THE CATALYTIC HYDROGENATION OF AROMATIC HYDROCARBONS UNDER HIGH PRESSURE AND HIGH TEMPERATURE.

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Introduction

In connection with the hydrogenation of aromatic hydrocarbons, numerous methods have been suggested by Sabatier,(1) Ipatiew(2) and Schroeter,(3)

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(1) Sabatier and Sendrens, *Compt. rend.*, **132** (1901), 1257.
(2) Ipatiew, *Ber.*, **40** (1907), 1281.
(3) Schroeter, *Ann.*, **426** (1922), 1

and their experimental studies indicate that the velocity of reduction is affected not only by the kind of catalyst employed and the pressure, but also by the chemical structure of the hydrocarbons. Very few investigators, however, have made a systematic survey of the relation between the catalytic reduction of aromatic hydrocarbons and their chemical constitution, and the present paper deals with this interesting problem.

Experimental.

The aromatic hydrocarbons which were used in the studies, were benzene, diphenyl, naphthalene, acenaphthene, anthracene, phenanthrene and pyrene, and they were all proved to be chemically pure except the phenanthrene, which contained a trace of a sulphur compound; their physical constants are shown in the table.

The reduced nickel used as a catalyst was made by heating nickel nitrate at about 300°C., and reducing it in a stream of hydrogen at 300°–320°C.; its activity was tested by its behaviour towards naphthalene.

Table 1.

Name	Appearance	d_4^{25}	n_D^{25}	B.P.	M.P.	Picrate	
						Appearance	M.P.
Benzene	Colourless liquid	0.8740	1.4972	—	—	—	—
Diphenyl	White thin plates	—	—	248–249 (756.5 mm.)	68.5–69.5	—	—
Naphthalene	White granular	—	—	212.5–213.5 (·58.2 mm.)	80–81	Pale yellow needles	150–150.5
Acenaphthene	White needles	—	—	266.5–267.5 (760.2 mm.)	93–94	Orange-red needles	160.8–161.8
Anthracene	White thin plates	—	—	—	212.5-213.5	Red needles	139–140
Phenanthrene	White powder	—	—	—	98–100	Orange yellow thin plates	141–142
Pyrene	Yellow tetrahedral crystals	—	—	about 280° (757.5 mm.)	148–149	Red needles	222–223

In the experiments, a weighed sample was placed in an autoclave with freshly reduced nickel in the proportion of 8% of the weight of the sample, and after the air in the autoclave had been replaced by hydrogen, the gas was subjected to the required pressure, and heated externally by electric resistance to a definite temperature. During the reaction, the apparatus was shaken by a machine to bring the substance in contact with the hydrogen, and the change of temperature and pressure in the reaction chamber was recorded every 15 minutes. When the pressure became constant, the autoclave was cooled and the reaction products separated and fractionated by distillation, and purified by distillation or recrystallization. Their physical and chemical properties were then studied.

In the hydrogenation of benzene with 76 hydrogen atmospheric pressures at 0°C., the reaction started at 40°C and the reaction velocity at 200° C. to form hexahydrobenzene was found by calculation to be $\frac{96 \text{ gr.}}{315 \text{ minutes}}=0.3$ (Fig. 1).

