ON THE THERMAL DECOMPOSITION OF AROMATIC ETHERS UNDER HIGH HYDROGEN PRESSURE.

By Toru OGAWA.

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It is a well known fact that diethyl ether on being heated to 550° – 770° C., decomposes into ethane and acetaldehyde(1); anisol(2) yields phenol and ethylene at 380 – 460°, and cyclohexyl phenyl ether decomposes at high temperatures into phenol and cyclohexene.(3)

Aromatic ethers such as diphenyl ether, as noticed by Graebe, on pyrolysis, yields diphenyleneoxide and other polymers with a small quantity of phenol and benzene.(4) This result seems to differ from that obtained with the aliphatic ethers or aliphatic and aromatic ethers mentioned above, and polymerization of diphenyl ether in the pyrolysis may be attributed to the weakness of the combining affinity of the hydrogen atom in the para or ortho position for the carbon atom, effected by the disruption of the linking between the carbon and the oxygen atom in the molecule.

The thermal decomposition of ethers should be promoted in the presence of catalysts and in fact, aliphatic ethers in the presence of Japanese acid clay are decomposed into alcohols and olefines at 200°(6); phenyl methyl ether by potash fusion at 180° produces phenol and anisol; and diphenyl ether by contact with metallic sodium heated to 180° – 200°, is decomposed into phenol and benzene.(7) The decomposition of diphenyl ether into phenol and benzene is promoted in the presence of reduced nickel and hydrogen, as observed by S. Komatsu and M. Masumoto(8), this decomposition being evidently accompanied by hydrogenation of the benzene nucleus:

$$C_6H_5\,O\,C_6H_5 \rightarrow C_6H_{11}OH + C_6H_{12}$$

It is, therefore, very interesting to study the pyrolysis of aromatic ethers in the presence of hydrogen under pressure, and in the present re-

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(1) *Ann.*, **14** (1835), 134; U. Nef. Ibid., **318** (1901), 198; E. Peytral, *Bull. Soc. Chim.*, **4** (1924), 35.

(2) Meyer u. Hofmann, *Monatsh.*, **38** (1917), 343.

(3) Skraup u. Beifuss, *Ber.*, **60** (1927), 1070.

(4) *Ber.*, **29** (1896), 1877.

(5) R. Nakai, This Bulletin, **5** (1930), 136.

(6) K. Kashima, Ibid., **5** (1930), 25.

(7) P. Shöringen, *Ber.*, **56** (1923), 176; K. Ziegler u. F. Thielmann, Ibid., **56** (1923), 1740.

(8) This Bulletin, **5** (1930), 241.

search, diphenyl ether, diphenylene oxide, α- and β-dinaphthylene oxides are used as the experimental material.

When diphenyl ether was heated in an autoclave at 500° for 1 hour with hydrogen under 100 atmospheric pressures at 0°, 90% of the ether was transformed into benzene and phenol, although W. Ipatiew(1) has reported that no appreciable reaction took place under such conditions.

The fact that the mol ratio of benzene, phenol and water in the reaction product is 1 : 0.4 : 0.3 indicates that in the pyrolysis the following reaction (1)

$$C_6H_5\,O\,C_6H_5 + H_2 = C_6H_5OH + C_6H_6 \quad \ldots\ldots \quad (1)$$

will be accompanied by either reaction (2) or (3):—

$$C_6H_5\,O\,C_6H_5 + H_2 = 2C_6H_6 + H_2O \quad \ldots\ldots \quad (2)$$

$$C_6H_5OH + H_2 = C_6H_6 + H_2O \quad \ldots\ldots \quad (3)$$

K. Kashima(2) and R. Nakai(3) have already claimed in the report on their experiments on aliphatic and aromatic ethers, that reaction (2) will take place mostly at higher temperatures, and reaction (3), in spite of the fact that it was not observed as expected in an experiment made by A. Kling and D. Florentin(4), was actually noticed by the writer and Takahashi(5) on heating phenol with hydrogen at 460°—490° for 2½ hours under 100 atmospheric pressures at 0°, the result being a fruitful yield of benzene and water.

Thus, the pyrolysis of diphenyl ether in the presence of hydrogen may be assumed to proceed mostly by reactions (1) and (2) and partly by reaction (3).

Decomposition of diphenylether at 250°, however, in the presence of reduced nickel and hydrogen under 100 atmospheric pressures at 0° is observed to produce cyclohexane and cyclohexanol in equimolecular quantities (0.65 mol), which result is on the whole very similar to that obtained by S. Komatsu(6) and W. Ipatiew(7), in which hydrogenation in the benzene nucleus happens first and is followed by the disruption of the linking between the oxygen and carbon atoms, thus:

$$C_6H_5{\cdot}O{\cdot}C_6H_5 + H_2 \rightarrow C_6H_{11}{\cdot}O{\cdot}C_6H_{11} \rightarrow C_6H_{11}OH + C_6H_{12}$$

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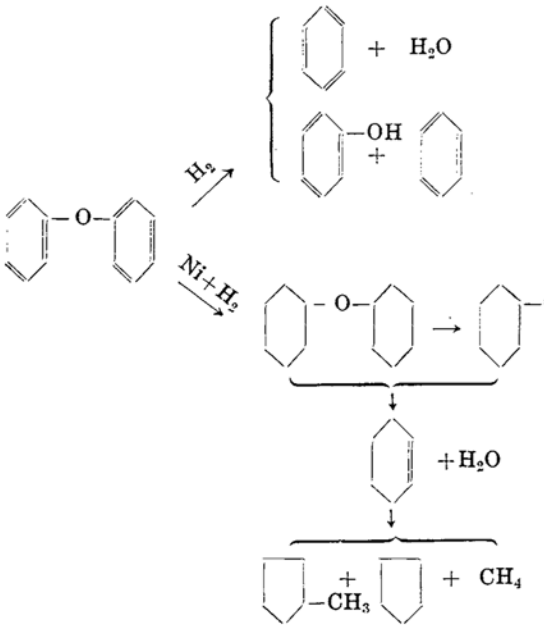
(1) *Ber.*, **60** (1927), 1963.
(2) Loc. cit.
(3) ,, ,,
(4) *Internat. Conf. Bit. Coal.*, **11** (1928), 523.
(5) Unpublished.
(6) Loc. cit.
(7) *Ber.*, **41** (1908), 1001.

