation of the anthracene.

The amount of cyclohexane produced by hydrogenation of benzene decreased from 7%, at 80°C, to 2%, at 140°C, and afterwards, increased to 34%, at 230°C. On the contrary, the hydrogenation of anthracene was much accelerated; the reaction began at 100°C, and 12.5% of tetrahydro-compounds was produced at 140°C, (the temperature giving minimum amount of cyclohexane), and at 180°C, half of the anthracene was converted. The conversion was much improved over the hydrogenation of anthracene alone, and the lowering of reaction temperature, equivalent to about 60°C, resulted from the addition of the benzene. It is interesting to note that the hydrogenation of benzene began at 200°C, at which temperature the conversion of anthracene was 95%. Refer to Tables V(B)14 and VI(B)14 and Figure 4(B)14.

It is concluded from these results that the following held true:

a. Benzene was first hydrogenated at temperatures below 100°C.

b. In the range of temperature from 100°C to 200°C, the hydrogenation of benzene was retarded, and the hydrogenation of anthracene was accelerated.

c. Over 200°C, benzene was freed from restraint of the anthracene and was converted to cyclohexane. At these temperatures, however, dehydrogenation of cyclohexane also took place and the benzene-cyclohexane equilibrium concentration ratio was about 1:1.

2. Hydrogenation of a mixture of 1 part of benzene and 2 parts anthracene:

The results of hydrogenation tests on a mixture of 1 part benzene and 2 parts anthracene are given in Table VII(B)14 and Figures 1(B)14 through 3(B)14. The hydrogenation of anthracene began at 140°C and its conversion was 50% at 200°C and 100% at 230°C. The conversion of benzene was higher than in the preceding experiment, amounting to 24% at 80°C, and it did not increase until the hydrogenation of anthracene was completed. This experiment also showed, that the hydrogenation of anthracene was accelerated by the presence of benzene and the hydrogenation of benzene took place after the former reaction was finished.

C. Hydrogenation of a Mixture of Anthracene and Cyclohexane

The author hydrogenated a mixture of equal parts of anthracene and cyclohexane at temperatures of 180°C, 200°C and 230°C. The results, summarized in Table VIII(B)14, showed that the hydrogenation of anthracene in this mixture was similar to its reaction in a mixture with benzene. No conversion of cyclohexane was observed.

From these results it was concluded, that the effects of benzene and cyclohexene on the hydrogenation of anthracene was similar.

III. CONCLUSIONS

The following conclusions were drawn with regard to the high-pressure hydrogenation of benzene and anthracene in the presence of a reduced nickel catalyst:

1. The hydrogenation of anthracene was accelerated by the existence of benzene, and the hydrogenation of the latter was retarded, taking place after the hydrogenation of anthracene was completed.

2. The effect of cyclohexane on the hydrogenation of anthracene was similar to that of benzene.

3. The results are of significance in connection with the hydrogenation of mixtures of aromatic compounds, such as coal-tar, and they give a suggestion as to methods for controlling reactions.

ENCLOSURE (B)14

Table I(B)14
HYDROGENATION OF BENZENE

Reaction temp.	Yield of cyclohexane
140°C	50 wt %
200°C	100 wt %
260°C	94 wt %

Table II(B)14
RELATIONSHIP BETWEEN REACTION RATE AND TIME (BENZENE)

Max. value of dp.dt.	Reaction temp.	Reaction time.
1.4 kg/min	140°C	1 hr. 20 min
3.1 kg/min	200°C	1 hr. 15 min
1.4 kg/min	260°C	1 hr. 50 min

Table III(B)14
HYDROGENATION OF ANTHRACENE

React. temp. (°C.)	Conversion (%)	Amount of hydrogenated product (% by wt.)			
		Dihydro Compd.	Tetrahydro Compd.	Octahydro Compd.	Perhydro Compd.
180°	5.1	0	5.1	0	0
200°	10.6	0	10.6	0	0
230°	100.	0	0	86.8	13.2
260°	100.	0	0	76.3	23.7

Table IV(B)14
RELATIONSHIP BETWEEN REACTION RATE AND TIME (ANTHRACENE)

Max. value of dp/dt.	React. temp.	Time of progress
0.3 kg/min	200°C	55 min.
1.4 kg/min	260°C	115 min

ENCLOSURE (B)14

Table V(B)14
HYDROGENATION OF MIXTURE OF BENZENE AND ANTHRACENE (1:1)

