ON THE CRACKING OF POLYCYCLIC COMPOUNDS.

By Shozo YAMAGUCHI.

Received June 23rd, 1934. Published August 28th, 1934.

When an organic compound is subjected to heat, the rise in the temperature of the molecule due to the increase of its vibratory energy, finally decomposes it into simpler molecules. Such a cracking of organic compounds is considered to occur by breaking a link between two certain atoms somewhere in the molecule, since the bonds in it are not all of the same strength.

The evidence so far studied has shown that in a cracking of a higher paraffin hydrocarbon, the rupture of a link of a C–C bond results in forming one or more molecules of an olefine hydrocarbon as a primary dissociation of the molecule; and in case of unsaturated hydrocarbons, the C=C bond, being approximately twice as strong as the C–C bond, will remain without rupture in the molecule.(1)

In monocyclic compounds, such as benzene and cyclohexane, the inner energy of the molecule being distributed equally to all the carbon atoms composing the ring, the cracking of the ring compound is entirely different from the open chain compounds as indicated in the experiments on both compounds by R. Conrad and his co-workers.(2)

The study of the thermal decomposition of polycyclic compounds will not only afford evidence for the energy distribution in the molecule, but also may add some important contribution to a theory for production of gasoline from heavy oily substances such as coal tars or petroleum. The present study, therefore, deals with naphthalene, quinoline, and isoquinoline of bicyclic compounds, and tricyclic anthracene, as they occur in petroleum and other tar products.

Although naphthalene is usually represented by a bicyclic formula consisting of two condensed benzene nuclei, on reduction with hydrogen and nickel catalyst it is transformed into tetraline. Its dipole nature being 0.7, the chemical and physical natures of naphthalene are represented by the structural formula of C. Harries and R. Willstätter(3), which has two different carbon rings, Fig. 1.

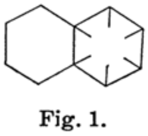

Fig. 1.

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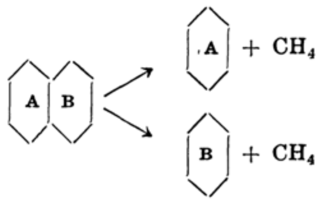
(1) F. O. Rice, "Free Radicals," 1933, p. 152; A. E. Dunstan, E. N. Hague, and R. V. Wheeler, *J. Soc. Chem. Ind.*, **50** (1931), 313; H. Gault and Y. Altchidjiam, *Compt. rend.*, **178** (1924), 2092; and also refer G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," 1932, p. 105.

(2) *Z. Elektrochem.*, **36** (1930), 654; "Free Radicals," 1933, p. 215.

(3) R. Müller, *Samm. Chem. u. Chem. Tech. Vorträge*, **30** (1928), 1.

The theory that naphthalene molecule is represented by a formula consisting of two benzene nuclei considered unequal in view of energy distribution, is advocated by Dr. S. Kimura in his study of hydronaphthalenes.(4) According to this hypothesis, on cracking, naphthalene will yield derivatives of benzene by disruption of the more unstable one of the two rings.

When naphthalene is heated in an autoclave under high pressure of hydrogen, the dissociation of the polycyclic compound into monocyclic free radicals may occur in one of two ways according to the stability of the rings :



The free radicals thus formed usually undergo secondary reaction to form complicated products. In order to minimize, if possible, the subsequent course of reaction of the free radicals produced in the primary decomposition, and also to intensify the cracking by the heat transfer, hydrogen under high pressure is used ; this will saturate the free valence of the fragments before polymerisation can occur. When naphthalene (100 g.) was heated at 500° for 5 hours in the presence of calcium chloride with hydrogen of 80 atmospheric pressures at 0°, 60 per cent. of the substance was cracked and the reaction product was found to consist of liquid and gaseous substances. The former consists of benzene and its homologues and the latter of methane and ethane, and their percentages in the product are given in Table 1.

The theoretical yields of methane in mols with the formation of 1 mol benzene or its homologues from 1 mol of naphthalene are as follows :

With	benzene	4 mols	methane
,,	toluene	3 ,,	,,
,,	xylene	2 ,,	,,

Table 1.