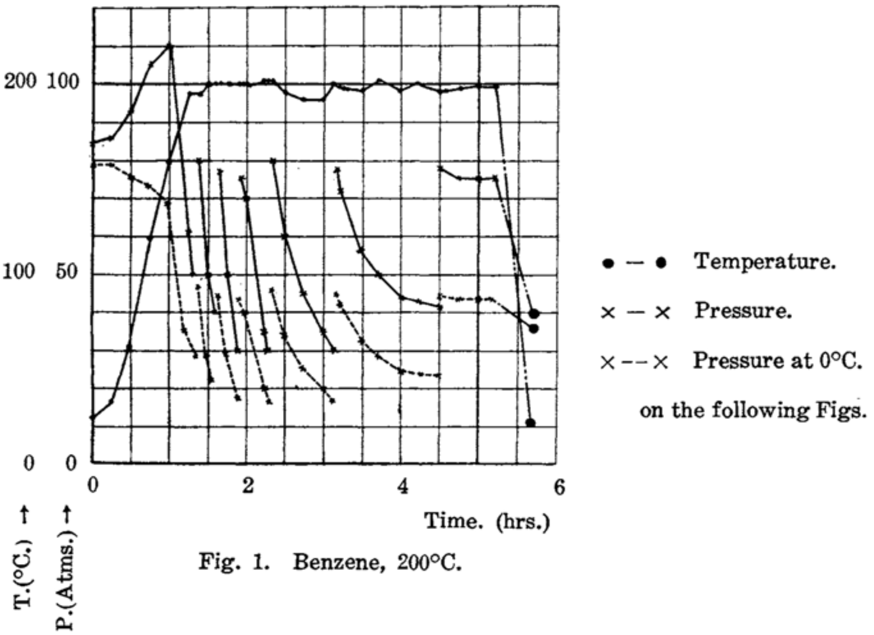

Fig. 1. Benzene, 200°C.

When diphenyl was hydrogenated catalytically with 95 hydrogen atmospheric pressures at 0°C., the initial temperature at which the reaction began was about 80°C., and dicyclohexyl was formed quantitatively at 200°C., the reaction velocity being $\frac{61}{225}=0.27$ (Fig. 2). Hydrogenation at 250°C. and under 95 hydrogen atmospheric pressures at 0°C., however, resulted in the formation of phenyl cyclohexane, owing to the partial oxidation of dicyclohexyl formed directly from diphenyl (Fig. 3). Naphthalene on reduction at 200°C. and under 91 hydrogen atmospheric pressures at 0°C., yields tetrahydronaphthalene which is converted into a

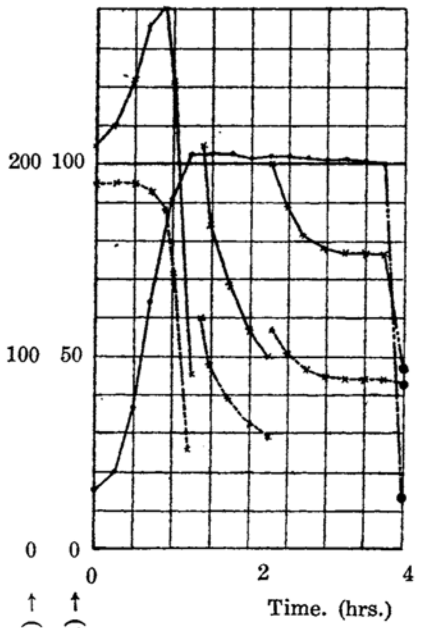

Fig. 2. Diphenyl, 200°C.

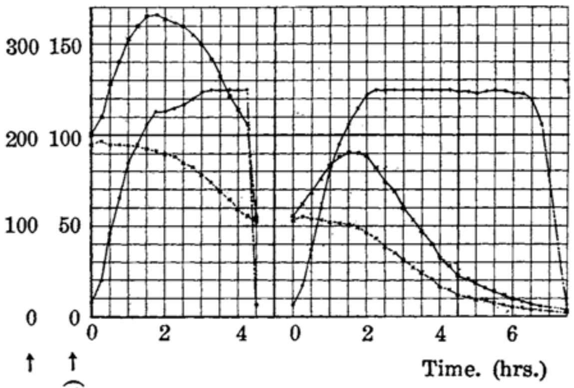

Fig. 3. Diphenyl, 250°C.

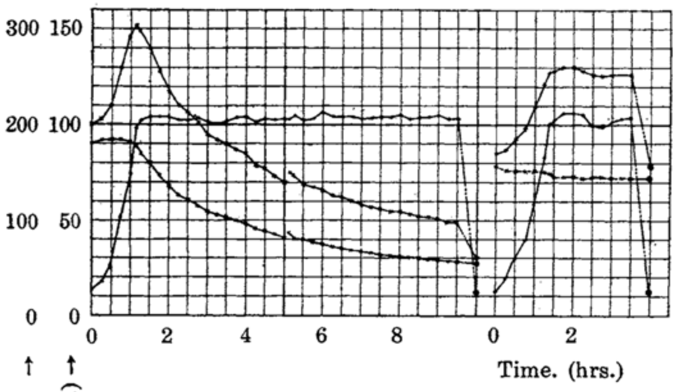

Fig. 4. Naphthalene, 200°C.