Reaction Temp. (°C)	Conversion of Anthracene %	Yield of Products from Anthracene (% by Wt.)				Conversion of Benzene (% by Wt)
		Dihydro Compd.	Tetrahydro Compd.	Octahydro Compd.	Perhydro Compd.	
80	0	0	0	0	0	6.8
100	0.6	0	0.6	0	0	2.9
120	6.8	0	6.8	0	0	3.4
140	12.5	0	12.5	0	0	2.1
160	39.3	2.0	37.3	0	0	2.4
180	46.7	3.1	43.6	0	0	3.9
200	95.0	15.4	79.6	0	0	8.0
230	100	0	0	87.3	12.7	33.5
260	100	0	0	83.4	16.6	49.9
300	100	0	0	64.1	35.9	50.8

Table VI(B)14
PROPERTIES OF GAS PRODUCED BY HYDROGENATION OF MIXTURE OF BENZENE AND ANTHRACENE (1:1)

Reaction Temp. (°C)	Yield (%)		
	C_nH_{2n}	C_nH_{2n+2}	n
230	0.3	0	-
260	0.6	3.3	1.3
300	0.4	2.0	1.8

ENCLOSURE (B)14

Table VII(B)14
HYDROGENATION OF MIXTURE OF BENZENE AND ANTHRACENE (1:2)

Reaction Temp. (°C)	Conversion of Anthracene %	Yield of Products from Anthracene(%byWt				Conversion of Benzene (% by Wt)
		Dihydro Compd.	Tetrahydro Compd.	Octahydro Compd.	Perhydro Compd.	
80	0	0	0	0	0	24.0
100	0	0	0	0	0	30.6
120	0	0	0	0	0	24.3
140	0.4	0	0.4	0	0	23.8
160	6.0	0	6.0	0	0	26.5
180	7.7	2.5	5.2	0	0	28.9
200	52.9	14.9	38.0	0	0	32.9
230	100	8.8	64.2	22.8	4.2	50.4
260	100	0	0	78.0	22.0	86.7
300	100	0	0	62.7	37.3	86.4

Table VIII(B)14
HYDROGENATION OF A MIXTURE OF ANTHRACENE AND CYCLOHEXANE (1:1)*

Reaction Temp. (°C)	Conversion of Anthracene (%)	Yield of Products from Anthracene (% by wt)			
		Dihydro Compd.	Tetrahydro Compd.	Octahydro Compd.	Perhydro Compd.
160	32.8	0	32.8	0	0
200	100	3.8	87.1	9.1	0
230	100	0	0	82.6	97.4

*No conversion of cyclohexane

ENCLOSURE (B)14

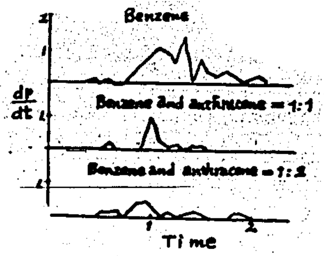


Figure 1(B)14

RELATION OF $\frac{dp}{dt}$ AND TIME IN THE HYDROGENATION AT 140°C

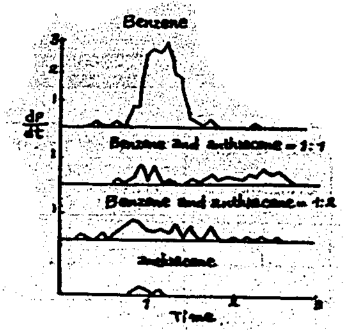


Figure 2(B)14

HYDROGENATION AT 200°C

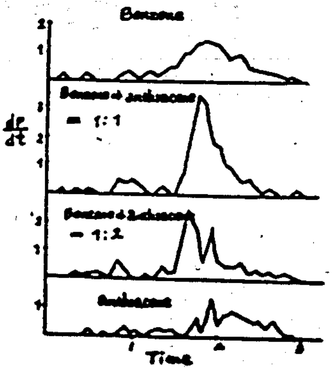


Figure 3(B)14

HYDROGENATION AT 250°C

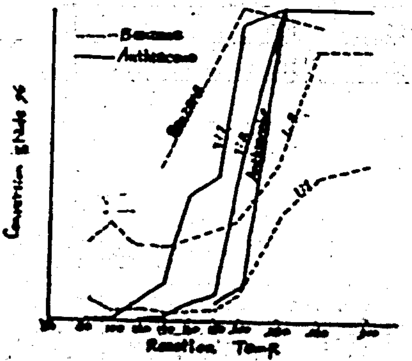


Figure 4(B)14

REACTION TEMPERATURE CONVERSION GRADE RELATION IN THE HYDROGENATION OF BENZENE, ANTHRACENE AND THEIR MIXTURE