Substance	Yield	No. of mols from 1 mol of naphthalene
Benzene	4.8 g.	0.08
Toluene	14.1 ,,	0.20
Xylene	18.0 ,,	0.22
Methane	4.8 ,,	0.40
Ethane	19.8 ,,	0.46

The actual yield of the gaseous hydrocarbons calculated as methane is 1.3 mols, which agrees with 1.36 mols of methane calculated from molar yield of benzene and its homologues based on

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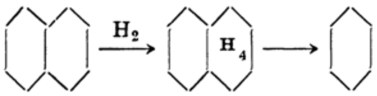
(4) *Mem. Coll. Sci. Kyoto Imp. Univ.*, A, **14** (1931), 307.

the theory shown above. The cracking of naphthalene under high pressure of hydrogen, therefore, may be represented by the following scheme when we take M. A. Sundgren's⁽⁵⁾ experiment on hydronaphthalene into consideration:



The cracking of anthracene was performed under the same conditions, and the compound was perfectly decomposed into 20 per cent. gaseous hydrocarbons such as methane and ethane, and 80 per cent. other hydrocarbons. The latter contained 47 per cent. naphthalene and its derivatives, 27 per cent. benzene and its homologues, and 10 per cent. dianthracene; the molar yield of benzene and its homologues is almost equal to that of naphthalene and its homologues. This fact indicates that two decomposition reactions occur simultaneously but with different velocities, namely the rupture of the B-ring and one of two A-rings (Table 2):

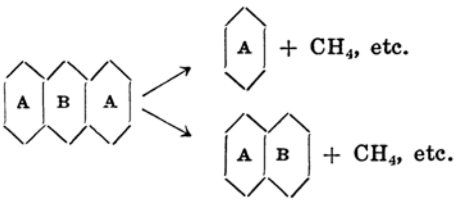


Table 2.

	Yield		
Benzene	6.4 g.	0.146 mol	0.55 mol
Toluene	14.3 ,,	0.295 ,,	
Xylene	6.2 ,,	0.113 ,,	
Naphthalene	15.8 ,,	0.220 ,,	0.58 ,,
Dimethyl-naphthalene	31.3 ,,	0.357 ,,	
Dianthracene	10.1 ,,	0.050 ,,	0.05 ,,
Methane	3.6 ,,	0.401 ,,	1.37 ,,
Ethane	16.3 ,,	0.967 ,,	

The hydrogenation of anthracene in the presence of a catalyst proceeds by adding the first two hydrogen-atoms to the B-ring, and the dihydro-compound thus formed will be instantly transformed into tetrahydro-com-

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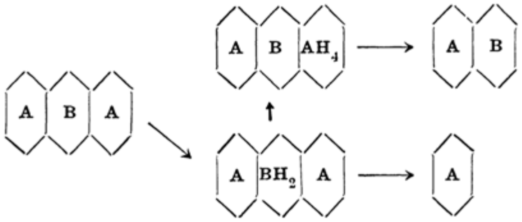
(5) "La décomposition pyrogénée du tétranaphtalène et du décanaphtalène." *Ann. Combustibles Liquides*, **5** (1930), 35; and refer Ipatiew and Orlow, *Ber.*, **60** (1927), 1950; **62** (1929), 711, 719, 1226; **63** (1930), 2179.

pound. Thus, cracking of anthracene under pressure of hydrogen produces dihydro-anthracene, which partly decomposes into benzene homologues and is partly converted into tetrahydro-anthracene. This in turn is cracked into naphthalene derivatives.



Quinoline and isoquinoline, which are bicyclic compounds, are formulated in the same way as naphthalene in which an α- or β-CH-group is replaced by N.

I

Quinoline

II

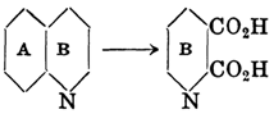
Isoquinoline

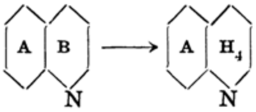
III

Naphthalene

Benzene nucleus A and pyridine nucleus B in the formulas I and II may evidently differ from each other in the energy content, since the heats of combustion of benzene and of pyridine are 787 cal. and 660 cal. respectively.

Such an assumption of the energy content of ring systems agrees with the fact that quinoline, when oxidized with potassium permanganate, opens the benzene nucleus with production of quinolinic acid, and that when quinoline is reduced with sodium and alcohol it takes up four atoms of hydrogen, forming tetrahydro-quinoline, the hydrogen atoms adding almost exclusively to the pyridine ring. The same phenomena occur of course in the case of naphthalene.





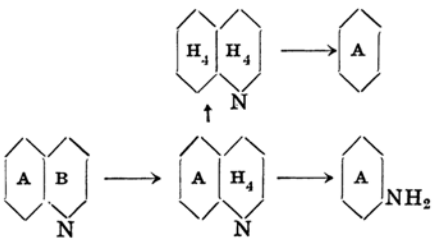
From these facts it is evident that when quinoline is cracked under high pressure of hydrogen at 450°, the pyridine nucleus in the quinoline molecule is reduced. The tetrahydro-compound so formed undergoes decomposition into benzene homologues or aniline derivatives, as naphthalene gives benzene homologues. As a matter of fact, when quinoline (50 g.) was heated at 450° for 4 hours with hydrogen of 80 atmospheric pressures at 0°, 90 per cent. of the substance was decomposed and 50 per cent. was composed of aniline and its homologues including methyl-indole; in other words, 1 mol of quinoline gave on cracking 0.5 mol of aniline-derivatives, 0.16 mol of hydrocarbons of cyclohexane and benzene homologues, and 0.21 mol of ammonia and amines (Table 3).