When the reaction was conducted at 500° C, methane, cyclopentane, methyl-cyclopentane and water were observed to occur in the reaction product with the yield in mol ratio, 2 : 0.2 : 0.4 : 1 respectively.

The formation of methyl-cyclopentane and cyclopentane is explained by assuming that cyclohexene which is formed as an intermediate product by dehydration from cyclohexanol or dicyclohexyl ether is in turn decomposed into cyclopentane and its derivative, as reported by S. Inoue(1) and by the writer and T. Yokota(2) in connection with their catalytic reaction of benzene and phenol under high temperature and high pressure in the presence of reduced nickel and hydrogen.

The chemical changes of diphenyl ether under high temperature and high hydrogen pressure with or without reduced nickel may be summarized as in the following scheme :—



When diphenylene oxide is treated with hydrogen at 500°C for 5 hours under 100 atmospheric pressures at 0°, benzene (0.14 mol), phenol (0.13 mol), *o*-hydroxydiphenyl (0.2 mol) and a small quantity of diphenyl are obtained with 30% of unchanged oxide in the reaction product.

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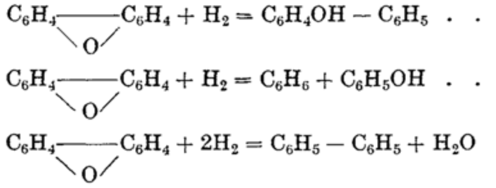
(1) This Bulletin, **1** (1926), 157.

(2) Ibid., **5** (1930), 266.

The main reaction in this case is represented analogously with the case of diphenyl ether, by the following scheme:



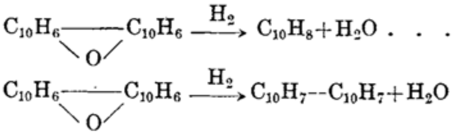
$$C_6H_4\underset{\diagdown O \diagup}{\text{———}}C_6H_4 + H_2 = C_6H_4OH - C_6H_5 \quad \ldots\ldots\ldots \quad (4)$$

$$C_6H_4\underset{\diagdown O \diagup}{\text{———}}C_6H_4 + H_2 = C_6H_6 + C_6H_5OH \quad \ldots\ldots\ldots \quad (5)$$

$$C_6H_4\underset{\diagdown O \diagup}{\text{———}}C_6H_4 + 2H_2 = C_6H_5 - C_6H_5 + H_2O \quad \ldots\ldots\ldots \quad (6)$$

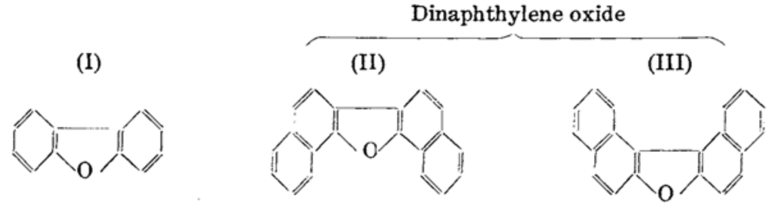
In other words, the disruption of the linking between the carbon and oxygen atoms proceeds first under the experimental conditions mentioned above; the effect of this is to weaken the linking connecting the two benzene nuclei, with the result that reaction (5) takes place properly, and the reactions (4) and (6) are compatible with reactions (1) and (2) in the case of diphenyl-oxide.

When 20 gr. of α- or β-dinaphthylene oxide were treated under conditions similar to those employed in the case of diphenylene oxide, the α-compound was decomposed completely into methane (3.8 gr.), benzene homologue (3.4 gr.), naphthalene (5.4 gr.) and a small amount of β-β'-dinaphthyl, and the β-isomer was converted into methane (4.8 gr.), benzene homologue (3.5 gr.), naphthalene (4.8 gr.), α-α'-dinaphthyl (2.5 gr.) and perylene (1.5 gr.), but no trace of naphthol was formed in either case. These results indicate that the behaviour of these two naphthylene oxides is not entirely the same as that of diphenylene oxide though they present by the anologous chemical constitutions (I), (II) and (III).



$$C_{10}H_6\underset{\diagdown O \diagup}{\text{———}}C_{10}H_6 \xrightarrow{H_2} C_{10}H_8+H_2O \quad \ldots\ldots\ldots \quad (7)$$

$$C_{10}H_6\underset{\diagdown O \diagup}{\text{———}}C_{10}H_6 \xrightarrow{H_2} C_{10}H_7\text{--}C_{10}H_7+H_2O \quad \ldots\ldots\ldots \quad (8)$$



Dinaphthylene oxide

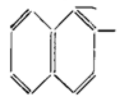
(I) (II) (III)

Diphenylene oxide α β

A free naphthylene radical (4) which is formed by disruption of the linking between the carbon and oxygen atoms and that between the carbon and carbon atoms connecting the two naphthalene nuclei, will decompose more easily than the phenylene radical (5) into methane and benzene homologue, and such a tendency of the free radical to decompose may be anticipated from the thermal reaction of naphthalene and benzene.

(V)

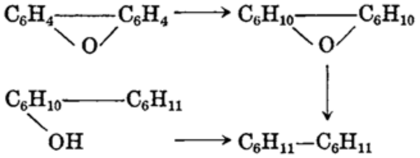
(IV')



In the presence of nickel and hydrogen, diphenylene oxide was converted at 200°C and 280°C into *o*-hydroxydicyclohexyl and dicyclohexyl. The reaction products differ in quantity according to the reaction temperature, as may be seen in the Table 1 and the experimental results indicate that the conversion of the ethylene oxide into dicyclohexyl is favorable at higher temperatures, due to dehydration of either *o*-hydroxydicyclohexyl or dicyclohexylene oxide, which are evidently formed by the catalytic hydrogenation of the oxide:

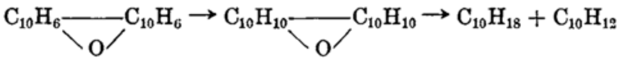
Table 1.