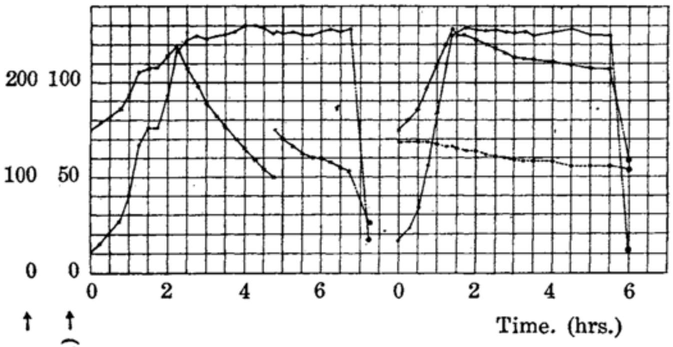

Fig. 5. Naphthalene, 250°C.

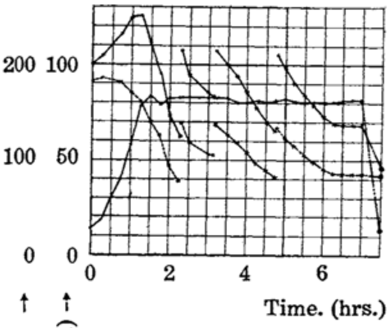

Fig. 6.

Tetrahydronaphthalene, 160°C.

decahydro-compound at 160°C. and under 91 atmospheric pressures. The hydrogenation of naphthalene seems to differ from that of tetrahydronaphthalene, the reaction in the former case having been observed to start with slow reaction velocity at about 140°C. under the conditions mentioned above, while that of tetrahydronaphthalene takes place at lower temperatures such as 80°C. (Figs. 4, 5, 6).

According to the principles of stereochemistry, there are two isomers in decahydronaphthalene, the cis- and trans-isomers, which have been studied by Mohr⁽¹⁾, Hückel⁽²⁾, Willstätter⁽³⁾, Eisenrohr⁽⁴⁾, and Zelinsky⁽⁵⁾. The proportion of the cis- to the trans-isomer in the writer's sample was found to be 90 : 10, the calculation being made by the aid of the index of refraction and the specific gravity of the two isomers as observed by Willstätter and Hückel (See Table 2). The catalytic reduction of naphthalene at high pressure and high temperature seems to be similar, so far as the reaction product is concerned, to the case of the reaction of naphthalene with platinum and hydrogen at ordinary temperatures, but not the same as in Sabatier's method, in which the trans-isomer predominates in the reaction product.

Table 2.

	Decahydronaphthalene	
	Cis-form %	Trans-form %
Calc. from Willstätter's data		
of index of refraction	81	19
of specific gravity	97	3
Calc. from Hückel's data		
of index of refraction	62	38
of specific gravity	73	27

Acenaphthene on the other hand behaves quite differently from naphthalene in the catalytic reduction, though they show similar chemical structure; the absorption of hydrogen begins at about 80°C. under 94 atmospheric pressures at 0°C, and decahydroacenaphthene is produced at 200°C, the

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(1) Mohr: *Ber.*, **55** (1922), 230.
(2) Hückel: *Ber.*, **58** (1925), 1449.
(3) Willstätter: *Ber.*, **56** (1923), 1388; **57** (1924), 683.
(4) Eisenrohr: *Ber.*, **57** (1924), 1639.
(5) Zelinsky: *Ber.*, **57** (1924), 2062.

reaction velocity being $\frac{103}{540} = 0.2$. The hydrogenation at higher temperatures (270°C.), however, produces tetrahydroacenaphthene due to the reverse reaction which occurs in the decahydro compound and which is favoured by higher temperatures (Fig. 7, 8).

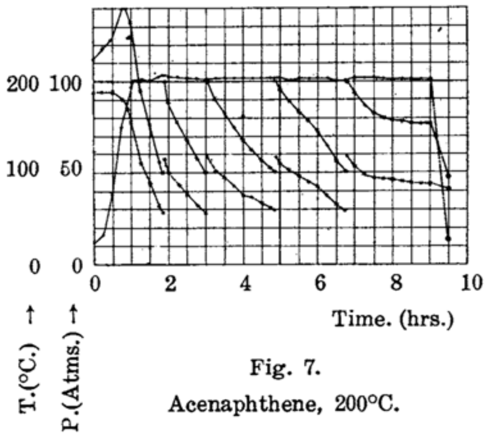


Fig. 7.
Acenaphthene, 200°C.