Table 3.

	Yield		
Aniline	2.7 g.	0.04 mol	0.5 mol
o-Toluidine	14.5 ,,	0.18 ,,	
o-Ethyltoluidine	5.6 ,,	0.06 ,,	
o-Propyltoluidine	3.5 ,,	0.03 ,,	
Methyl-*o*-toluidine	1.6 ,,	0.02 ,,	
Ethyl-*o*-toluidine	1.2 ,,	0.03 ,,	
Methyl-indole	15.4 ,,	0.16 ,,	
Cyclohexane	2.0 ,,	0.03 ,,	0.16 ,,
Methylcyclohexane	1.4 ,,	0.03 ,,	
Ethylcyclohexane	1.7 ,,	0.03 ,,	
Propylcyclohexane	3.6 ,,	0.04 ,,	
Toluene	0.5 ,,	0.007 ,,	
Ethyl-benzene	0.5 ,,	0.006 ,,	
Propyl-benzene	0.5 ,,	0.004 ,,	
Ammonia	1.37 ,,	0.21 ,,	0.21 ,,
Methane	2.70 ,,	0.44 ,,	0.70 ,,
Ethane	3.00 ,,	0.26 ,,	

The experimental results resemble those gained from the experiments on the cracking of hydroquinoline by Padoa and his co-workers.(6)

The cracking of quinoline, therefore, will be represented by the following scheme in which hydroquinoline is supposed to be formed during the process of cracking.



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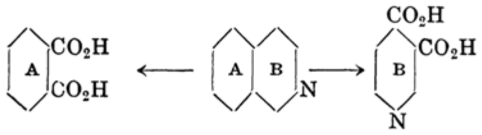
(6) Padoa, Carughi, and Seagliarini, *Chem. Zentr.*, 1906, II, 1011; 1908, II, 114.

To our astonishment, no traces of pyridine and its homologues are present in the cracking product of quinoline. Then it follows that benzene and pyridine nuclei in the quinoline molecule are not equivalent in energy content. Such a consideration on the bicyclic compound may be applied to isoquinoline in which benzene and pyridine nuclei occur as in the quinoline molecule. However, the structural difference is evidently manifested in the result of oxidation with potassium permanganate; quinolinic acid is formed from quinoline, while phthalic acid and cinchomeronic acid are formed from isoquinoline :



Thus the stability of the pyridine ring is greater in isoquinoline than in quinoline.

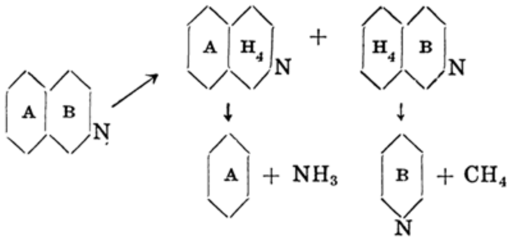
In fact, the cracking of isoquinoline at 450° gives 5 per cent. pyridine and its homologues, 38 per cent. toluene and other aromatic hydrocarbons, about 10 per cent. of unchanged material, and 9 per cent. gaseous products.

The molar yields of the cracked substances are 0.06 mol pyridine bases, 0.4 mol aromatic hydrocarbons, and 0.65 mol gaseous bases (Table 4).

Table 4.

	Yield		
Pyridine	1.3 g.	0.03 mol	0.1 mol
Methyl-pyridine	1.6 ,,	0.03 ,,	
Dimethyl-pyridine	1.9 ,,	0.03 ,,	
Toluene	4.3 ,,	0.06 ,,	0.4 ,,
o-Xylene	12.6 ,,	0.15 ,,	
Indane	18.5 ,,	0.20 ,,	
Dimethyl-anthracene	2.3 ,,	0.01 ,,	
Ammonia	4.3 ,,	0.65 ,,	0.65 ,,
Methane	2.7 ,,	0.43 ,,	0.61 ,,
Ethane	2.2 ,,	0.18 ,,	

The writer, therefore, suggests the following reactions in the cracking of isoquinoline as the most probable :



In conclusion, in the cracking of polycyclic compounds under high pressure of hydrogen, the more reactive ring takes first hydrogen atoms and the hydrogenated ring breaks before the other. There exists an optimum temperature for cracking which depends upon the chemical nature of substances; above this temperature the dehydrogenation becomes predominant. The manner of the ring rupture of the polycyclic compounds would be foreseen from their behaviour in catalytic reduction or in other words from the study of the energy content of ring systems.

Experimental.

The naphthalene, anthracene, quinoline, and isoquinoline used in the experiments were all proved to be fairly pure by their physical constants as shown in Table 5.

Table 5.