	$C_6H_4\text{—O—}C_6H_4$	$+H_2$	$\longrightarrow C_6H_{10}(OH)-C_6H_{11}$	$+\ C_6H_{11}-C_6H_{11}$	$+H_2O$
200°	1 mol.	8.4 mol.	0.47 mol.	0.33 mol.	0.15 mol.
280°	1 mol.	9.3 mol.	0.25 mol.	0.54 mol.	0.69 mol.



$$\begin{tikzcd} C_6H_4\text{—O—}C_6H_4 \arrow[r] & C_6H_{10}\text{—O—}C_6H_{10} \arrow[d] \\ C_6H_{10}(OH)\text{—}C_6H_{11} \arrow[r] & C_6H_{11}-C_6H_{11} \end{tikzcd}$$

Such an interpretation of the chemical changes occurring during the catalytic hydrogenation of the ethylene oxide may be applied to the catalytic reaction of α- and β-dinaphthylene oxides in the presence of reduced nickel. As a matter of fact, α-dinaphthylene oxide does not present any change in the presence of reduced nickel at 225°, while the β-isomer is transformed first into octa-hydrodinaphthylene oxide at 200°. At 500°, formation of methane, cyclohexane homologue, decalin and tetralin was noticed, and the reaction is explained by assuming that hydronaphthylene, formed as an intermediate reaction product by dehydration of hydronaphthalene oxide, was converted into tetralin and decalin by catalytic reduction on the one hand, and on the other decomposed into methane and cyclohexane homologue; this assumption is based on the fact that naphthalene is converted by catalytic hydrogenation under high pressure and temperature into methane and cyclohexane homologue.



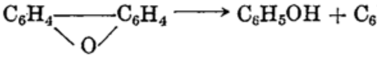
$$C_{10}H_6\underset{\diagdown O\diagup}{-\!\!-\!\!-}C_{10}H_6 \rightarrow C_{10}H_{10}\underset{\diagdown O\diagup}{-\!\!-\!\!-}C_{10}H_{10} \rightarrow C_{10}H_{18} + C_{10}H_{12}$$

In order to investigate the catalytic effects of reduced copper, ferric oxide and Japanese acid clay on the thermal decomposition of diphenylene oxide, it was treated in the presence of each of these catalysts and of hydrogen at 500° under 100 atmospheric pressures at 0°. The reaction product was observed to consist, in each case, of benzene, phenol, diphenyl and *o*-hydroxydiphenyl, and the amount of water and of benzene produced by the reaction was greatest with Japanese acid clay, ferric oxide and copper following in that order, as will be seen from the following Table 2.

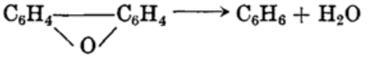
Table 2.

Catalyst	Water produced %	mol ratio of benzene and phenol
—	0.7	1.2 : 1
Cu	3.4	2.1 : 1
Fe_2O_3	5.4	2.7 : 1
Japanese acid clay	6.0	4.1 : 1

From these experimental results, the writer is inclined to believe that the chemical reaction of diphenylene oxide in the presence of a catalyst and hydrogen under high temperature and pressure, proceeds by the processes represented as follows:

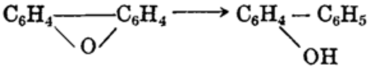


$$C_6H_4\underset{\diagdown O\diagup}{-\!\!-\!\!-}C_6H_4 \longrightarrow C_6H_5OH + C_6H_6 \quad (5)$$



$$C_6H_4\underset{\diagdown O\diagup}{-\!\!-\!\!-}C_6H_4 \longrightarrow C_6H_6 + H_2O \quad (9)$$

$$C_6H_4OH - C_6H_5 \longrightarrow C_6H_6 + H_2O \quad (10)$$



$$C_6H_4\underset{\diagdown O\diagup}{-\!\!-\!\!-}C_6H_4 \longrightarrow \underset{\diagdown OH}{C_6H_4} - C_6H_5 \quad (4)$$

The reactions (9) and (10) which are not occur at 280° and 100 atmospheric pressures at 0° with or without reduced nickel, are promoted in the presence neither copper oxide, ferric oxide nor Japanese acid clay heated at 500°C.

Experimental.

The apparatus employed in the experiments consisted of a cylindrical autoclave of about 2.5 litres capacity, which was heated externally by electric resistance, and mounted horizontally so to rotate, as may be seen in the Fig. 1.

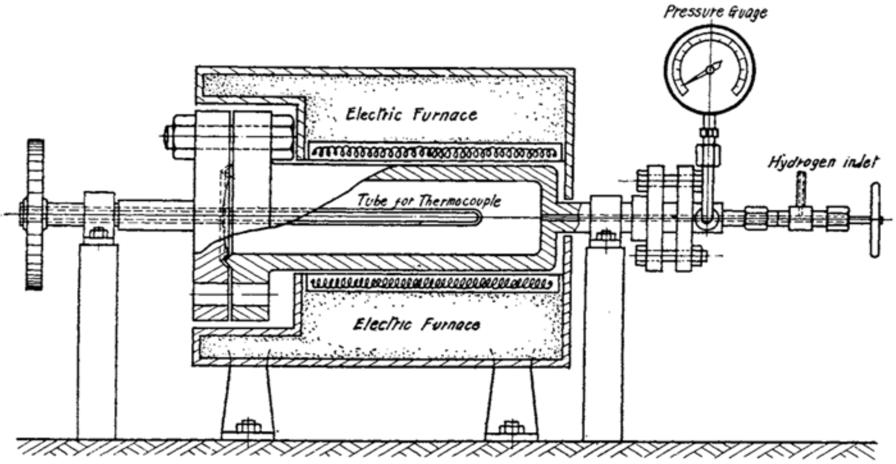


Fig. 1.

In each experiment, the sample, with or without a catalyst (10%) was put into the autoclave, hydrogen was introduced from a cylinder to produce 100 atmospheric pressures at 0°C, and this was heated to the required temperature. The changes in the pressure during the reaction were observed at intervals of 5 minutes. When the reaction was finished, the volume and the density of the gas in the apparatus were measured, and the chemical composition of the gas and liquid or solid reaction products was examined carefully by chemical and physical methods.

