[CONTRIBUTION FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Chemical Nature of Coal Hydrogenation Products. I. Initial Resolution by Chromatography on Alumina[1]

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Introduction

For the elucidation of the structure of polymeric substances, chemical degradation to identifiable moderate-molecular weight fragments is one of the most informative methods. Since bituminous coal is considered to be a network polymer[3] resulting from the chemical interaction of plant material, this method of clarifying the chemical nature of coal is being studied in this Laboratory. Oxidation,[4] halogenation,[5] hydrolysis,[6] and hydrogenation[7] have been and are being employed as tools for this degradation.

In the hydrogenation process a modified technique has been used to promote the formation and isolation of truly primary hydrogenation products. Previous workers (7) have reported the use of lower reaction temperatures, the use of no vehicle or pasting agent, and the use of a catalyst which does not promote the hydrogenation of the aromatic ring. The use of a coal–catalyst mixture which has been ground together, the use of a cold-head receiver on the hydrogenation autoclave, and the use of chromatographic analysis and ultraviolet absorption spectra in the resolution and characterization of the volatile primary hydrogenation products are reported in the present work. The grinding together of the coal and the catalyst and the use of the cold-head receiver have increased the yield of degradation products to the extent that 75% of the carbon on a dry ash-free basis has been liquefied and/or gasified.

Experimental

Coal–Catalyst Mixture.—Sufficient coal-catalyst mixture for one hydrogenation experiment was prepared by mixing 100 g. of minus 200-mesh Pittsburgh Seam coal from the Edenborn mine[8] and 20 g. of Adkins catalyst (calcium–copper–chromium oxide) or by grinding in a pebble mill for forty-eight hours.

Autoclave with Cold-Head Receiver.—The autoclave (1.1 liters) was of the usual design with a modified head with a sidearm connected to a water-cooled condenser mounted above a receiver (0.1 liter)[9] as shown in Fig. 1, and was so supported during use that the distillation tube was on the upper side to prevent the reactants from being transferred mechanically to the receiver. The autoclave was heated by an electric furnace provided with an insulated cover to prevent condensation of the products of hydrogenation in the autoclave head and manifold.

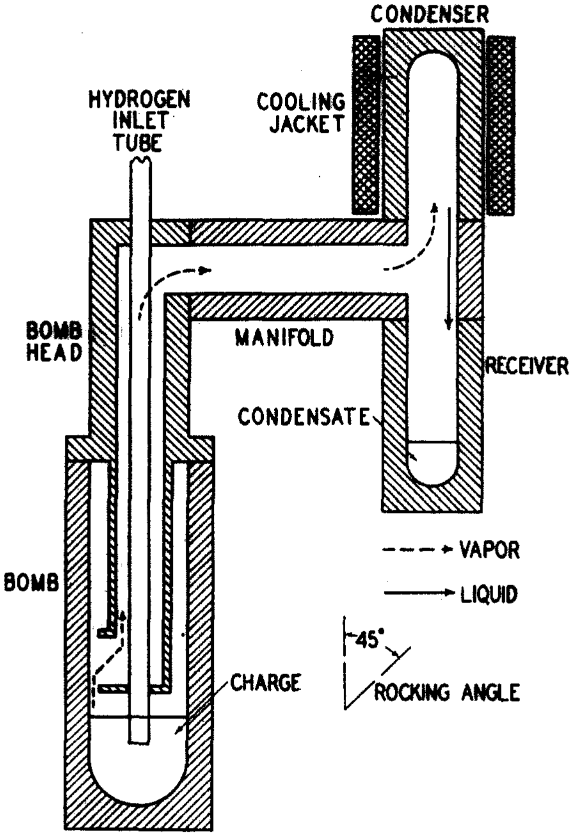

Fig. 1.—Diagrammatic sketch of hydrogenation autoclave.

