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

Nuclear Structure of the Water-soluble Polycarboxylic Acids from the Oxidation of Bituminous Coal: The Decarboxylation Reaction[1]

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Aqueous suspensions of the copper salts of the yellow, water-soluble, polycarboxylic aromatic acids produced by the controlled oxidation of aqueous alkaline suspensions of bituminous coal have been decarboxylated at a temperature of 250°. The volume of CO_2 produced indicated 96–99% removal of carboxyl groups. From the decarboxylation products, which were investigated in an exploratory qualitative manner, there were isolated and identified benzene, naphthalene, biphenyl, biphenylene oxide, phenanthrene, benzophenone, fluorenone, phenol, benzoic acid, the lactone of 2-hydroxybiphenyl-2′-carboxylic acid, pyridine, quinoline, α-, β-, γ-phenylpyridine and β-naphthoquinoline. A discussion is presented of the relationships of these compounds to some of the nuclei of the aromatic acids produced by the oxidation of bituminous coal, and to some of the fundamental units which comprise the coal structure.

The controlled oxidation of aqueous suspensions of bituminous coals has produced yellow, water-soluble, polycarboxylic aromatic acids in yields of 50–60% by weight of coal charged.[3] A knowledge of the nuclear structure of these acids is of importance for possible commercial applications of these acids as well as for extrapolation of this knowledge for a better understanding of the fundamental units which comprise the coal structure.

The nuclei of these acids were parts of the complex coal "molecule" that were resistant to further degradation under these oxidation conditions; they do not necessarily exist, *per se*, as individual entities in coal.

For the purpose of investigating the structure of the coal "molecule," the type of nucleus isolated may be of greater significance than the quantities isolated, since it can be shown that these quantities are a function of the reaction conditions; and that some of these nuclei isolated in minor quantities are intermediate oxidation products which for diverse reasons escaped complete oxidation and which can be used to reconstruct the course of oxidation.

Decarboxylation of these acids would appear to be an excellent means for the study of these nuclei. However, previous attempts at decarboxylation, employing an aqueous solution of the sodium salts of these acids, required a temperature of 450°, leading to extensive nuclear condensations and was, therefore, of limited use in establishing the nuclear structure of these acids.[4]

It has been shown that the use of copper or copper salts of acids significantly lowers the temperature necessary for decarboxylation.[5] In this work, aqueous suspensions of the copper salts of 2000 g. of the acids produced by the oxidation of bituminous coal have been decarboxylated to the extent of at least 95% at a temperature of only 250°, with a resulting minimum of secondary condensations. In all cases approximately 50% of the theoretical amount of basic copper carbonate necessary to react with all the carboxyl groups was used. This was to avoid the presence of unreacted carbonate ion which, under the decarboxylation conditions, would produce CO_2 and lead to erroneous results in computing the percentage of decarboxylation which had occurred, based on the amount of CO_2 produced. It was believed that during the course of the reaction normal metathesis would occur, regenerating the copper salts of those unreacted acids.

Since the products of this decarboxylation reaction were worked up in an exploratory qualitative manner, the quantities of materials reported represent only the minimum quantity present. The polynuclear carbocyclic and heterocyclic nature of these acids has been unequivocally demonstrated by this work and an understanding of some of the units comprising the coal "molecule" has been obtained.

Experimental[6]

Decarboxylation Procedure.—The copper salts of the acids produced by the alkaline oxidation of a bituminous coal were prepared by dissolving 100 g. (0.37 mole) of these acids in 100 ml. of water. Basic copper carbonate, $CuCO_3 \cdot Cu(OH)_2$, 38 g. (0.17 mole), was added in small quantities with stirring. To ensure the completion of the reaction, after cessation of the evolution of CO_2 the reaction mixture was stirred and heated for 30 minutes on a steam-bath.

This aqueous suspension of the copper salts of these acids was made up to a volume of 200 ml. and charged to a 1070-ml. stainless steel, externally heated, rocking autoclave. The autoclave was flushed several times with nitrogen and then pressured to 20 p.s.i.g. of nitrogen. Heating and rocking of the autoclave was started and maintained for 24 hours after reaching the reaction temperature of 250°. After cooling to room temperature the volume of gas in the autoclave was measured by venting through a "Precision" wet test meter (Precision Scientific Co., Chicago, Ill.) and a sample of this gas was analyzed. From the volume of gas produced and analysis of the gas for carbon dioxide it was possible to determine the percentage of decarboxylation which had occurred. A small amount of carbon dioxide remained in the autoclave, dissolved in the aqueous phase.

By this method 2000 g. of these acids was decarboxylated in 20 runs of 100 g. each. Typical runs produced about 1.15 cu. ft. of gas whose carbon dioxide content was about 95%, corresponding to about 99% decarboxylation.