1. Diphenyl Ether. (A) Diphenyl ether (50 gr.) prepared(1) from monochlorobenzene and phenol by the catalytic action of copper, showing m. p. 28.0°; b. p. 247°–249 (760 mm.), $d_4^{30} = 1.0711$; $n_D^{30} = 1.5773$, was heated with hydrogen at 490° for 1 hour under a pressure of 100 atmos-

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(1) F. Ullmann and P. Sponagel, *Ber.*, **38** (1905), 2211.

pheres at 0°. A fall of 6 atmospheric pressures was observed, which corresponds to 1.2 gr. or 2 mol hydrogen, and the gas in the autoclave was determined to be composed of 99.4% hydrogen and 0.3% saturated hydrocarbon, probably methane.

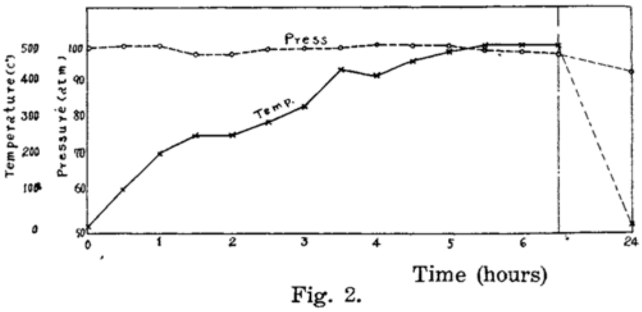

Fig. 2.

The liquid substance (45 gr.) produced by the reaction with water (1.5 gr.), was divided by fractional distillation into the following 3 fractions.

Fraction	B. p.	Yield (gr.)	d_4^{25}	n_D^{25}	Remarks
1	75°—85°	22	0.8724	1.4970	Benzene
2	180°—190°	11	—	1.5411	Phenol
3	250°—260°	6.5	1.0724	1.5779	Diphenyl-ether

Fractions (1) and (2), as indicated by their physical constants, are assumed to be composed of benzene and phenol respectively, and this was confirmed in the case of the former substance by changing it into nitrobenzene, and of the second by the reaction with ferric chloride and caustic soda.

The third fraction agrees in its constants with diphenyl ether.

(B) *In the presence of reduced nickel.* (1) When 50 gr. of the sample were heated at 250° for 2 hours with hydrogen under 100 atmospheric pressures at 0°, in the presence of reduced nickel (5 gr.) which had been previously prepared from nickel oxide by reduction with hydrogen at 280°, a fall of 22 atmospheric pressures was noticed.

The amount of hydrogen absorbed and that of the gases produced during the reaction were found by calculation to be 4.8 gr. (8.0 mol.) and

2.9 gr. respectively (Fig. 3) from the analytical results of the gas in the autoclave:

$$CO = 0.1; \quad H_2 = 98.4; \quad C_nH_{2n+2} = 1.5:$$

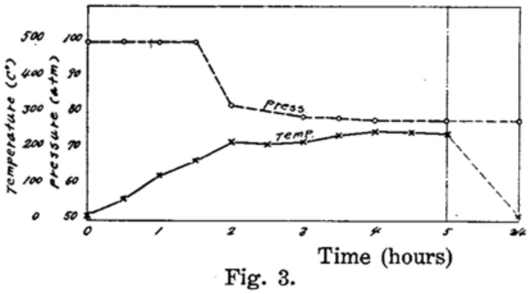

Fig. 3.

The liquid reaction product (47.5 gr.) separated from water (0.2 gr.) and the catalyst, was fractionated into 3 parts:

	B.p.	Yield
1	70°–175°	40 gr.
2	175°–250°	2.5 ,,
3	above 250°	1.0 ,,

After repeated fractionation, the physical constants of each fraction were studied:

Fraction	B. p.	Yield (gr.)	d_4^{25}	n_D^{25}	Remarks
1	79°–85°	14.5	0.7769	1.4241	Cyclohexane
2	158°–165°	20.0	0.9464	1.4610	Cyclohexanol
3	238°–242°	1.5	0.989	1.470	Dicyclohexyl-ether

Fraction 1 was confirmed to be composed of cyclohexane from its behaviour towards bromine or a mixture of nitric and sulphuric acids, and also from its physical constants. The physical properties of the 2nd fraction agree with those of pure cyclohexanol ($d_4^{25} = 0.9469$; $n_D^{25} = 1.4635$).

The third fraction was assumed from the physical constants to be composed of dicyclohexyl ether, which has been prepared by S. Komatsu and M. Masumoto⁽¹⁾ from diphenyl ether by catalytic reduction.

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(1) S. Komatsu and M. Masumoto, loc. cit.

(2) Diphenyl ether (50 gr.) was heated at 500° for 2 hours with reduced nickel (5 gr.) and hydrogen under a pressure of 100 atmospheres, the fall in the pressure was 28.5 atm. at 0°, (Fig. 4) and 7 gr. of hydrogen (12 mol) were used in the reduction, and the gaseous product was composed of hydrogen and methane in the proportion H : $CH_4 = 92.7 : 7.3$.

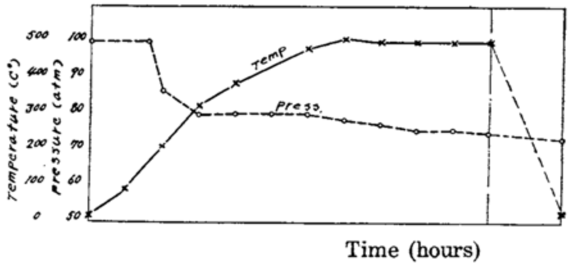

Fig. 4.

5.4 Gr. of water and 13.6 gr. of liquid substance were obtained from the autoclave, with 22.0 gr. of liquid substance of low boiling point, which escaped with the gaseous products from the autoclave when it was opened, and were absorbed with active carbon. The liquid reaction product found in the autoclave was all distilled at below 120°, and was fractionated carefully, and the physical constants of each fraction studied :

Fraction	B. p.	Yield (gr.)	d_4^{15}	n_D^{15}	Remarks
1	55°—65°	5.0	0.7556	1.4160	Cyclopentane
2	65°—75°	3.0	0.7633	1.4214	Methyl-cyclopentane
3	75°—78°	0.5	0.7769	1.4242	Cyclohexane

Fractions 1, 2 and 3 were identified by their physical constants and chemical properties with cyclopentane, methyl cyclopentane and cyclohexane respectively.