Hydrogenation Procedure.—The coal–catalyst mixture (120 g.) was placed in the autoclave under a cold hydrogen pressure of 1800 p. s. i. Rocking of the autoclave was begun when the reaction temperature was reached and was stopped at the end of the reaction time. After cooling, the receiver and contents were weighed, the distillable material (about 60 g.) removed with the aid of benzene and the receiver dried and its tare weight determined. The solid residue (about 55 g.) was removed mechanically from the bomb proper and weighed.

Processing of the Hydrogenation Distillate.—The benzene solution of the distillable oils with the water of hydrogenation were transferred to a separatory funnel and the water (about 6 ml.) separated. The benzene solution, after drying with anhydrous sodium sulfate, was adsorbed on a short column (6.0 × 2.2 cm.) of activated alumina–Super-Cel (1:1) and the purified material removed by elution with 200 ml. of benzene. The amount of material removed in this short column treatment was determined by extruding the column[10] after

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[1] (a) From the thesis submitted to Carnegie Institute of Technology in partial fulfilment of the requirements for the degree of of Doctor of Science; (b) presented in part before the Division of Gas and Fuel Chemistry at the 106th meeting of the American Chemical Society, Pittsburgh, Pa., Sept. 1943.

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[3] H. C. Howard, *J. Phys. Chem.*, **40**, 1103 (1936).

[4] H. C. Howard in "Chemistry of Coal Utilization," H. H. Lowry, editor, John Wiley and Sons, Inc., New York, N. Y., 1945, chapter 9.

[5] J. F. Weiler, *ibid.*, chapter 8.

[6] H. C. Howard, *ibid.*, chapter 11.

[7] J. F. Weiler, *ibid.*, chapter 10.

[8] A. C. Fieldner, *et al.*, Tech. Paper 525, U. S. Bureau of Mines, 1932.

[9] The cold-head receiver was designed and used originally by J. F. Weiler of this Laboratory.

[10] John Turkevich, *Ind. Eng. Chem.. Anal. Ed.*, **14**, 792 (1942).

elution, transferring it to a Soxhlet and extracting it exhaustively with benzene–methanol, and was found in Run 4 to amount to 3% of the material put through the column.

Chromatography of Hydrogenation Products.—The stabilized distillate, after removal of the benzene–methanol solvent by distillation at the pressure of the water pump, was dissolved in 250 ml. of petroleum ether (30–60°) and chromatographed using a long column (50 × 4.8 cm.) of activated alumina–Super-Cel (1:1) and the same solvent (1000 ml.) as developer. The extruded column, after separation into the four bands based on its appearance in ultraviolet light, was extracted in a Soxhlet with methanol–benzene. The filtrate from the chromatogram was combined with the extract from the lowest band (Band I). A typical chromatogram is shown diagrammatically in Fig. 2.

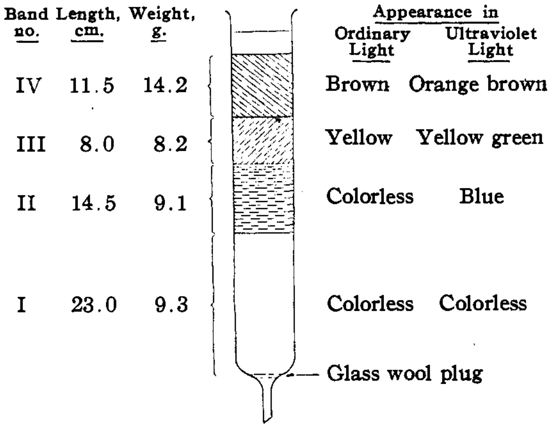

Fig. 2.—Diagrammatic chromatogram of hydrogenation products.

Hydrogenation Time–Temperature Studies.—To determine the yield of distillate as a function of time and temperature, hydrogenations were made over the temperature range 350 to 400° from twenty-four to seventy-two hours. Coal–catalyst mixtures prepared both by simple mixing and by grinding in a pebble mill for forty-eight hours were used. The data and yields on a dry ash-free basis are given in Table I.