	B. p.	M. p.	n_D^{25}	d^{25}
Naphthalene	215-218	81°	—	—
Anthracene	—	216°	—	—
Quinoline	235-238°	—	1.6238	1.0894
Isoquinoline	238-240°	—	1.6239	1.0984

In the experiment, a weighed sample was introduced into an autoclave, and after the air in it was replaced by hydrogen, and the hydrogen gas was raised to the required pressure, it was heated externally to the required temperature by an electrical resistance furnace.

During the reaction, the autoclave was shaken by a machine to bring the substances in agitated state, and changes of temperature and pressure during the reaction were recorded every ten minutes.

After the reaction the apparatus was cooled. The volume of gas in it was measured, and the chemical composition and physical properties of the gas and of other reaction products were examined carefully.

(1). **Naphthalene.** When naphthalene (100 g.) was heated for 6 hours with a small amount of calcium chloride at 500° with hydrogen of 71 atmospheres at 0°, a fall of 11 atmospheric pressures was observed.

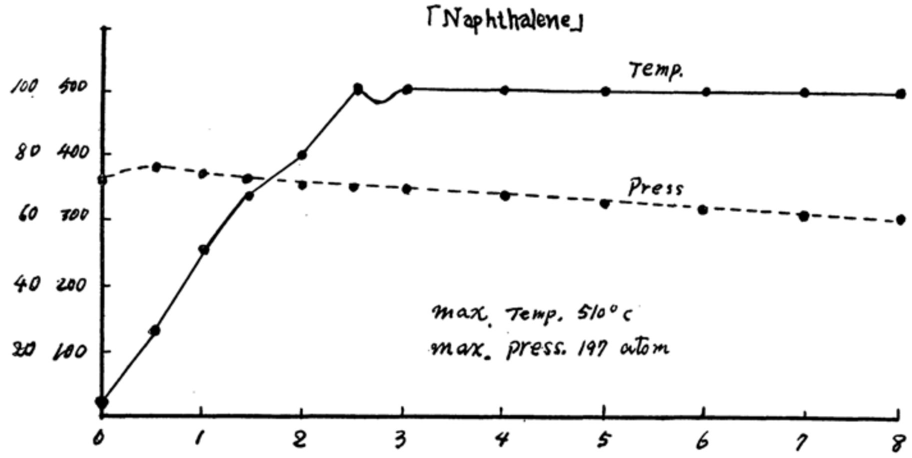


Fig. 2.

The gas in the autoclave was determined to be composed of 84.9 per cent. of H_2, 10.3 per cent. of C_2H_6, 4.6 per cent. of CH_4, and 0.2 per cent. of C_nH_m. The reaction product (67 g.) in the autoclave consisted of liquid and solid substances, which were separated by filtration. The solid substance separated from the liquid amounted to 10 g. and was found to be naphthalene, for, after it was purified by recrystallization from alcohol, it melted at 81°, and its picrate at 151°. The liquid reaction product (65 g.) was subjected to fractional distillation under 759.5 mm. pressure over metallic sodium and separated into six fractions with the physical constants shown in Table 6.

Table 6.

Fraction	B. p.	Yield (g.)	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		

The fractions 1 and 2, as indicated by their physical constants. were assumed to be composed of benzene and toluene respectively; the former was confirmed by changing it into nitrobenzene and then reducing it to aniline, and the latter was oxidized to benzoic acid (m.p. 121°) by potassium permanganate.

The fractions 3 and 4 were supposed from their physical constants to be a mixture of *o*-xylene and ethyl-benzene.

The fraction 5, consisting of naphthalene, xylene, and ethyl-benzene, was treated with picric acid in an alcoholic solution in order to separate naphthalene. The picrate separated from volatile hydrocarbons by distillation under reduced pressure amounted to 4.8 g., from which pure naphthalene was isolated in a yield of 1.2 g. The mixture of hydrocarbons separated from naphthalene weighed 3.6 g., and from its boiling point 124–145°, refractive index $n_D^{25} = 1.4981$, and density $d_4^{25} = 0.8695$, the proportion of xylene and ethyl-benzene was calculated to be about 7:3. Fraction 3 was composed of naphthalene as shown by the physical properties and also by the formation of the picrate.

(2) **Anthracene.** Anthracene (100 g.) was heated at 500° for 6 hours with 10 g. of calcium chloride and hydrogen of 84 atmospheric pressures at 0°. The fall in the pressure was 17.6 atmospheres at 0°. The gaseous product was composed of 89.1 per cent. of H_2, 3.2 per cent. of CH_4, 7.6 per cent. of C_2H_6, and 0.1 per cent. of C_nH_m. From the reaction product 10 g. of solid and 74 g. of liquid ($d_4^{25} = 0.984$, $n_D^{25} = 1.584$) were isolated.