The liquid reaction substance found in the gaseous products, was also examined and found to be composed of cyclopentane and methyl cyclopentane by the usual treatment, as will be seen in the following table :—

Fraction	B.p.	Yield (gr.)	d_4^{15}	n_D^{15}	Remarks
1	55°—65°	2.0	0.7545	1.4142	Cyclopentane
2	65°—75°	1.2	0.7635	1.4218	Methyl cyclopentane

2. Diphenylene Oxide. Diphenylene oxide prepared from phenol by destructive distillation with lead oxide, and purified by fractional distillation and recrystallization from alcohol solution, shows b.p. 284° (760 mm); m.p. 83°; m.p. of picrate 99°.

When 50 gr. of the sample was heated with hydrogen at 500° for 2 hours under a pressure of 100 atmospheres at 0°, no appreciable change in the pressure was noticed, and therefore, it was heated again with a new supply of hydrogen, at 500°C for 2 hours (Fig. 5), and 1.5 gr. (2.5 mols.) of hydrogen were utilized in the reaction.

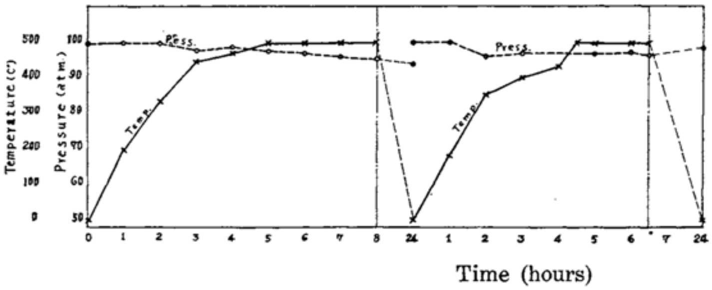

Fig. 5.

The gas in the autoclave consisted only of hydrogen.

An oily reaction product (43 gr.) separated from water (0.4 gr.) was fractionated into 4 fractions with the follwing physical constants:

Fraction	B.p.	Yield (gr.)	d_4^{25}	n_D^{25}	Remarks
1	75°–90°	3.3	0.7819	1.4919	Benzene
2	170°–190°	3.5	1.0356	1.5358	Phenol
3	260°–280°	10	—	—	—
4	280°–290°	13.7	—	—	—

Fractions 1 and 2 were confirmed to be composed of benzene and phenol respectively.

Fraction 3 melting at 70°–80°, was treated with a dilute caustic alkali solution, and the amorphous substance separated on acidifying the solution with acid, was recrystalized from petroleum ether in colorless needle crystals which melted at 58° and boiled at 283°, 760 mm. These physical properties of the writer's sample being different from those of *o*-hydroxydiphenyl mentioned by Hönigschmidt⑴ (b.p. 275°, m.p. 56°) and Hirsh⑵ (m.p. 67°), it was analysed with the following results:

Subst. = 0.1045; CO_2 = 0.3240; H_2O = 0.0570 gr. Found: C = 84.55; H = 6.06.
Calc. for $C_{12}H_{10}O$: C = 84.70; H = 5.88.

Fraction (4) consists of a substance which shows m.p. 83°, after being purified from an alcohol solution, it was identified with diphenylene oxide.

(B) *In the presence of reduced nickel.* (1) 100 Gr. of diphenylene oxide were heated at 200° for 3 hours with hydrogen and reduced nickel under 100 atmospheric pressures at 0°. The fall in the pressure was 45.3 atmospheres which correspond to 10 gr. or 8.5 mol of hydrogen (Fig. 6).

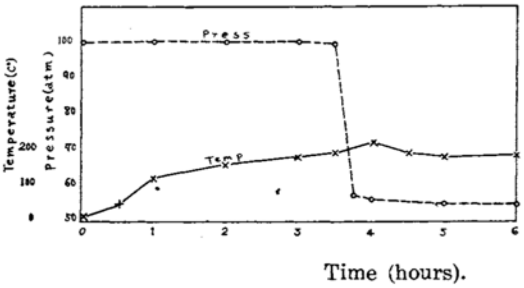

Fig. 6.

The gas in the autoclave was composed of hydrogen.

The liquid reaction product (107.0 gr.) separated from water (2.7 gr.) was fractionated carefully and the physical constants of the main fraction studied:

Fraction	B. p.	Yield (gr.)	d_4^{25}	n_D^{25}
1	Below 255°	7.3	—	—
2	255°–265°	32.5	0.9391	1.4898
3	265°–275°	51.1	0.9791	1.4962
4	Over 275°	2.0	—	—

The third fraction was a colorless liquid with a characteristic odour, showing no coloration with ferric chloride and no reaction with hydroxylamine; the analytical results are as follows:

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(1) Hönigschmidt, *Monatsh.*, **22** (1901), 568.
(2) Hirsh, *Ber.*, **23** (1890), 3710.

Subst. = 0.1056; CO_2 = 0.3028; H_2O = 0.1141 gr. Found: C = 78.2; H = 12.1
Calc. for $C_{12}H_{22}O$: C = 79.12; H = 12.09.

These results agree fairly well with those of *o*-hydroxydicyclohexyl mentioned by Wallach.⁽¹⁾

The second fraction was assumed to be a mixture of *o*-hydroxydicyclohexyl ($C_{12}H_{22}O$, C = 79.1; H = 12.1) and dicyclohexyl ($C_{12}H_{22}$, C = 86.7; H = 13.3) from its physical constants and the analytical results:

Subst. = 0.1423; CO_2 = 0.4197; H_2O = 0.1692 gr. Found: C = 80.4: H = 13.3.

(2) When 100 gr. of diphenylene oxide were heated at 280° for 2 hours with hydrogen and reduced nickel under a pressure of 100 atmospheres at 0°, there was a fall of 50 atmospheric pressures, which indicated that 10.7 gr. (9 mol.) of hydrogen were absorbed.

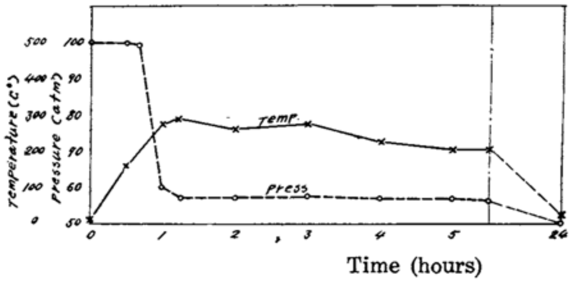

Fig. 7.