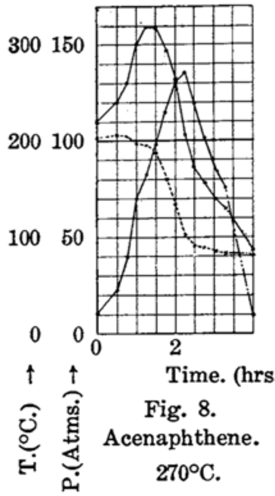


Fig. 8.
Acenaphthene.
270°C.

The reduction of anthracene is noteworthy in that the absorption of hydrogen begins at about 100°C. and the reaction by which the substance is converted into its octahydro-compound proceeds very quickly at 200°C., as was indicated by a fall of 30 atmospheric pressures in the pressure of the autoclave. Also, further reduction of the compound into perhydroanthracene will takes considerably longer time, as may be seen from Fig. 9.

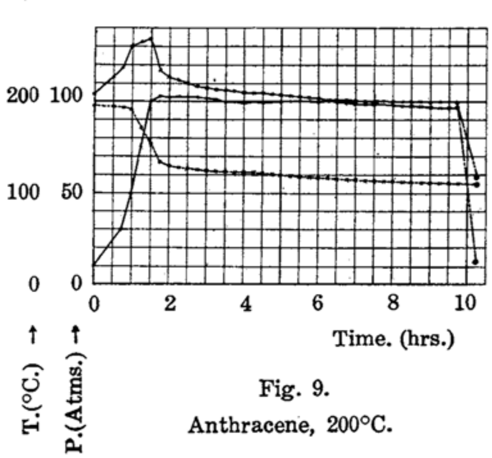
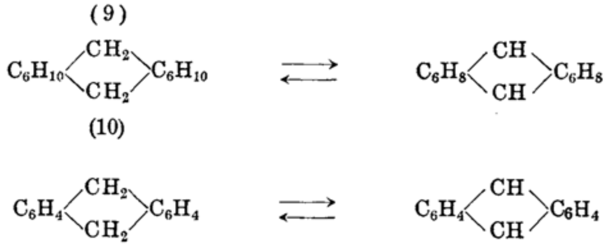


Fig. 9.
Anthracene, 200°C.

The reaction product consisted of three substances; the first was in the form of colourless crystals melting at 72°C., (Found: C=90.5; H=10.5) identified with the octahydroanthracene obtained by Godchot⁽¹⁾ and Schroeter⁽²⁾; the second, colourless crystals melting at 61°C., was proved to be perhydroanthracene by elementary analysis (Found: C=87.7; H=12.3); and the third, a liquid substance, was found by elementary analysis (Found: C=87.1; H=12.3) and by reference to its physical constants to be an isomeric substance with the perhydro-compound. The proportion of these substances in the reaction product was 1 : 3 : 2.

The fact that octahydroanthracene occurs with perhydro-compounds in the reaction product, indicates that two hydrogen atoms combined with carbon atoms, (9) and (10), in perhydroanthracene were removed on heating, as we experienced in the case of dihydroanthracene, resulting in octahydroanthracene as a reaction product.



$$C_6H_{10}\left\langle\begin{matrix}\overset{(9)}{CH_2}\\ \underset{(10)}{CH_2}\end{matrix}\right\rangle C_6H_{10} \rightleftarrows C_6H_8\left\langle\begin{matrix}CH\\ CH\end{matrix}\right\rangle C_6H_8$$

$$C_6H_4\left\langle\begin{matrix}CH_2\\ CH_2\end{matrix}\right\rangle C_6H_4 \rightleftarrows C_6H_4\left\langle\begin{matrix}CH\\ CH\end{matrix}\right\rangle C_6H_4$$

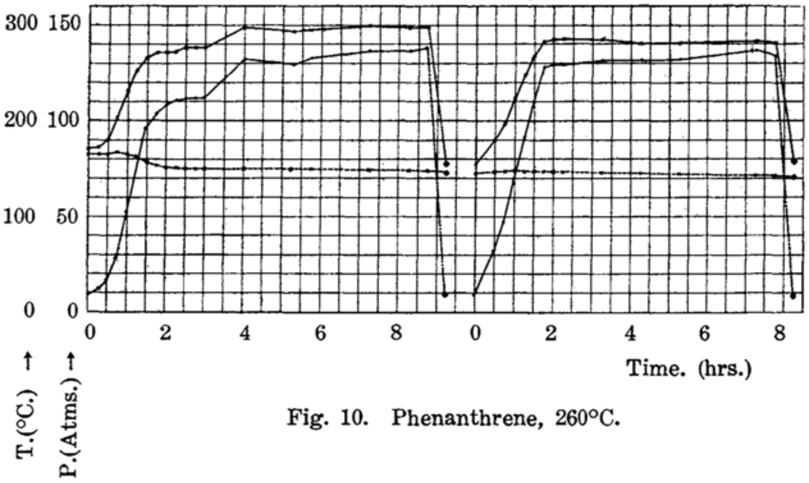


Fig. 10. Phenanthrene, 260°C.

