ACTION OF REDUCED NICKEL AND HYDROGEN ON AROMATIC HYDROCARBONS UNDER HIGH PRESSURE AND TEMPERATURE.

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The reduction of benzene was assumed to proceed by the following steps:

$$C_6H_6 + H_2 = C_6H_8 + 0.8 \text{ cal.}$$
$$C_6H_8 + H_2 = C_6H_{10} + 25 \text{ cal.}$$
$$C_6H_{10} + H_2 = C_6H_{12} + 27.8 \text{ cal.}$$
$$C_6H_{12} + H_2 = C_6H_{14} + 11 \text{ cal.}$$

which were investigated comprehensively by Stohmann(1) in the series of his thermochemical studies of organic compounds, and he concluded that the jump in heat-toning between the first and second terms of the series compared with the two following, as well as between the third and fourth, indicates a fundamental difference of structure between benzene and its di- and tetra-hydrobenzenes, and also between tetrahydro- and hexahydrobenzenes, viz., that the benzene molecule is in the most stable state by packing together by the bonds and the combination by them in di- and tetra-hydrocompounds more loosely, reaching again a high degree of stability in hexahydrobenzene, and such observation led him to reject the Kekulé formula for benzene.

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(1) *J. prakt. Chem.*, **48** (1893), 447; **49** (1894), 260.

The structural formula for naphthalene proposed by Graebe was also rejected by Bamberger(1), and lately by Willstätter(2) from their studies of its reduction.

According to Professor Sabatier(3) benzene begins the catalytic hydrogenation to cyclohexane in presence of reduced nickel at 70° and proceeds with increased velocity as the temperature is increased to about 300°, and above this temperature there is no formation of cyclohexane, but the conversion of the latter into benzene and decomposition into methane and carbon have started. Under similar conditions naphthalene yields tetralin and decalin which decompose at high temperature into methane and benzene homologues.

When benzene and naphthalene treated in presence of nickel oxide at high temperature and under pressure, the experimental results(4) are on the whole very similar to those obtained by Sabatier's method.

The catalytic action of reduced nickel at high temperature and under pressure, apart from these theoretical considerations on the structure of aromatic hydrocarbons, would afford an idea for the cracking process in which permanent gas and volatile fuels for internal combustion engines are prepared from heavy hydrocarbons, and the formation of these compounds is regarded generally as depending on the temperature and pressure at which the process is carried out, with or without catalyst and hydrogen, and the present investigation was so carried out.

In the experiment, 100 gr. of pure benzene, b.p. 80°–80.5° (761 mm.), $n_D^{25}=1.498$, were introduced in an autoclave of 2 litres capacity, with 5 gr. of reduced nickel and hydrogen, and heated at 470° for 1 hour, under pressure of 80 atmospheres at 0°, after cooling the apparatus, the depression of pressure of hydrogen was 35 atm. at 0°, which corresponds to 2.7 mol %. (Fig. 1.) The gas in the autoclave was analysed with the following results:

CO_2	CO	C_nH_{2n}	C_nH_{2n+2}	H_2	n
0.1	—	—	1.4	98.5	1.2

The liquid reaction product was 92% in yield for theory, and on being fractionated:

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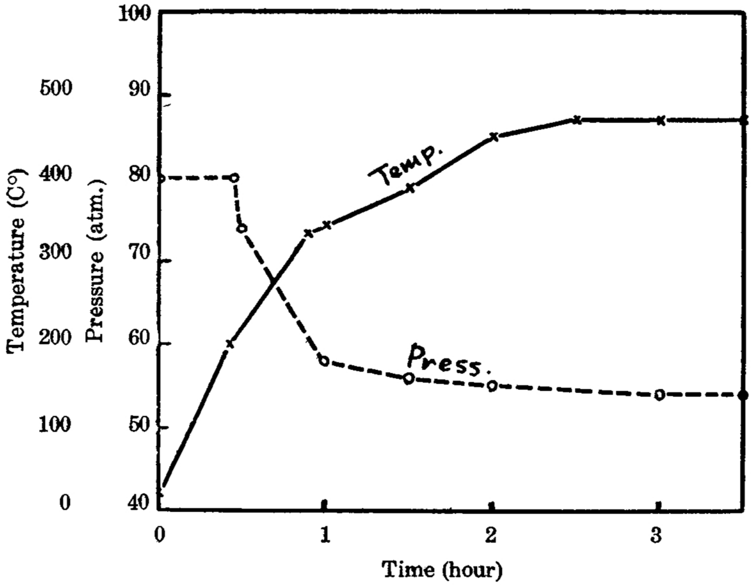
(1) *Ann.*, **257** (1890), 47.