104.0 Gr. of liquid reaction product was obtained, with 7.3 gr. of water, and the former was fractionated carefully and the physical constants of each fraction studied:

Fraction	B. p.	Yield (gr.)	d_4^{25}	n_D^{25}
1	Below 237°	1.2	—	—
2	237°–240°	53.8	0.8958	1.4794
3	240°–245°	19.8	0.9049	1.4811
4	245°–250°	6.6	0.9253	1.4842
5	Over 250°	5.0	0.9485	1.4881

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(1) O. Wallach, *Ber.*, **40** (1907), 70.

The 2nd fraction, which showed no reaction with a mixture of nitric and sulphuric acids, gave the following analytical results:

Subst. = 0.1378; CO_2 = 0.4342; H_2O = 0.1617 gr. Found: C = 85.9; H = 13.1.
Calc. for $C_{12}H_{22}$: C = 86.74; H = 13.26.

These experiments indicate that the fraction consisted of dicyclohexyl.

The 3rd fraction was assumed to be a mixture of dicyclohexyl and hydroxydicyclohexyl from its physical constants.

(3) When 50 gr. of diphenylene oxide were heated with hydrogen and nickel at 500° for one hour under pressure, the fall in pressure was observed to be 28.5 atmospheres. (Fig. 8).

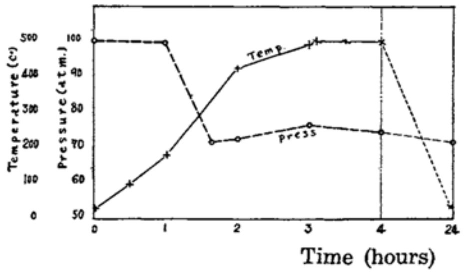

Fig. 8.

From the composition of the gas in the autoclave shown in the table, the amount of hydrogen absorbed by the reaction was calculated and found to be 7.8 gr. (13 mol.)

H_2	C_nH_{2n}	C_nH_{2n+2}	n
87.7	—	12.3	1.4

Liquid product (22.0 gr.) and water (4.8 gr.) were obtained by the reaction and the former was fractionated repeatedly and the physical constants of each fraction were studied:

Fraction	B. p.	Yield (gr.)	d_4^{15}	n_D^{15}	Remarks
1	68°—75°	8.7	0.7662	1.4226	Methyl-cyclopentane
2	78°—82°	2.5	0.7844	1.4279	Cyclohexane

Fractions 1 and 2, as their physical constants indicate, are composed of methylcyclopentane and cyclohexane respectively. Moreover, 7.4 gr. of methyl-cyclopentane (b.p. 50—75°, $d_4^{15} = 0.7635$; $n_D^{15} = 1.4218$) were isolated from 19.6 gr. of the liquid reaction product which escaped with hydrogen gas from the autoclave when it was opened, and absorbed by active carbon.

(C) *In the presence of ferric oxide.* Diphenylene oxide (50 gr.) was heated at 500° for 5 hours with hydrogen and ferric hydroxide ignited at 350°, under pressure, and no appreciable change in the pressure was noticed, as is indicated in Fig. 9. The gas in the autoclave was composed of,

CO_2	CO	H_2	C_nH_{2n}	C_nH_{2n+2}	n
—	0.2	97.5	—	2.3	1.5

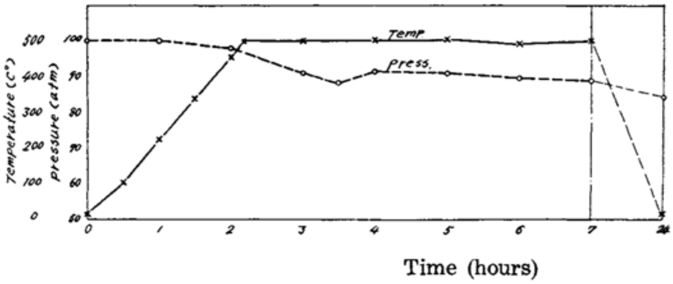

Fig. 9.

An oily reaction product (37.2 gr.) separated from water (2.7 gr.) was fractionated and the physical constants of each fraction studied:

Fraction	B.p.	Yield (gr.)	d_4^{25}	n_D^{25}	Remarks
1	75°—85°	6.5	0.8580	1.4820	Benzene
2	175°—200°	3.0	1.0335	1.5369	Phenol
3	200°—260°	3.5	—	—	—
4	260°—280°	11.0	—		Mixture of *o*-hydroxydiphenyl and diphenyl
5	280°—290°	2.0	(83°)		Diphenylene oxide

Fractions 1 and 2, as indicated by their physical constants are composed of benzene and phenol respectively, and this was confirmed by chemical methods. The 4th fraction was treated with dilute caustic alkali solution, to separate *o*-hydroxydiphenyl from diphenyl, and the former showed b.p.

283°, (760 mm), m.p. 58° after purification and a part insoluble in alkali, which melted at 70° after being purified by distillation and crystallization, was confirmed to be diphenyl.

Fraction 5 was assumed to be composed mostly of diphenylene oxide from its melting point, which showed no depression on mixing with pure diphenylene oxide.

(D) *In the presence of reduced copper*. Diphenylene oxide (50 gr.) was heated at 500° for 3 hours with hydrogen under 100 atmospheric pressures at 0°, in the presence of reduced copper (5 gr.) which had been previously prepared from copper oxide by reduction with hydrogen at 200°.

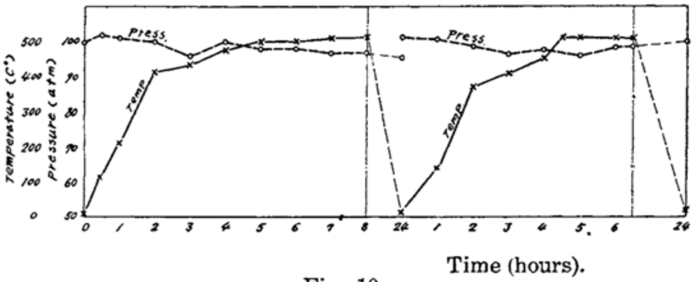

Fig. 10.

The gas in the autoclave was composed of hydrogen and saturated hydrocarbon, and the hydrogen absorbed by the reaction was calculated as 5 mols.