TABLE I

SUMMARY OF HYDROGENATION DATA FOR TIME–TEMPERATURE STUDIES

Run	Temp., °C.	Time, hr.	Distillate, g.	Water, ml.	Residue, g.	Benzene soluble distillate g.	%
1	350	24	23.4	6.1	92.5	17.8	19.4
2	375	24	38.2	6.0	77.0	32.2	35.0
3	375	48	42.6	6.8	68.6	35.8	38.9
4	375	48	42.0	5.7	70.9	36.3	39.5
5	400	24	51.2	7.6	56.7	43.6	47.3
6[a]	375	24	42.7	6.4	72.2	36.3	39.5
7[a]	375	48	52.3	8.0	60.9	44.3	48.1
8[a]	375	72	60.5	5.0	52.1	55.5	60.3

[a] Coal and catalyst were ground together for forty-eight hours in a pebble mill.

Preparation of Hydrogenation Products in Quantity.—In order to obtain sufficient material for separation into fractions, seven additional hydrogenations were made using the pebble mill-ground coal–catalyst mixture at 375° for seventy-two hours. A summary of the data and results are shown in Table II. The stabilized water-free distillates from Runs 3–15, excluding No. 5, were chromatographed separately into four fractions which in turn were combined until approximately 100 g. of each was collected.

TABLE II

SUMMARY OF DATA FOR HYDROGENATIONS AT 375° FOR SEVENTY-TWO HOURS

Run	Total yield of distillate, g.	Yield of water, ml.	Weight of residue, g.	Yield of benzene soluble products, g.	%[a]
8	60.5	5.0	52.0	55.5	60.3
9	61.0	9.6	51.4	51.4	55.9
10	59.4	9.5	56.6	49.9	54.2
11	63.6	7.8	50.4	55.9	60.7
12	59.4	5.0	53.4	54.4	59.1
13	61.1	6.0	52.3	55.1	59.8
14	59.3	6.2	53.3	53.1	57.7
15	60.2	6.0	52.1	54.2	58.9
Average	60.6	6.9	52.7	53.7	58.3

[a] Percentages are based on dry, ash-free coal.

Examination of the Hydrogenation Residue.—The residues from Runs 8 and 13 containing 39.2 and 39.0% carbon, respectively, were combined (48.9 g.) and extracted in a Soxhlet with petroleum ether. There was obtained 6.1 g. of soluble material and by subsequent Soxhlet extraction with benzene 8.9 g. of additional material was recovered. The molecular weight of the benzene soluble material was determined as 925 by the boiling-point elevation of benzene. The insoluble residue remaining after these extractions (34.9 g.) contained 27.4% carbon, corresponding to 13.1% of the carbon in the original coal.

Characterization of Chromatographic Fractions.—The cumulative material from each of the bands was rechromatographed separately to remove traces of material from other bands and the following data were obtained upon each: refractive index, molecular weight, ultraviolet absorption spectra, and per cent. carbon, hydrogen, nitrogen, sulfur and oxygen (by difference). They are shown in Table III and Fig. 3.

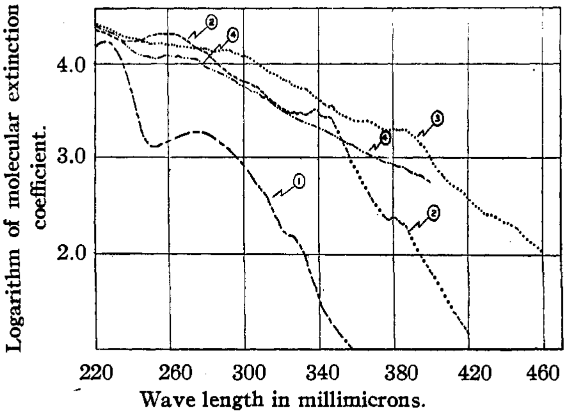

Fig. 3.—Ultraviolet absorption spectra of the four chromatographic bands: (1) band I, (2) band II, (3) band III, (4) band IV.

The ultraviolet light absorption spectra were determined in methanol using a Beckmann Model DU Spectrophotometer.