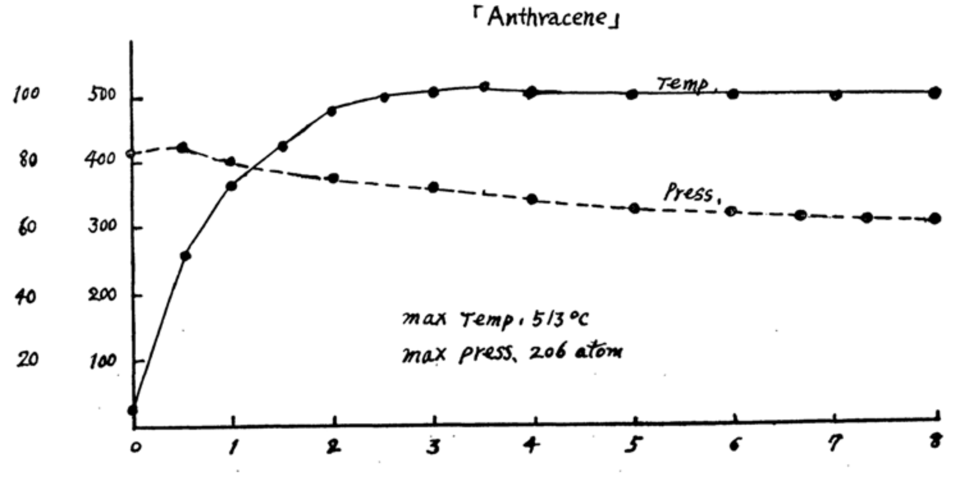


Fig. 3.

The liquid reaction product (70 g.) was fractionated over metallic sodium as shown in Table 7.

Table 7.

Fraction	B. p.	Yield (g.)	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			
6	220–240	13.5	Liquid with crystals		Naphthalene
7	240–270	13.5	Resin with crystals		
8	270–350	5.0			
9	Residue	5.1			

The fractions 1 and 2 were identified by their physical and chemical properties with benzene and toluene respectively; and the fractions 3 and 4 were assumed to be mixtures of xylene and ethyl-benzene from their physical constants.

Fractions 5 and 6, containing some crystals which amounted to 14.9 g. and showed m.p. 78°, were confirmed to be naphthalene from the melting point and the analytical results of the substance purified by recrystallization from alcohol.

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

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

Fractions 7 and 8, both being viscous liquids containing some solid substances, 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 a red picrate melting at 162–172° was isolated.

Lastly, there was a solid residue which was practically insoluble in alcohol, ether, and benzene, and showed a melting point 242–243° after purified by recrystallization from ether solution. These properties quite agree to those of dianthracene prepared by Graebe and Lieberman, and by

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(7) "Beilsteins Handbuch der Organischen Chemie," 4th Ed. Vol. V, p. 567 and Vol. VI, p. 2721, b. p. 242–243°, m.p. 37–38°, picrate m.p. 116–117°.

Ordendorff and Cameron,(8) from anthracene, and on analysis it gave the following results:

Found: C, 93.85; H, 5.41. Calculated for $(C_{14}H_{10})_2$: C, 94.38; H, 5.61%.

(3) **Quinoline.** When quinoline (50 g.) was heated at 450° for 4 hours with hydrogen of 80 atmospheric pressures, the fall in the pressure was 42.5 atmospheres at 0° and 42.5 g. of a liquid substance besides a gaseous product was obtained. The gas was determined to be of the following composition:

62.4% H_2, 17.3% CH_4, 11.5% C_2H_6, 0.4% C_nH_m. and 8.0% NH_3.

Through repetition of the same experiments four times, and after removal of lower boiling fractions (below 100°) by distillation, 162.5 g. of the liquid product was obtained. It was then treated with dilute sulphuric acid in order to separate hydrocarbons from bases.

The bases were fractionated into two fractions, and the fraction boiling below 230° was separated by means of meta-phosphoric acid into primary and secondary bases. The yield of each fraction is shown below:

162.5 g.	Hydrocarbons			43.0 g.
	Bases	below 230° (81.4 g.)	primary	60.5 ,,
			secondary	9.6 ,,
		above 230°		24.6 ,,
		loss		24.8 ,,

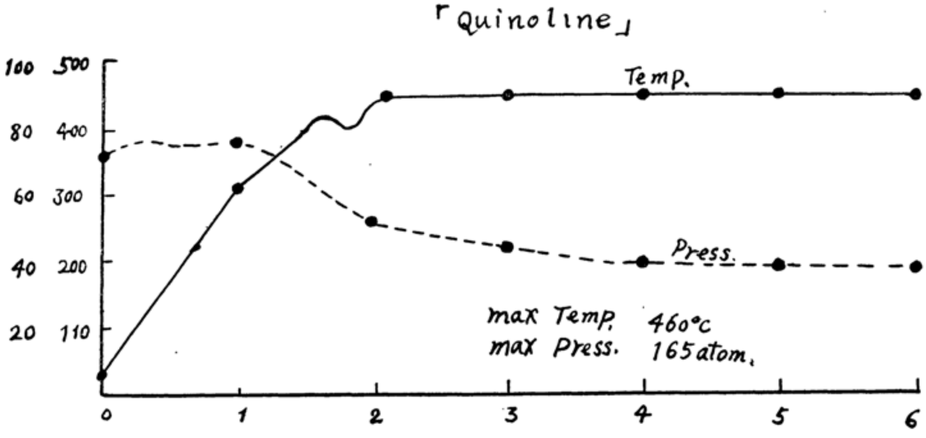

Fig. 4.