H	C_nH_{2n+2}	n
97.4	2.6	1.1

40 Gr. of the oily reaction product with 1.7 gr. of water were obtained, and were fractionated :

Fractions 1 and 2 were assumed by their physical constants to be composed mainly of benzene and phenol respectively.

Fraction	B.p.	Yield (gr.)	d_4^{25}	n_D^{25}	Remarks
1	75°—82°	6.8	0.8659	1.4904	Benzene phenol
2	170°—190°	3.8	1.0414	1.5428	*O*-hydroxy diphenyl
3	220°—280°	18	—	—	Diphenyl
4	Above 280°	2	—	—	Diphenylene oxide

O-hydroxydiphenyl and a small quantity of diphenyl were isolated from fraction (3).

(E) *In the presence of Japanese acid clay.* (3) Diphenylene oxide (50 gr.) was heated at 500° for 10 hours with hydrogen under pressure in the presence of Japanese acid clay (5 gr.). (Fig. 11).

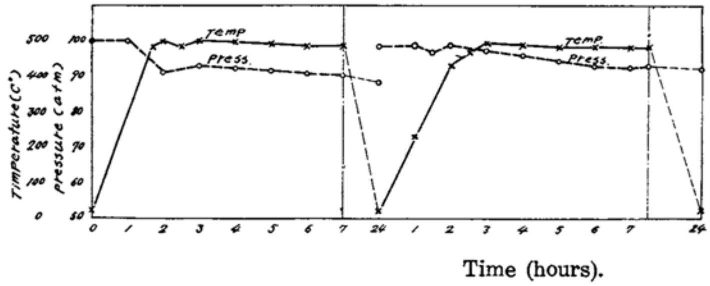

Fig. 11.

From the composition of the gases in the autoclave we learned that the loss of hydrogen was 11 mol but 6.9 gr. of saturated hydrocarbon were generated by the reaction.

	H_2	C_nH_{2n+2}	n
I	97.4	2.6	1.1
II	98.3	1.7	—

27 Gr. of an oily substance with 3.0 gr. of water were obtained by the reaction, and the former was fractionated carefully and the physical constants of each fraction studied :

Fraction	B.p.	Yield (gr.)	d_4^{25}	n_D^{25}	Remarks
1	79°—85°	7.5	0.8683	1.4925	Benzene
2	175°—185°	2.3	1.0227	1.5310	Phenol
3	260°—300°	15.0	(60°—70°)		Mixture of *o*-hydroxydiphenyl and diphenyl
4	280°—300°	2.3	(82°—83°)		Diphenylene oxide

Fractions 1 and 2, as their physical constants indicate, are composed of benzene and phenol respectively. From the 3rd fraction, *o*-hydroxydiphenyl and diphenyl were isolated, and the 4th fraction was assumed to be composed mainly of diphenylene oxide.

3. **Dinaphthylene Oxide.** α- and β-Dinaphthylene oxides were prepared⁽¹⁾ from the corresponding naphthol (α or β) by distillation with lead oxide, and purified by treating with alkali solution and recrystallization from hot benzene solution.

	α-Dinaphthylene oxide	β-Dinaphthylene oxide
B. p.	255°–260° (5 mm)	250°–260°–(5 mm)
M. p.	181°	155°
M.p. of picrate	173°	158.5°

(A) *α-Dinaphthylene Oxide.* (1) α-Dinaphtylene oxide (20 gr.) was heated at 500° for 3 hours with hydrogen under 100 atm. pressures at 0° and the fall in the pressure was 14 atmospheres. (Fig. 12).

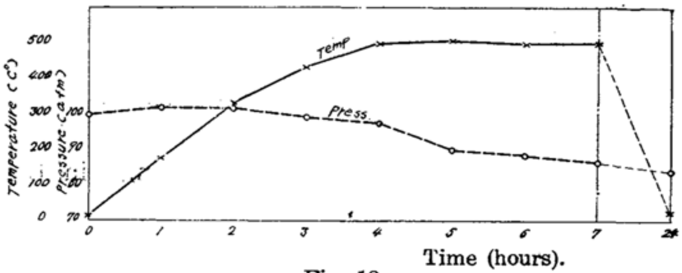

Fig. 12.

The gas in the autoclave was composed of hydrogen (89.7%) and saturated hydrocarbons (10.3% ; n=1) and the latter amounted to 3.8 gr.

Liquid product, (16.8 gr. $d_4^{25}=0.9801$; $n_D^{25}=1.5840$), was fractionated :

Fraction	B.p.	Yield (gr.)	d_4^{25}	n_D^{25}
1	80°–125°	2.7	0.8802	1.4956
2	125°–140°	0.7	0.8894	1.5080
3	180°–200°	1.0		
4	200°–250°	5.4		
5	250°–280°	0.6		
6	residue	2.8		

Fractions 1 and 2 were assumed to be composed of benzene and its homologue by their physical constants and also by the formation of nitro-compounds with a mixture of sulphuric and nitric acids, and of benzoic and phthalic acids on oxidation by potassium permanganate solution.

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(1) W. Knecht u. J. Unzeitig, *Ber.* **13**, 1724; C. Graebe, Ann., **209** (1881), 132; O. Hönigschmidt, *Monatsh.*, **22** (1901), 561; O. Eckstein, *Ber.*, **38** (1905), 3661.

Fraction 3 which showed no reaction with ferric chloride solution or alkali solutions, yielded a small amount of naphthalene on distillation.

Fraction 4, on recrystallization from hot alcohol yielded white crystals melting at 80°, and was confirmed to be hydro-naphthalene by conversion into picrate melted at 149°. From the higher fraction, 0.5 gr. of white tabular crystals with a pale blue fluorescence was isolated which melted at 184° after being recrystallized from hot alcohol solution and gave an organe yellow picrate melting at 184°. It was assumed to be β-β'-dinaphthyl, and to confirm this assumption, it was analysed:

Subst. $=0.0142$; $CO_2=0.0290$; $H_2O=0.0076$ gr.

Found: $C=94.1$; $H=5.9$; Calc. for $C_{20}H_{14}$; $C=94.48$; $H=5.52$.

(2) *In the presence of nickel.* α-Dinaphthylene oxide (20 gr.) was heated with hydrogen at 225° for 2 hours in the presence of reduced nickel under 100 atm. pressures at 0°, no appreciable change in the substance being noticed.