Discussion

The use of the cold-head receiver on the autoclave has simplified greatly the recovery of products from the hydrogenation of coal as compared with methods used by previous workers.[7] In a one-step hydrogenation procedure conversion of more than 60% of the carbon on a dry ash-free

TABLE III

SUMMARY OF ANALYTICAL DATA ON PRODUCTS AND FRACTIONS

		Edenborn coal[a]	Petroleum ether soluble products	Chromatographic fractions			
				Band I	Band II	Band III	Band IV
Weight, grams		92.0	40.8[b]	9.3	9.1	8.2	14.2
Refractive index, 20°/D		...	...	1.5317	1.6319	1.6419	1.6401
Ultimate analysis	C, %	82.83	86.88	89.07	91.36	88.32	83.81
	H, %	5.80	8.44	10.78	7.72	7.85	7.09
	N, %	1.58	1.44	..	0.40	2.57	2.47
	S, %	1.01	0.23	..	..	0.13	0.18
	O, %[c]	8.80	3.00	..	.50	1.10	6.50
Carbon hydrogen ratio		1.19	0.86	0.69	.99	0.94	0.96
Molecular weight		...	...	228[d]	284[e]	304[e]	280[e]
Average molecular formula		...	...	$C_{17}H_{25}$	$C_{22}H_{22}$[f]	$C_{22}H_{22}N_{0.5}O_{0.2}$	$C_{19}H_{21}ON_{0.5}$

[a] Calculated on a dry, ash-free basis from analyses by this Laboratory. [b] The loss of approximately 25% of the product represents the combined loss due to chromatographic adsorption and stripping of low boiling materials. [c] Per cent. oxygen calculated by difference. [d] Micro Rast method in camphor. [e] Ebullioscopic method in benzene (Menzies–Wright). [f] Calculated on the basis of 100% carbon and hydrogen.

basis into petroleum ether soluble products is now possible. Also by virtue of the reduction of the number of steps in the hydrogenation procedure from ten to one, the handling losses are greatly decreased. This improvement in the hydrogenation procedure increases the significance of conclusions concerning the original coal structure and the hydrogenation reaction mechanism, since the primary products are free to distill out of the reaction zone rapidly and secondary reactions are minimized.

The distribution of the carbon of the original coal, dry, ash-free basis, in the hydrogenation products, Fig. 4, is as follows: (1) 61.3% in the petroleum ether soluble distillate; (2) 14.0% in the residue as material soluble in petroleum ether and/or benzene; (3) 13.1% in the residue as material insoluble in petroleum ether and/or benzene; and (4) 11.6% in gaseous products and loss. LeClaire[11] reported the following distribution for the hydrogenation of Pittsburgh Seam coal at 350° using the technique of Biggs and Weiler[12]: (1) 68.6% as petroleum ether soluble material; (2) 7.6% as benzene soluble material; (3) 6.5% as insoluble material in the residue and (4) 17.3% as gaseous products and handling loss. The total soluble products by the two procedures is essentially the same, 75.3 and 76.2%. The percentage of insoluble material found in the residue in this work is greater, 13.1 as compared to 6.5%; on the other hand, the sum of gaseous products plus loss is less, 11.6 as compared to 17.3%.

An examination of Table III indicates the effectiveness and usefulness of chromatographic adsorption in the initial resolution of the complex mixtures resulting from the hydrogenation of coal. Separation into four distinct bands takes place according to the degree of aromaticity and functional group content in such a way that the oxygen-, nitrogen- and sulfur-containing compounds are concentrated in Bands III and IV leaving only carbon- and hydrogen-containing compounds in the first two bands.

Bands I and II are essentially mixtures of hydrocarbons, with a marked difference in aromaticity as shown by increasing carbon/hydrogen ratio, refractive index, and fluorescence. Bands III and IV are composed of the most highly condensed aromatic compounds as evidenced by the refractive indices and ultraviolet absorption spectra and the oxygen-, nitrogen- and sulfur-compounds as shown by ultimate analyses.