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(1) Godchot: *Ann. Chim.*, (8) **12** (1907), 1168.
(2) Schroeter: *Ber.*, **57** (1924), 2003.

In the reduction of phenanthrene, the reaction proceeded very slowly at 260°C. partly owing to the presence of some poisonous sulphur compound in it, and the product contained only 6% of tetrahydrophenanthrene (Fig. 10), which was separated from phenanthrene unchanged. The reduction was repeated with a new supply of hydrogen and reduced nickel, and octahydrophenanthrene was formed by heating at 175°C. for about 30 hours, which was identified from the physical properties. (Fig. 11).

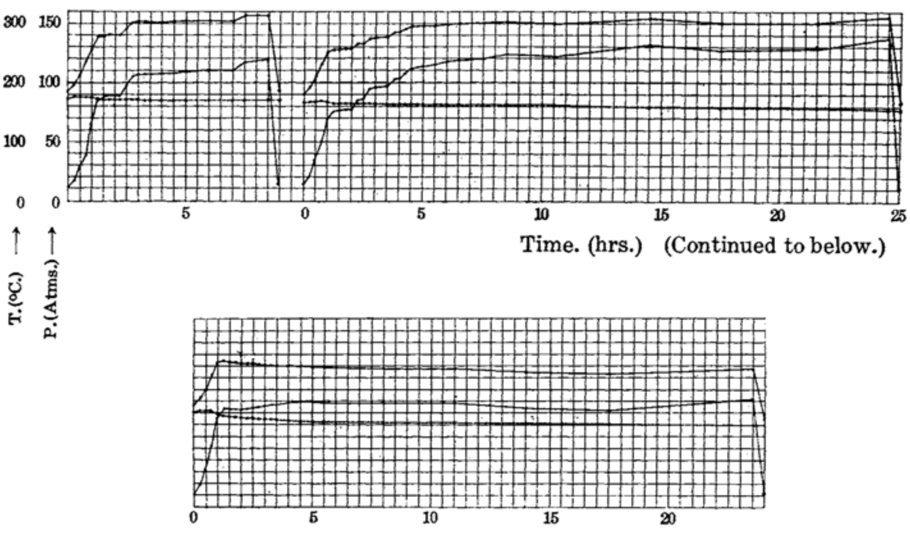


Fig. 11. Tetrahydrophenanthrene, 175°C.

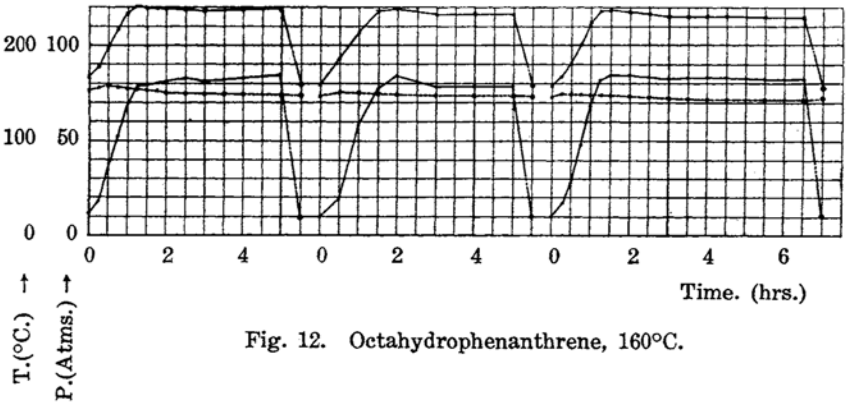
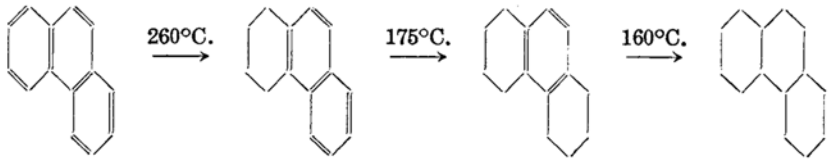


Fig. 12. Octahydrophenanthrene, 160°C.