(B) *β-Dinaphthylene Oxide.* (1) β-Dinaphthylene oxide (20 gr.) was heated at 500° for 3 hours under the same conditions as above, and the fall in the pressure was 18 atm. at 0° (Fig. 13).

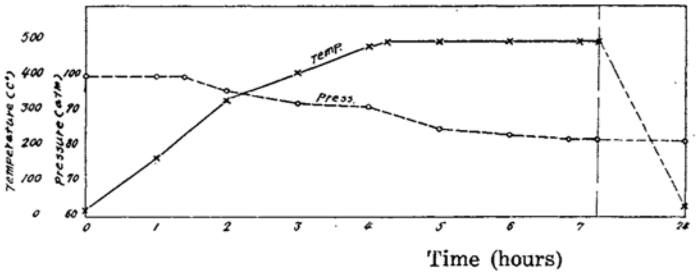

Fig. 13.

From the composition of the gases in the autoclave [hydrogen (86.3 %) and methane (13.7 %)], the amount of hydrogen absorbed and of methane produced were calculated and found to 1.6 gr. (11.5 mol.) and 4.8 gr. (4.3 mol.) respectively.

The oily reaction product (14.7 gr.) was fractionated with the following result:

Fraction	B.p.	Yield (gr.)	d_4^{25}	n_D^{25}
1	100°–150°	2.5	0.8719	1.4963
2	150°–180°	1.0	0.8894	1.5058
3	180°–200°	1.3		
4	200°–250°	4.8		
5	250°–280°	0.7		
6	120°–250° (4 mm)	2.5		
7	250°–320° (4 mm)	1.5		

The first fraction was confirmed to be composed of benzene homologues by chemical methods as in the case of the α-compound.

The amount of fractions 3 and 5 was very small, and no alkali-soluble matter was observed to occur.

Fraction 4 was confirmed to be composed of naphthalene. From fraction 6, white tabular crystals melting at 156°, identical in their properties with α-α'-dinaphthyl, were obtained and analysed:

Subst. = 0.1215; CO_2 = 0.4215; H_2O = 0.0561 gr. Found: C = 94.6; H = 5.2. Calc. for $C_{20}H_{14}$; C = 94.48; H = 5.52.

Fraction 7, a reddish viscous liquid, yielded yellowish tabular crystals on being treated with benzene solution and then acetic acid; they melted at 247° and formed a deep brown picrate melting 250°. These facts and the colour reaction to conc. sulphuric acid indicate that the compound is identical with perylene.

(2) β-Dinaphthylene oxide (20 gr.) was heated with hydrogen in the presence of reduced nickel at 200° for 2 hours, the fall in the pressure being 11 atmospheres. (Fig. 14).

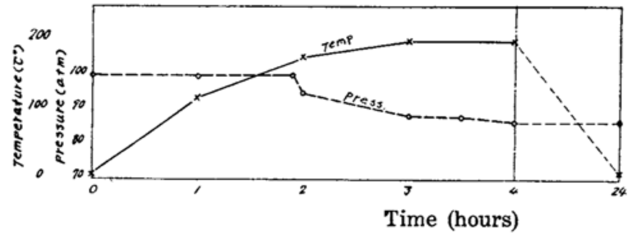

Fig. 14.

A colourless jelly-like matter which distilled out at 225°–280° (6 mm), was obtained as a reaction product. The yield was 17 gr. On analysis it gave the following results:

Subst. = 0.1106; CO_2 = 0.3509; H_2O = 0.0729 gr. Found: C = 86.52; H = 7.37.

On treating the product with hot alcohol, 5 gr. of white needle crystal melting at 140° were isolated.

Subst. = 0.1069; CO_2 = 0.3396; H_2O = 0.0708 gr. Found: C = 86.6; H = 7.4.
Calc. for $C_{20}H_{20}O$: C = 86.95; H = 7.24.

It yielded an orange yellow picrate which melted at 145.5°–146.5° (not sharp). From these results the needle crystals were assumed to be octahydrodinaphthylene oxide.

(3) When 20 gr. of β-dinaphthylene oxide were heated at 500° for one hour in the presence of reduced nickel under high pressure, the hydrogen lost and the methane generated were found, by calculation, to be 2.5 gr. (16.5 mol.) and 5.5 gr. respectively (Fig. 15), since the gaseous reaction product was composed of 87 % hydrogen and 12.3 % methane.

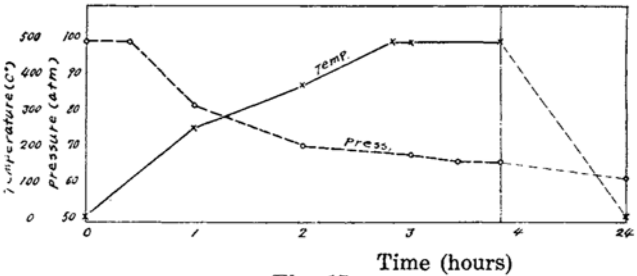

Fig. 15.

A pale yellow liquid product (13.9 gr.) was fractionated as usual, and the physical constants of each fraction studied:

Fraction	B.p.	Yield (gr.)	d_4^{25}	n_D^{25}
1	67°—90°	1.2	0.7623	1.4204
2	90°—160°	2.6	0.8246	1.4615
3	160°—190°	2.3	0.8584	1.4831
4	190°—197°	0.7	0.9074	1.5010

Fractions 1 and 2 were assumed by their physical constants to be composed of cyclohexane and its homologue, and this was confirmed by transforming them into benzene $n_D^{25}=1.4995$ and toluene $n_D^{25}=1.4955$ respectively by dehydrogenation with reduced nickel heated at 350°.

Fractions 3 and 4 were assumed to be composed of decalin and tetralin by the study of their physical constants, and also of their catalytic oxidation into naphthalene by contact with reduced nickel at 350°.

In conclusion, the writer wishes to express his gratitude to Vice-Admiral S. Kishimoto, Director of the Imperial Naval Fuel Depot, who gave him permission to publish this paper; 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 work; and also to Professor S. Komatsu of the Kyoto Imperial University, whose advice and encouragement have been invaluable.

March 1931. Naval Fuel Depot, Imperial Japanese Navy,
Tokuyama.