Band I is a mixture of paraffins, naphthenes and aromatics of varying molecular weights. The absence of compounds containing more than two condensed six-membered rings is indicated by the lack of fluorescence. However, the fluorescence of such compounds may be quenched by traces of others being present. The difference between Band I and Band II is revealed further by the ultraviolet absorption spectra in Fig. 3. The lack of fine structure is due to the similarity of the compounds present whose absorption maxima are slightly out of phase, and the lower intensity of absorption is due to the presence of compounds low in molecular weight and aromaticity. Although the spectrum of Band I lacks fine structure and intensity of absorption, the envelope corresponds in general to that of a mixture of benzene and naphthalene derivatives with a predominance of the former. The spectrum does not exclude such compounds as di-naphthyls, fluorenes, acenaphthenes and phenanthrenes, but as yet no hydrocarbon with a five-membered ring has been identified in primary degradation products of coal. They have been isolated from carbonization products. On the other hand, the presence of paraffins in Band I has been shown by the isolation and analysis of a $C_{30}H_{62}$ hydrocarbon.

Band II consists mainly of aromatic hydrocarbons with three or more condensed six-membered rings as indicated by the pronounced fluorescence and by the zone of absorption of ultraviolet light which is shifted to longer wave lengths.

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(11) Claire D. LeClaire, THIS JOURNAL, 63, 343 (1941).

(12) B. S. Biggs and J. F. Weiler, *ibid.*, 59, 369 (1937).

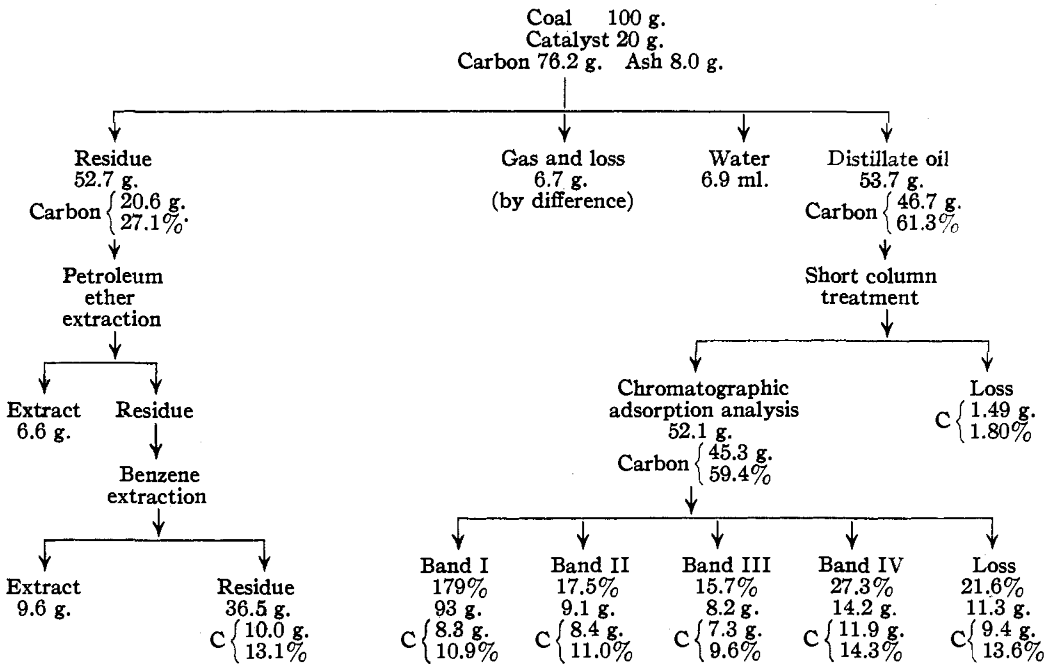

Fig. 4.—Distribution of hydrogen products.

Band II contains, in addition to highly condensed aromatic hydrocarbons, compounds containing about one-third the nitrogen (of the original hydrogenation products) and about one-tenth the oxygen or one-sixth nitrogen and one-hundredth the oxygen originally present in the coal.

Band IV on the other hand contains two-thirds the nitrogen and nine-tenths the oxygen originally present in the moisture-free hydrogenation distillate, or one-fourth the nitrogen and one-ninth the oxygen originally present in the coal.