To convert the octahydro-compound into perhydrophenanthrene, it was heated with hydrogen at about 160°C. for 5 hours under 77 atmospheric pressures at 0°C., and the yield of the pure compound was only 13% (Fig. 12). The catalytic reduction of phenanthrene may be represented by the following scheme:



Thus, the behaviour of phenanthrene towards reduced nickel and hydrogen at high temperature and high pressure, is, on the whole, similar to that of its isomeric anthracene, both being viewed as diphenylene compounds; the group CH=CH in the phenanthrene molecule, by which two benzene rings are joined, is very difficult to keep in a reduced state at higher temperatures since these two carbon atoms, as we noticed in the oxidation of phenanthrene, are situated in a more reactive state than the other carbon atoms due to lack of uniformity in distribution of energy in the molecule.

The hydrogenation of pyrene was more difficult than that of the other hydrocarbons. The hexahydro-compound was formed with theoretical

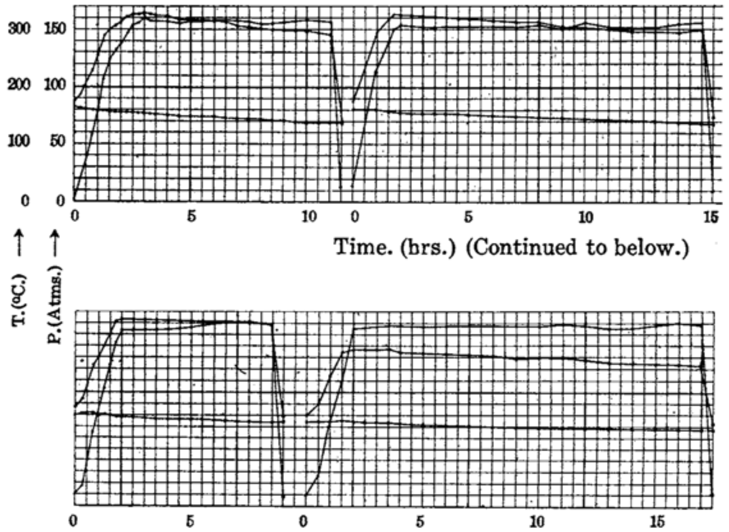


Fig. 13. Pyrene, 300°C.

yield when pyrene was heated with hydrogen at 300°C. for 52 hours under about 80 atmospheric pressures at 0°C. (Fig. 13); its physical properties, the results of elementary analysis (Found: C=92.2; H=7.7) and m.p. of picrate (118–119°C.) were identical with those of di-peri-di-trimethylene naphthalene obtained by Goldschmidt.⁽¹⁾

Hexahydropyrene was regarded from the point of view of structure chemistry as a derivative of naphthalene or acenaphthene, and the catalytic reduction with reduced nickel and hydrogen at high temperature and pressure leads to a similar conclusion. When heated with hydrogen at 210°C. for 20 hours under 92 atmospheric pressures at 0°C., it yielded a substantial amount of decahydropyrene (Fig. 14), which was by further catalytic reduction at 240°C. for 40 hours under 107 atmospheric pressures at 0°C., converted into perhydropyrene (Fig. 15). There are two isomeric forms of the perhydro-compound, the one consisting of colourless needles, m.p. 87–88°C., and the other being a liquid, b.p.=162–166°C. at 9.5 mm.; they were

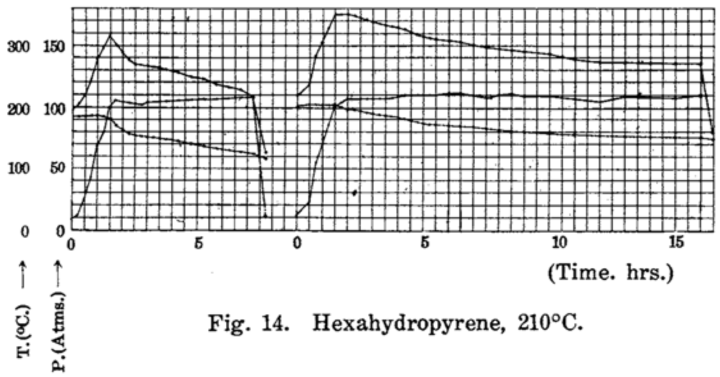


Fig. 14. Hexahydropyrene, 210°C.