(2) *Ber.*, **45** (1912), 1478.

(3) "La catalyse en chimie organique," (1920), p. 171, 221.

(4) W. N. Ipatiew "Aluminiumoxyd als Katalysator in der organischen Chemie," (1929), 78.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Pressure (atm.)
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200
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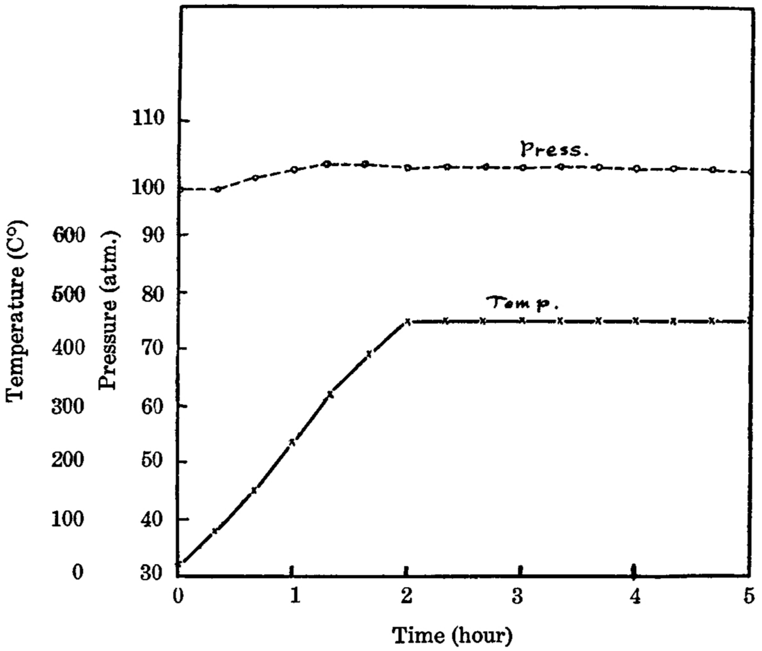
Temp.
Press.
0
1
2
3
Time (hour)

Fig. 1.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60
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40
30
Press.
Temp.
0
1
2
3
4
5
Time (hour)

Fig. 2.

	Fraction	Yield	n_D^{25}	d_4^{25}
1	77°–79°	55%	1.433	0.7843
2	79°–80.7°	30%	1.433	0.7806

The two fractions showing no reaction with bromine, were treated with a mixture of nitric and sulphuric acids, and show b.p. 80°–82°, $n_D^{25}=1.423$, $d_4^{25}=0.777$ which agree with the constants for cyclohexane.

When 166 gr. of pure cyclohexane heated in presence of hydrogen and 20 gr. reduced nickel in the autoclave at 450° for 3 hours under 100 atmospheric pressures at 0°, no appreciable change on pressure was noticed as indicated in Fig. 2, and the liquid substance in the autoclave boils from 80° to 85°, and thus cyclohexane is confirmed to be a stable compound under the above conditions, and the same is also noticed of benzene treated with hydrogen at 460° for 1 hour, and 100 atmospheric pressures at 0°.

While, benzene heated for 5 hours with hydrogen in presence of reduced nickel at 500°, under pressure of 100 atmospheres at 0°, undergoes the hydrogenation which follows with decomposition of the hydrogenated compound into methane on the one hand, and on the other into aromatic hydrocarbons. (Fig. 3).