The inability of the alumina to retain the nitrogen-containing compounds in one fraction is explainable by assuming that some of the nitrogen is in molecules which also contain hydroxyl groups that have a greater affinity for the basic adsorbent. Thus a compound containing both basic nitrogen and acidic oxygen would be more strongly adsorbed than if it contained only the basic nitrogen. Since Band IV contains such a large proportion of the oxygen, the latter must be principally in the form of phenolic hydroxyl groups. These phenols apparently are low in molecular weight and account for the low average molecular formula of Band IV.

Thus chromatographic adsorption permits the separation of the bulk of the hydrocarbons from the nitrogen-, sulfur- and oxygen-containing compounds and concentrates the latter almost completely in one fraction and separates the hydrocarbons into two fractions according to their aromatic content.

The similarity of the molecular weights of the four fractions excluding the low molecular weight material in Band I points to the production of a range of carbon skeletons by primary depolymerization and thermal cleavage of the coal polymer. This is accompanied by the partial hydrogenolysis of the hetero atoms to water, hydrogen sulfide, and ammonia. The production of these cleavage products in various degrees of saturation could take place by catalytic hydrogenation concurrently with intermolecular disproportionation of hydrogen.[13] As a result of this phenomenon a given compound could appear in several bands in varying degrees of hydrogenation.

Thus no conclusions as to the degree of hydrogenation in the original coal polymer can be drawn from the degree of saturation after catalytic hydrogenation. However, the identity of the carbon skeletons should be of great structural significance especially if they retain the hetero atoms by their original linkages.

Acknowledgment.—The author wishes to acknowledge the assistance of Miss F. A. Lawrence in carrying out the spectra determinations and the ultimate analyses. He also wishes to express his appreciation to Dr. H. C. Howard and Dr. R. C. Jones for suggestions and advice in carrying the research.

Summary

1. A study has been made of the chemical nature of the primary hydrogenation products of coal prepared by the high pressure catalytic hydrogenation of a Pittsburgh Seam coal in an autoclave modified to permit the simultaneous hydrogenation and distillation of the volatile products into a cooled receiver.

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[13] M. Orchin, THIS JOURNAL, 66, 535 (1944).

2. By chromatographic adsorption these products have been initially resolved into four characteristic fractions according to their aromatic content and the presence or absence of oxygen, nitrogen and sulfur.

3. By a study of the ultraviolet spectra and ultimate analyses, information has been obtained concerning the structure of the components of these various fractions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Reduction of Certain Organic Compounds in Liquid Ammonia[1]

BY GEORGE W. WATT, CECIL M. KNOWLES[2] AND L. O. MORGAN[3]

Earlier publications[4-9] show that addition of sodium to liquid ammonia solutions containing an organic compound together with a substance containing active hydrogen (*e. g.*, ammonium salts, methanol or water) sometimes leads to reduction products that differ from those obtained upon addition of sodium to liquid ammonia solutions containing only the organic compound. Some additional examples are presented in the present paper.

Experimental

Materials.—In addition to reactants prepared and/or purified as previously described,[8,9] the following purified reactants were employed: nitrobenzene, b. p., 210°; 1-nitronaphthalene, m. p., 61°; 1-naphthylamine, m. p., 50°; 2-nitrofluorene, m. p., 156°.

Methods.—The reduction reactions employing only the organic compound and sodium were conducted by Method II as described previously.[9] Reduction by means of ammonium bromide and sodium was effected as described by Knowles and Watt,[9] and a similar procedure was employed when methanol (10 g./200 ml. of liquid ammonia) and sodium were used. In conformity with observations recorded previously,[9] the interaction of the organic compounds and sodium alone was accompanied by series of intense colorations. For example, in the case of 1-nitronaphthalene, green, blue, purple and maroon colored liquid ammonia solutions were observed before the appearance of the characteristic blue color that denoted the presence of excess sodium. *No such color changes were observed when either ammonium bromide or methanol was employed.*

The essential numerical data are given in Table I.