Initial Separation of the Decarboxylation Products.—The decarboxylation products were transferred from the autoclave to a 2-l. round-bottom flask. The autoclave was thoroughly rinsed with a dilute sodium hydroxide solution and the washings added to the flask containing the decar-

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[1] Presented before the Division of Gas and Fuel Chemistry, American Chemical Society, March 31, 1954, Kansas City, Mo.

[2] Atlantic Research Corporation, Alexandria, Va.

[3] C. H. Ruof, T. R. Savich and H. C. Howard, THIS JOURNAL, **73**, 3873 (1951).

[4] B. Juettner, R. C. Smith and H. C. Howard, *ibid.*, **57**, 2322 (1935).

[5] H. Schrader and H. Walter, *Ges. Abhandl. Kenntnis Kohle*, **6**, 79 (1921); H. Gilman and M. B. Lousinian, *Rec. trav. chim.*, **52**, 156 (1933).

[6] The spectra referred to in this paper have been deposited as Document number 4288 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints or $1.25 for 35 mm. microfilm payable to: Chief, Photoduplication Service, Library of Congress.

boxylation products. This solution was made alkaline to litmus and after refluxing for a half-hour was exhaustively steam distilled.

A light yellow oil, fraction A, was recovered from the distillate by ether extraction and freed of nitrogen bases by washing with dilute hydrochloric acid. The steam-volatile neutral oil, fraction A-1, was dried over anhydrous potassium carbonate. The steam-volatile nitrogen bases, fraction A-2 were recovered by alkaline wash and ether extraction.

The steam-non-volatile material was filtered through a Büchner funnel and the black tarry residue extracted with acetone in a Soxhlet extractor. There was obtained an acetone-soluble material, fraction B, and an acetone-insoluble residue, fraction E.

The filtrate was extracted in a continuous liquid–liquid extractor with benzene followed by ether. The solvents were removed from the benzene and ether extracts and the recovered extracts were combined and added to fraction B. The alkaline raffinate of this extraction was designated as fraction F.

This procedure was followed for each of the 20 runs, and similar classes of materials were combined for isolation and identification of individual components.

Isolation and Identification of Individual Components. Fraction F.—This fraction, consisting of a solution of the sodium salts of acids, phenols and lactones, was saturated with gaseous carbon dioxide. The precipitated mixture of black viscous and light brown crystalline material was removed by filtration. After rinsing with ether to remove adsorbed phenolic materials, this precipitate was extracted with acetone in a Soxhlet extractor. There was obtained an acetone extract, fraction C-2 and a light brown crystalline residue.

The filtrate, still saturated with carbon dioxide, was thoroughly extracted with ether and methyl ethyl ketone (MEK). This extract was combined with the ether rinsings of the carbon dioxide precipitated materials and was designated as fraction C-1. The light brown crystalline residue described above was dissolved in the raffinate which was then acidified with hydrochloric acid. The resulting light brown crystalline precipitate, fraction D, was removed by filtration and the filtrate thoroughly extracted with MEK. The solvent was removed by distillation and the resulting crystalline material added to fraction D.

Fraction D.—This material was sublimed at 100° (10 mm.). The white crystalline sublimate, 85 g., m.p. 120.5–121.5°, was identified as benzoic acid by mixed melting point and infrared spectrum.

Anal. Calcd. for $C_7H_6O_2$: mol. wt., 122; equiv. wt., 122. Found: mol. wt., 122.8; equiv. wt., 122.5.

The residue, 80 g., consisted of inorganic salts, largely silica and sodium chloride.

Fraction C-1.—This brown viscous material was acidified with phosphoric acid and steam distilled. The distillate was extracted with ether and, after removal of the solvent, the extract, which had a strong phenolic odor, was distilled in a vacuum model Piros–Glover spinning band column (H. S. Martin & Co., Evanston, Ill.). There was obtained 11.7 g. of phenol, b.p. 120° (100 mm.), which solidified on standing and which was identified by infrared spectrum and through its tribromo derivative, m.p. 92–93°, undepressed by mixture with an authentic sample.

The steam-non-volatile residue was recovered by ether and acetone extraction and dried over anhydrous sodium sulfate. The solvents were removed by distillation and the extract distilled *in vacuo*. Two grams of phenol and 10 g. of a yellow crystalline material boiling at 150–200° (6 mm.) were removed. This yellow material was identified as the lactone of 2-hydroxybiphenyl-2′-carboxylic acid by methods which will be described later.