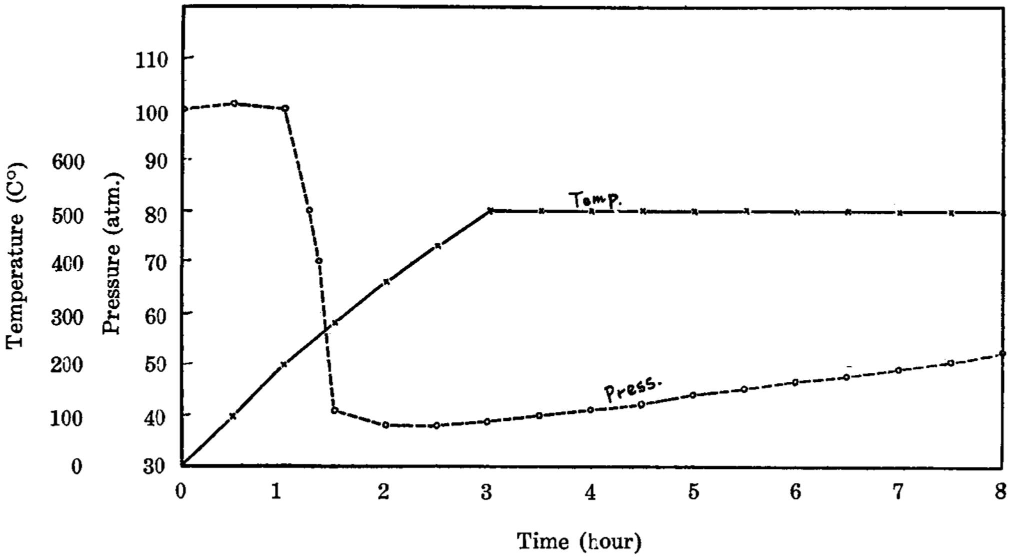

Fig. 3.

The reaction products are 28% gas, 41% liquid hydrocarbons and 14% coke. The gas was composed of 94.5% methane and 5.5% hydrogen. The liquid product was fractionated as follows:

Fraction	B.p.	%	n_D^{25}	d_4^{25}
1	48°- 65°	0.6	1.413	—
2	65°- 75°	1.4	1.446	0.789
3	75°- 85°	6.5	1.492	0.859
4	85°-120°	5.5	1.494	0.866
5	120°-180°	2.3	1.502	0.875
6	180°-250°	2.6	1.551	0.942
7	250°-300°	2.3	1.603	1.012
8	300°-320°	1.5	1.651	1.07
9	Residue	3.6	—	—

These results indicate that the fractions are composed of aromatic hydrocarbons, and benzene and toluene occur in fractions 3 and 4.

When benzene was first heated with hydrogen in presence of the catalyst under 200° and 100 atmospheric pressures at 0° for 2 hours, 3.9 mol % of hydrogen were absorbed, and the product was again heated at 500° for 3 hours with a new supply of hydrogen of 78 atmospheric pressures, and a depression of 17 atm. was noticed. (Fig. 4.) The reaction product was 5.4% methane and 95% of a liquid substance which was composed of cyclopentane, methyl cyclopentane and cyclohexane as will be seen in the following table:

Fraction	B.p.	Yield	d_4^{25}	n_D^{25}
1	48°-65°	2.9	0.744	1.409
2	65°-75°	28.7	0.753	1.415
3	75°-85°	31.7	0.772	1.424
4	85°-90°	0.4	—	1.423

The formation of cyclopentane, methyl cyclopentane with cyclohexane from benzene by catalytic reduction at high temperature and under pressure, is explained by assuming the formation of cyclohexene which is formed from cyclohexane by dehydrogenation and converted by isomerisation into methyl cyclopentane. The latter phase of the reactions has al-

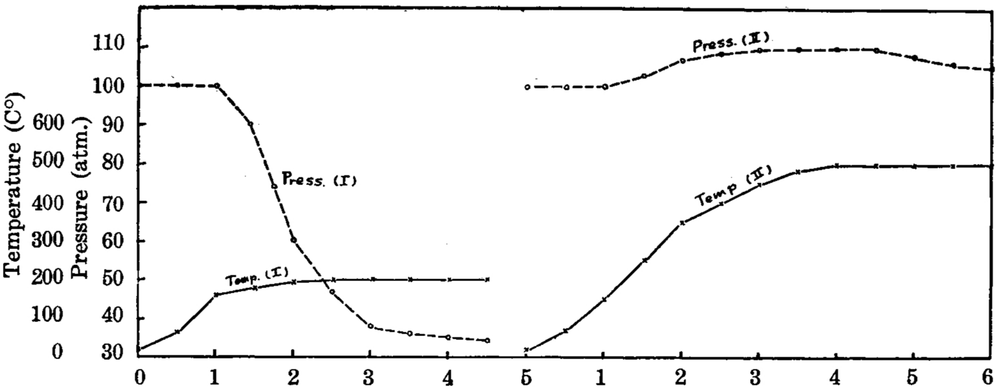

Fig. 4.

ready been noticed by Dr. H. Inoue⁽¹⁾ in his study on the catalytic action of Japanese acid earth on cyclohexanol and its drivatives, where cyclohexanol by passing on the catalyst heated at 200° was converted into cyclohexene, while at a high temperature, such as 330°, methyl cyclopentane occurred in the reaction product, which was actually derived from cyclohexene by the contact action of the catalyst at high temperature.

Such a view for the conversion of cyclohexane into cyclohexene was also accepted by D. T. Jones⁽²⁾ in the transformation of cyclohexane, heated to 500° in contact with porous porcelain, into hydrogen, ethane, benzene and some olefine hydrocarbons.