Nitrobenzene.—From an ether extract of the product of reduction with ammonium bromide and sodium, aniline was isolated in 85% yield as the hydrochloride, m. p. 198°, and as acetanilide, m. p. 114°. Similarly, using methanol and sodium, aniline was isolated as the hydrochloride, m. p. 198°, and in 92% yield as 2,4,6-tribromoaniline, m. p. 119°.

Anal. Calcd. for $C_6H_4NBr_3$: N, 4.25. Found: N, 4.53.

The identity of the derivatives was established by determination of the melting points of mixtures with authentic samples.

TABLE I

DATA ON REDUCTION REACTIONS IN LIQUID AMMONIA

Compound reduced Name	Compound reduced g.-mole	Gram-atoms Na/mole compound reduced Added	Gram-atoms Na/mole compound reduced Unreacted[a] excess	Gram-atoms Na/mole compound reduced Consumed[b]
Compound reduced + sodium[c,d]				
1-Naphthylamine	0.0145	6.97	4.93	2.04
1-Nitronaphthalene	.0319	8.95	1.05	7.90
2-Nitrofluorene	.0168	14.05	4.37	9.68
Compound reduced + ammonium bromide + sodium				
Nitrobenzene	.0340	7.06	1.17	5.89
1-Naphthylamine	.0250	4.47	3.38	1.09
1-Nitronaphthalene	.0094	13.23	12.14	1.09[e]
2-Nitrofluorene	.0095	7.08	7.08	0
Compound reduced + methanol + sodium				
Nitrobenzene	.0413	6.63	0.75	5.88
1-Nitronaphthalene	.0114	10.39	1.91	8.48
2-Nitrofluorene	.0052	17.48	6.50	10.98

[a] Measured in terms of molecular hydrogen liberated and collected (1) upon addition of ammonium bromide following addition of excess sodium, or (2) during the reactions that ensued upon addition of sodium to the liquid ammonia solutions containing the "Compound reduced" and excess ammonium bromide or methanol. In the latter cases, this mode of presentation of data is not intended to imply the necessity of direct interaction of sodium and the compound reduced. [b] This is equivalent to the "Reaction ratio" tabulated in earlier publications.[9] [c] See ref. 9, Table I, footnote *d*. [d] Reactions conducted by Method II as described in ref. 9 [e] Because of the slight solubility of 1-nitrophthalene in liquid ammonia, reduction was very slow. Use of 20 ml. of toluene as a diluent led to a value of 4.30 gram-atoms of sodium/mole of 1-nitronaphthalene.

1-Naphthylamine.—Following reduction with sodium, the residue that remained after repeated extraction with cold water consisted of pure 5,8-dihydro-1-naphthylamine, m. p. 37–38°. The benzylidene derivative formed by reaction with benzaldehyde and recrystallized from petroleum ether melted at 69°.

Anal. Calcd. for $C_{17}H_{15}N$: N, 6.01. Found: N, 5.92.

The benzylidene derivative was hydrolyzed with dilute hydrochloric acid, the benzaldehyde removed by steam distillation and the residual oil crystallized from petroleum ether to afford the original base, m. p., 37–38°. The melting points of both the amine and its benzylidene derivative correspond to those reported by Rowe and Levin.[10]

Reduction with ammonium bromide and sodium was slow and incomplete. The reaction product appeared to

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[1] This work was supported in part by grants from The University Research Institute, Project No. 25.

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[3] Present address: Radiation Laboratory, University of California, Berkeley, California.

[4] Wooster and Godfrey, THIS JOURNAL, **59**, 596 (1937).

[5] Fuller, Lieber, and Smith, *ibid.*, **59**, 1151 (1937).

[6] Wooster, U. S. Patent 2,182,242, December 5, 1939.

[7] Cappel and Fernelius, *J. Org. Chem.*, **5**, 40 (1940).

[8] Knowles and Watt, *ibid.*, **7**, 51 (1942); **8**, 540 (1943).

[9] Knowles and Watt, THIS JOURNAL, **65**, 410 (1943).

[10] Rowe and Levin, *J. Chem. Soc.*, **117**, 1574 (1920).