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(8) *Ann. d. Chem. Spl.*, **7** (1870), 265; *Am. Chem. J.*, **17** (1895), 666.

(a) Primary bases. This fraction (55 g.), set free from the phosphate, was fractionated into 5 fractions with the physical constants given in Table 8.

Table 8.

Fraction	B. p.	Yield (g.)	n_D^{25}	d_4^{25}	Remarks
1	180–190	4.8	1.5736	1.0075	Aniline
2	190–200	25.2	1.5731	0.9984	*o*-Toluidine
3	200–210	9.8	1.5655	0.9842	*o*-Ethyl-aniline
4	210–220	6.0	1.5612	0.9778	*o*-Propyl-aniline
5	220–230	3.0	1.5623	0.9860	
Loss		6.2	—	—	

Fractionts 1 and 2, as indicated by their physical constants, are assumed to be composed mainly of aniline and of toluidine respectively, and it was confirmed by the melting points of their picrates: 164° and 212–213° respectively.

The toluidine showed the physical constants, $d_4^{25} = 0.9950$, and $n_D^{25} = 1.5703$, and gave the following analytical results:

Found: C, 78.37; H, 8.84; N, 12.51. Calc. for C_7H_9N: C, 78.5; H, 8.4; N, 13.1%.

Fractions 3 and 4 were assumed from their physical constants to be composed of ethyl- and propyl-anilines, and it was confirmed by converting them into benzoates melting at 147–148° and 117–118° respectively. On analysis they gave the following results:

Found: C, 79.49; H, 6.60. Calc. for $C_{16}H_{17}N$: C, 80.00; H, 6.60%.
Found: C, 80.03; H, 6.90. Calc. for $C_{17}H_{19}N$: C, 80.0; H, 7.50%.

(b) Secondary bases. This fraction (9.6 g.) was fractionated as shown in Table 9.

Table 9.

Fraction	B. p.	Yield (g.)	n_D^{25}	d_4^{25}	Remarks
1	196–200	1.1	1.5641	0.9792	
2	200–210	2.3	1.5601	0.9754	Methyl-*o*-toluidine
3	210–220	2.0	1.5520	0.9674	Ethyl-*o*-toluidine
4	220–230	0.2	1.5538	—	
5	230–240	0.2	—	—	
6	above 240°	3.8	—	—	

Fractions 1, 2, and 3 were assumed from their physical constants to be mixtures of methyl-*o*-toluidine and ethyl-*o*-toluidine, and they gave the following analytical results:

Fraction 2. Found: C, 78.40; H, 9.0. Calc. for $C_8H_{11}N$: C, 79.35; H, 9.09%.
Fraction 3. Found: C, 80.48; H, 8.79. Calc. for $C_9H_{13}N$: C, 80.00; H, 9.63%.

(c) The fraction boiling above 220° was fractionated as shown in Table 10.

Table 10.

Fraction	B. p.	Yield (g.)	n_D^{25}	d_4^{25}	Remarks
1	-230	1.2	1.5624	0.9863	
2	230–240	8.7	1.5636	0.9867	Quinoline
3	240–250	3.0	1.5685	1.0004	Methyl-indole
4	250–260	2.3	1.5740	1.0067	
5	260–270	2.0	1.5784	1.0295	
6	above 270°	5.3	—	—	

Fraction 2 was assumed to consist mainly of quinoline from its physical constants, and it was confirmed by transforming it into a picrate of m.p. 203–203.5°, and isolating quinoline (b. p. 207–208°, $n_D = 1.640$, $d_4^{25} = 1.0895$) by the action of alkali on the picrate.

The fraction boiling above 240° gave a sodium salt when heated with metallic sodium or sodium amide. The alcoholic solution of this fraction gave cherry red colour to a pine chip moistened with concentrated hydrochloric acid. These facts indicate that the fraction was a mixture of indole derivatives.

(d) Hydrocarbons. The fraction boiling below 100° was combined with the neutral part of higher boiling points separated from bases, and the whole substance amounted to 43 g. It was fractionated over metallic sodium into 15 fractions as shown in Table 11.

Table 11.