According to Ipatiew cyclohexane at high temperatures such as 600° appears to be more stable than n-hexane, and the isomerization of cyclohexane into methyl cyclopentane takes place under high pressure and in presence of alumina, but with ordinary pressure, even at 760°, there is no such isomerization.⁽³⁾ These facts are in harmony with the writers' case that cyclohexane and methyl cyclopentane occur in the product from benzene by catalytic reduction, but there is no formation of n-hexane.

Naphthalene. Although naphthalene⁽⁴⁾ itself gives no benzene on pyrolysis, dihydronaphthalene, tetralin and decalin pyrolyse at about 400° in forming hydrogen and naphthalene as chief products with some methane,

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(1) This Bulletin, **1** (1926), 219.
(2) *J. Chem. Soc.*, **107** (1915), 1582.
(3) *Ber.*, **37** (1904), 2961; **44** (1911), 2987.
(4) Egloff, *J. Soc. Chem. Ind.*, **35** (1916), 920.

ethane, benzene and unsaturated hydrocarbons.(1) In order to study the behavior of these hydrocarbons toward the catalyst and hydrogen at high temperature and under pressure, pure naphthalene b.p. 215°; m.p. 80°, was heated with hydrogen at 460°–500° under 80 atmospheric pressures at 0°, and no appreciable reaction was noticed to occur in the treatment. A similar situation is also noticeable even in presence of ferric oxide or copper oxide.

When, however, 100 gr. of naphalene in presence of 5 gr. of reduced nickel and hydrogen are heated at 470° and under 80 atmospheric pressures at 0° (Fig. 5.) yield 5% methane and 91% of a liquid substance which seems by fractional distillation to be composed of benzene homologue and tetralin as indicated in the table:

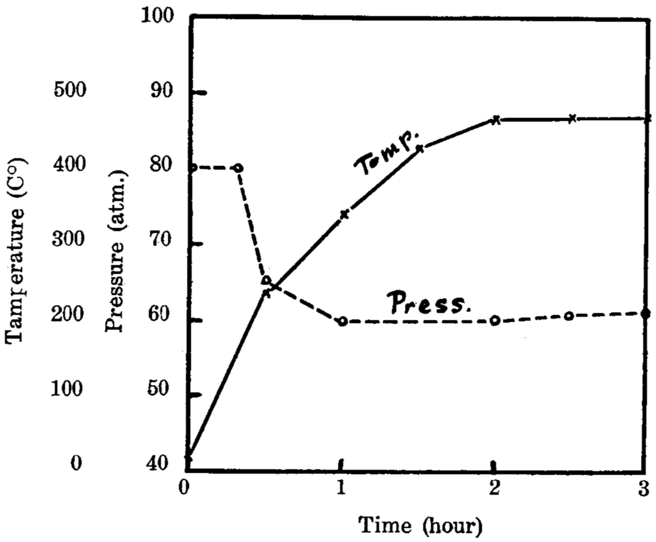

Fig. 5.

	Fraction	Yield	d_4^{25}	n_D^{25}	Remark
1	100°–150°	7 %	0.825	1.487	Benzene homologue
2	150°–180°	8 ,,	0.895	1.498	
3	180°–190°	18 ,,	0.901	1.502	Tetralin
4	190°–200°	26 ,,	0.935	1.521	
5	200°–210°	26 ,,	0.962	1.542	
6	Residue	2 ,,	—	—	

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(1) Jones, loc. cit.

Tetralin. When 100 gr. of tetralin, b.p. 206° (760 mm.) treated in presence of hydrogen and the catalyst under the same conditions described in the case of naphthalene (Fig. 6.), 5.6% methane and 92% of a liquid substance are formed and the latter is composed of benzene homologue and decalin.

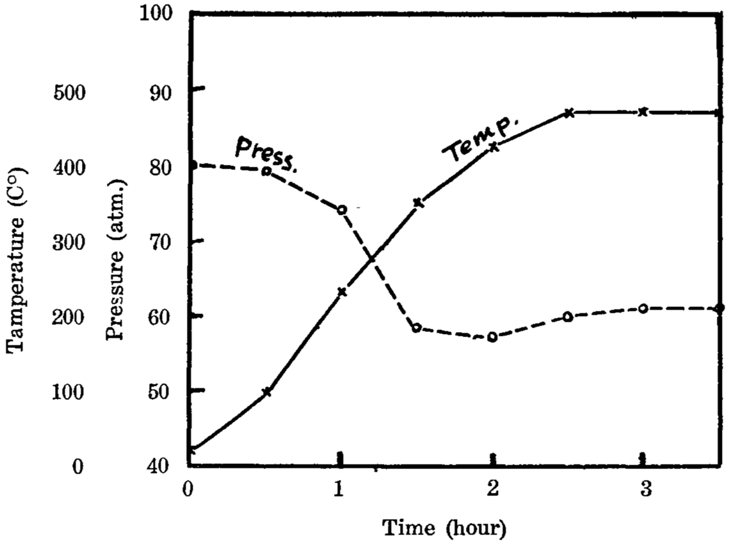

Fig. 6.