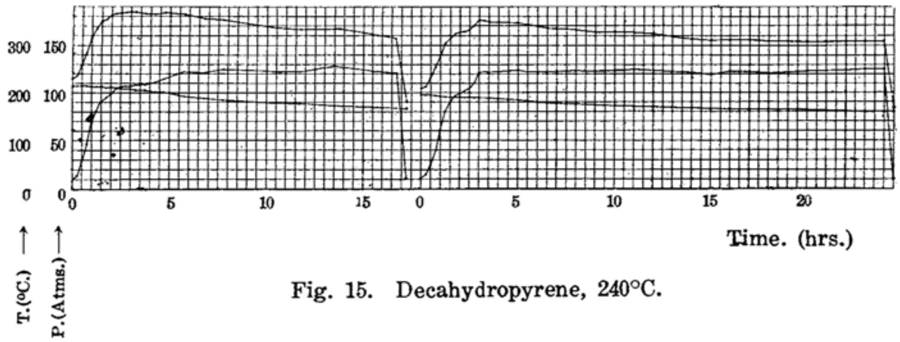


Fig. 15. Decahydropyrene, 240°C.

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(1) Goldschmidt: *Ann.*, **351** (1907), 218.

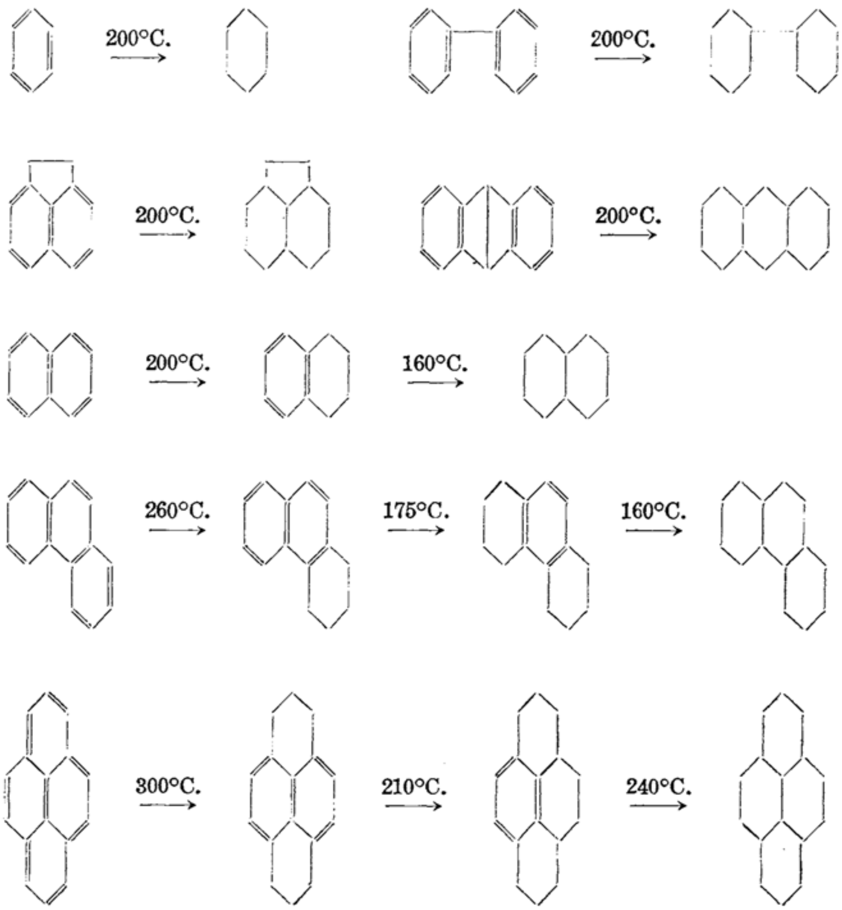
Table 3. The conditions and results of hydrogenation.