Fraction	B. p.	Yield (g.)	n_D^{25}	d_4^{25}	Remarks
1	-70	0.3	—	—	
2	70–80	1.8	1.4275	0.7655	
3	80–90	1.8	1.4291	0.7666	Cyclohexane
4	90–100	0.7	1.4328	0.7780	
5	100–110	1.5	1.4481	0.7935	Methyl-cyclohexane
6	110–120	1.5	1.4662	0.7818	
7	120–130	0.8	1.4661	0.8246	
8	130–140	1.4	1.4080	0.8245	Ethyl-cyclohexane
9	140–150	2.1	1.4730	0.8341	
10	150–160	1.5	1.4733	0.8391	
11	160–170	3.0	1.4800	0.8717	Propyl-cyclohexane
12	170–180	0.8	1.4928	0.8936	
13	180–190	1.6	1.5027	0.9031	
14	190–200	1.0	—	—	
15	Residue	19.4	—	—	

By fractional distillation of fractions 2 and 3, fairly pure cyclohexane (2.1 g., b. p. 80–81°, $n_D^{25} = 1.4281$, $d_4^{25} = 0.7748$) and a mixture of cyclohexane and methyl-cyclopentane were obtained. On analysis the cyclohexane gave the following results :

Found : C, 86.07 ; H, 13.98. Calc. for C_6H_{12} : C, 85.71 ; H, 14.29%.

Fractions 4, 5, and 6 were assumed, from their physical constants, to be composed mostly of methyl-cyclohexane with some aromatic hydrocarbons. After washing with concentrated sulphuric acid, redistillation gave a fraction (2.1 g.) with properties (b. p. 102–104°, $n_D^{25} = 1.4358$, $d_4^{25} = 0.7710$) agreeing to methyl-cyclohexane, and on analysis it gave the following result :

Found : C, 85.78 ; H, 14.10. Calc. for C_7H_{14} : C, 85.71 ; H, 14.29%.

Fractions 7, 8, and 9 appeared from their physical constants to consist of ethyl-cyclohexane and some aromatic hydrocarbons. After treating them with concentrated sulphuric acid, a fraction (1.2 g., b. p. 132–133°, $n_D^{25} = 1.4479$, $d_4^{25} = 0.7791$) corresponding to ethyl-cyclohexane was isolated.

Found : C, 85.84 ; H, 13.81. Calc. for C_8H_{16} : C, 85.81 ; H, 14.29%.

Fractions 10 and 11 were confirmed to be composed mostly of propyl-cyclohexane. By fractional distillation after washing with sulphuric acid, 1.5 g. of the pure substance was obtained. The physical properties and analytical results of the isolated compound were as follows :

B. p. 153–156° ; $n_D^{25} = 1.4751$; $d_4^{25} = 0.8347$.

Found : C, 86.00 ; H, 13.46. Calc. for C_9H_{18} : C, 85.71 ; H, 14.29%.

Since the residue gave a sodium salt and contained nitrogen, it was assumed to be an indole derivative.

(4) **Isoquinoline.** Isoquinoline (50 g.) was heated at 450° for 4 hours with hydrogen of 80 atmospheric pressures ; the fall in the pressure was 33 atmospheres at 0°.

The gas in the autoclave was composed of 59.2 per cent. of H_2, 15.9 per cent. of CH_4, 6.9 per cent. of C_2H_6, 0.5 per cent. of C_nH_m, and 17.1 per cent. of NH_3. The oily reaction product amounted to 40.4 g. (80.7%).

By repeating similar experiments several times, 282 g. of the liquid reaction product was obtained. It was first separated from the fraction boiling below 100°, and the higher fraction was then treated with dilute sulphuric acid in order to separate it into basic and neutral substances.

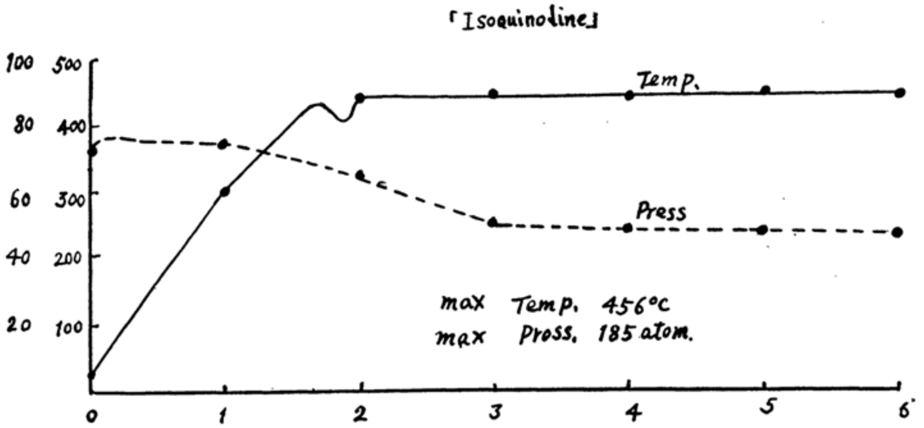

Fig. 5.