	Fraction	Yield	d_4^{25}	n_D^{25}	Remark
1	85°–180°	28 %	0.845	1.454	Benzene homologue
2	180°–185°	39 ,,	0.874	1.473	
3	185°–188°	18 ,,	0.879	1.477	Mostly decalin
4	188°–191°	5 ,,	0.889	1.483	
5	Residue	2 ,,	—	—	

Decalin. 200 gr. of pure decalin, b.p. 188° (760 mm.) heated with 20 gr. reduced nickel and hydrogen to 450° under 100 atmospheric pressures at 0° for 3 hours (Fig. 7), 3% methane and 97% of a liquid substance of the following compositions are formed.

When decalin is heated in presence of reduced nickel and hydrogen at 450° under 100 atmospheric pressures at 0°, only one part of the compound was decomposed into cyclohexane derivatives, while tetralin and naphthalene under similar conditions tend to be transformed into benzene homologues and decalin and benzene homologues and tetralin respectively.

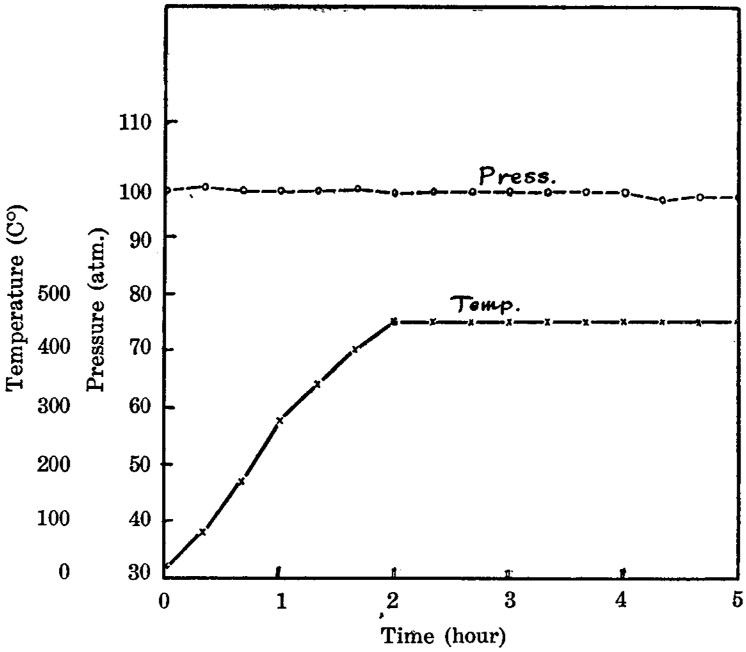

Fig. 7.

	Fraction	Yield	d_4^{15}	n_D^{20}	Remark
1	29°- 90°	3 %	0.777	—	Cyclohexane and its homologue
2	90°-130°	6 ,,	0.785	1.437	
3	130°-150°	7 ,,	0.826	1.451	
4	150°-188°	81 ,,	0.872	1.469	Mostly decalin
5	188°-192°	2 ,,	0.889	1.476	

The fact that tetralin decomposes into benzene homologues with fruitful yield is in favour of the view that the naphthalene molecule is in a more stable state than tetralin. The stability of hydronaphthalene again reaches a maximum in decahydronaphthalene. The relation in chemical behavior among naphthalene and its reduced compounds by the process of cracking in presence of reduced nickel and hydrogen is on the whole very similar to that among benzene and its hydrogenated compounds.

In conclusion, the writers wish to express their sincere thanks to Vice-Admiral S. Kishimoto, Director of the Imperial Naval Fuel Depot, who gave them permission to publish this paper; to Engineer-Captain Viscount M. Kawase, Chief of the Scientific Research and Experimental Branch, for their kindness in enabling them to take part in this work; and also to Professor S. Komatsu of the Kyoto Imperial University, whose advice and encouragement have been invaluable.

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