Number of experiment	Aromatic compound	Wt. (gr.)	Reaction temperature (°C)	Initial pressure at 0°C.	Hydrogen absorbed.		Time (hr.-min.)	Reaction product.							
					atms. (obs.)	atms. (calc.)		Hydroaromatic compound	Yield (gr.)	d_4^{25}	n_D^{25}	M.R. obs.	M.R. calc.	B. P. (°C.)	M.P. (°C.)
7	Benzene	100	200	76	182	168	5–15	Hexahydrobenzene	96	0.7741	1.4235	27.69	27.70	80–80.5 (759.5 mm.)	
21	Diphenyl	65	,,	95	115	98	3–45	Dicyclohexyl	61	0.8833	1.4772	53.20	53.22	231–233	
67	,,	40	250	95	91	92	11–0	Phenylcyclohexane	37	0.9431	1.5313	52.56	51.82	234–236	
8	Naphthalene	100	200	91	71	67	13–0	Tetrahydronaphthalene	91	0.9675	1.5392	42.79	42.58	201.5–203.5	
9	,,	,,	250	69	74	67	12–15	Tetrahydronaphthalene	92	0.9678	1.5396	42.80	42.58	201.5–203.5	
18	Terahydro-naphthalene	,,	160	91	119	97	7–0	Decahydronaphthalene	97	0.8881	1.4753	43.82	43.87	189–191	
22	Acenaphthene	,,	200	94	168	142	9–0	Decahydroacenaphthene	103	0.9488	1.4996	51.24	51.06	235–237	
66	,,	,,	270	102	62	57	3–20	Tetrahydroacenaphthene	96	1.0065	1.5550	50.42	49.62	245–248	
31	Anthracene	28	200	97	42	41	9–45	Octahydroanthracene	7					160–163 (13 mm.)	72–73
								Perhydroanthracene	14					150–155 (13 mm.)	60.5–61
								Perhydroanthracene	4.5	0.9747	1.5275	60.67	60.25	150–155 (13 mm.)	
33	Phenanthrene	100	260	83	13	42	16–30	Tetrahydrophenanthrene	7.2	1.0777	1.6322	58.96	57.92	170–180 (18 mm.)	
43	Tetrahydro-phenanthrene	53	175	87	19	23	56–30	Perhydrophenanthrene	0.7	0.9630	1.5323	61.87	60.25	150–160 (18 mm.)	
								Octahydrophenanthrene	40	1.0232	1.5726	59.91	58.85	160–170 (18 mm.)	
44	Octahydro-phenanthrene	15	160	77	3	9	16–30	Perhydrophenanthrene	2.0	0.9609	1.5261	61.41	60.25	155–165 (25 mm.)	
39	Pyrene	65	300	82	39	39	51–30	Hexahydropyrene	65						131–132
40	Hexahydropyrene	93	210	92	60	38	23–15	Decahydropyrene	89	1.0522	1.5713	66.28	65.89	196.5–201.5 (18 mm.)	
41	Decahydropyrene	70	240	107	40	40	40–45	Perhydropyrene	50						86.8–87.8
								Perhydropyrene	14	0.9828	1.5228	67.84	67.29	162–166 (9.5 mm.)	

proved to isomers so by elementary analysis (Found : C=87.9 ; H=12.1 for solid isomer and C=87.8 ; H=12.1 for the liquid) and also by their physical properties.

The method described above for the hydrogenation of aromatic hydrocarbons in the presence of reduced nickel under high pressure and at high temperature, has many advantages when applied to the synthesis of hydroaromatic compounds compared with the method of Sabatier or those proposed by Ipatiew and others, but in order to get the required hydrogenated compounds the reduction procedure shown in the table should be adhered to.

Table 4.



As will be seen in the above tables, aromatic hydrocarbons made up of two or more benzene rings, may be divided into two groups from the point of view of catalytic hydrogenation; the one can be hydrogenated completely by one experimental condition as we noticed in the case of benzene, but in the case of the other group to which naphthalene and phenanthrene belong, complete hydrogenation can be achieved only through two or more steps of reaction, with changes in the experimental conditions, especially in the reaction temperature.

In conclusion, the writer wishes to express his gratitude to Vice-Admiral G. Yamashita and Vice-Admiral S. Kishimoto, the former and the present Director respectively of the Imperial Naval Fuel Depot, and to Engineer Captain Viscount M. Kawase, Chief of the Scientific Research and Experimental Branch, for their kindness in enabling him to take part in this research, and also to Professor S. Komatsu of the Kyoto Imperial University, whose advice and encouragement have been invaluable.

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