(a) Basic substance. The basic substance (65.0 g.) was fractionated into 15 fractions as shown in Table 12.

Table 2.

Fraction	B. p.	Yield (g.)	n_D^{25}	d_4^{25}	Remarks
1	110–120	4.4	1.4928	0.9706	Pyridine
2	120–130	2.2	1.4975	0.9360	
3	130–140	2.0	1.4973	0.8971	Methyl-pyridine
4	140–150	0.9	1.5009	0.8982	
5	150–160	0.6	1.5070	0.9274	
6	160–170	—	—	—	
7	170–180	4.2	1.5161	0.9436	
8	180–190	1.6	1.5310	0.9631	Dimethyl-pyridine
9	190–200	1.0	1.5454	0.9821	
10	200–210	—	—	—	
11	210–220	2.5	1.5588	0.9911	
12	220–230	3.0	1.5632	1.0141	
13	230–240	15.1	1.5753	1.0333	Isoquinoline
14	240–250	12.1	1.5860	1.0550	
15	250–260	3.4	1.5911	1.0544	

Fraction 1 was composed mostly of pyridine as indicated by its characteristic odour and physical constants. Further it was confirmed by transforming it into a picrate melting at 167°.

Fractions 2, 3, 4, and 5 were composed mostly of methyl-pyridine as seen from physical constants. By deriving a picrate and recrystallizing it from alcohol several times, 0.4 g. of pure methyl-pyridine was obtained. The pure picrate melted at 165°.

Fractions 7, 8, and 9, composed mainly of dimethyl-pyridine, were converted into a picrate to isolate the pure base. The free base (3.4 g.) isolated showed b.p. 176–179°, $n_D^{25} = 1.5161$, and $d_4^{25} = 0.9439$.

Fractions 13 and 14 were composed mostly of isoquinoline as seen from their physical constants. The pure picrate (4.8 g.), isolated from 4.0 g. of these fractions, melted at 223°. The recovered free base (2.7 g.) gave the following analytical results:

Found: C, 83.59: H, 6.18. Calc. for C_9H_7N: C, 83.72; H, 5.42%.

(b) Hydrocarbons. The neutral substance separated from the bases was combined with hydrocarbons boiling below 100°, and the whole amounted to 203 g. It was fractionated by distilling repeatedly over metallic sodium into 10 fractions as shown in Table 13.

Table 13.

Fraction	B. p.	Yield (g.)	d_4^{25}	n_D^{25}	Remarks
1	-100	1.5	—	—	
2	100–110	1.0	0.7642	1.4308	
3	110–120	10.0	0.8240	1.4771	Toluene
4	120–130	2.5	0.8511	1.4941	
5	130–140	2.8	0.8592	1.4960	
6	140–150	26.9	0.8568	1.5000	Xylene
7	150–160	13.8	0.8687	1.5042	
8	160–170	10.8	0.8728	1.5025	
9	170–180	45.9	0.8918	1.5132	Indane
10	180–190	9.3	0.9155	1.5253	

Fractions 3, 6, and 9 were assumed from their physical constants to be composed mostly of toluene, *o*-xylene, and indane respectively.

For the identification of the compounds occurring in these fractions, the substances were oxidized with potasium permanganate, and after purification by distillation they were analyzed with the results given in Table 14.

Table 14.

	Fraction 3	Fraction 6	Fraction 9
B. p.	110–112°	140–145°	172–175°
n_D^{25}	1.4909	1.5009	1.5273
d_4^{25}	0.8539	0.8732	0.9370
Acid obtained by oxidation	Benzoic acid	Phthalic acid	Phthalic acid
Found	C, 91.41 ; H, 8.92	C, 90.76 ; H, 9.15	
Calculated	for C_7H_8 C, 91.30 ; H, 8.70	for C_9H_{10} C, 91.52 ; H, 8.48	

Lastly, from the final fraction two yellow crystalline substances were obtained, one, amounting to 1.1 g., melted at 202-206°, and the other (2.1 g.) at 239°. The former was confirmed from its analytical results to be α-methyl-anthracene.

Found: C, 93.60; H, 5.89. Calc. for $C_{15}H_{12}$: C, 93.75; H, 6,25%.

In conclusion, the writer wishes to express his sincere thanks to Vice-Admiral Y. Yoshioka, and Rear-Admiral M. Ueda, the former and the present Directors of the Imperial Naval Fuel Depot, and to Rear-Admiral Viscount M. Kawase, and Engineer-Captain R. Kinashi, the former and the present Chiefs of the Scientific Research and Experimental Branch, for their kindness in enabling him to take part in this work, and to Prof. S. Komatsu of the Kyoto Imperial University whose advice and encouragement have been invaluable, and also to Mr. G. Fujii, whose kind assistance enabled him to complete the experiment.

The Scientific and Experimental Branch,
The Imperial Naval Fuel Depot, Tokuyama.