Fraction C-2.—This material was distilled *in vacuo*. The yellow crystalline material which was collected at 150–200° (6 mm.) was washed with cold dilute sodium carbonate solution. Benzoic acid (6 g.) and phenol (1.3 g.) were recovered from the carbonate extract. The yellow crystalline residue, 37 g., could be recrystallized from dilute methanol to give a white crystalline material which was identified as the lactone of 2-hydroxybiphenyl-2′-carboxylic acid, m.p. and mixed m.p. 92–93° (literature 93°).[7] A derivative, 2-methoxybiphenyl-2′-carboxylic acid, was prepared, m.p. and mixed m.p. 148–149° (literature 150–152°).[7]

The brown resinous residue which was distilled in a molecular still at 100° (0.005 mm.) gave an additional 2 g. of this lactone. The residue from this molecular distillation, 23 g., was a dark brown resinous material: mol. wt., 390.5 (ebullioscopic in acetone); C, 81.40; H, 4.18; residue, 1.21; O (by diff.), 13.21; empirical formula, $C_{7.8}H_{4.8}O$; mol. formula, $C_{26.6}H_{16.4}O_{3.4}$. This residue may be in part a mixture of polymeric forms of the lactone of 2-hydroxybiphenyl-2′-carboxylic acid with more complex lactones of the same general structure.

Fraction A-1.—This steam-volatile neutral material, 93 g., was distilled in a column of 10 theoretical plates. The first 17% of the charge was removed at atmospheric pressure, and the next 5% at 63 mm. before fractionation was discontinued at 130°.

Benzene (15 g.) was isolated and was identified as its *m*-dinitro derivative, m.p. 89–90° (literature 89–89.5°).[8] The 5 g. of distillate obtained at reduced pressure, and which solidified upon standing, was treated in alcohol with picric acid, and from the purified picrate, m.p. 149–150°, 4 g. of naphthalene, m.p. 79.5–81°, was recovered by steam distillation. The infrared and ultraviolet spectra of this material were identical with those of authentic naphthalene.

The filtrate from the naphthalene picrate was made alkaline and steam distilled. Biphenyl, 1 g., was recovered, m.p. and mixed m.p. 68–70° (literature 70°).[8] The infrared and ultraviolet spectra were identical with those of biphenyl.

The residue from the distillation of fraction A-1, 71.4 g., consisted of a mixture of ketones and aromatic hydrocarbons. This residue, A-1-R, was dissolved in pentane and chromatographed on bentonite. The bentonite non-adsorbed material, 52.9 g., gave a negative test with 2,4-dinitrophenylhydrazine (2,4-DNP). Fractional freezing gave 18.7 g. of a liquid material, A-1-R-I, and 31.7 g. of a white crystalline material, A-1-R-II. Both fractions gave negative tests with 2,4-DNP.

The bentonite-adsorbed material, 22.7 g., was steam distilled to give 8.5 g. of a light yellow, easily steam-volatile material, A-1-R-III, and 14.2 g. of a material very slowly volatile with steam, A-1-R-IV. Both fractions gave positive tests with 2,4-DNP. These four fractions were distilled in a Piros–Glover column.

Fraction A-1-R-I: The plot of the fractionation data of this material is shown in Fig. 1. The materials which were isolated and identified are indicated on this plot. Approximately 2 g. of naphthalene and 7.5 g. of biphenyl were identified as previously described.

Approximately 3 g. of biphenylene oxide was isolated, m.p. and mixed m. p. 85–86° (literature, 86°).[8] The infrared and ultraviolet spectra of this material and authentic biphenylene oxide were identical. The 1,3,5-trinitrobenzene (1,3,5-TNB) derivative was prepared, m.p. 95–96° (literature 96°).[8] The infrared spectrum of this 1,3,5-TNB derivative and that of the derivative of authentic biphenylene oxide were identical.

Approximately 3.5 g. of phenanthrene was isolated, m.p. and mixed m.p. 98.5–99.5° (literature 100°),[8] m.p. 1,3,5-TNB, 157–158° (literature 158°).[8] The infrared and ultraviolet spectra of this material and authentic phenanthrene were identical. The infrared spectrum of this 1,3,5-TNB derivative and that of this derivative of authentic phenanthrene were identical.

Approximately 1.5 g. of an as yet unidentified liquid material was recovered. *Anal.* C, 91.35; H, 6.37; O (by diff.), 2.28.

Fraction A-1-R-II: A large loss of material occurred when the still pot cracked during distillation. The plot of the fractionation data is shown in Fig. 2. Approximately 11 g. of biphenyl, 0.7 g. of biphenylene oxide and 0.5 g. of phenanthrene were identified by the methods described previously.

Fraction A-1-R-III: Four grams of the β-isomer of benzophenone was isolated. Seeding with a small crystal of benzophenone converted the liquid β-form to the crystalline, stable α-form, m.p. 47–48° (literature 48°)[8]; 2,4-DNP, m.p. and mixed m.p. 237.5–238.5° (literature 238–239°).[8] The infrared spectra of this material and its 2,4-DNP were identical with those of benzophenone and the 2,4-DNP of benzophenone.

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[7] J. D. Brooks, *Research*, 5, 196 (1952).

[8] E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941.

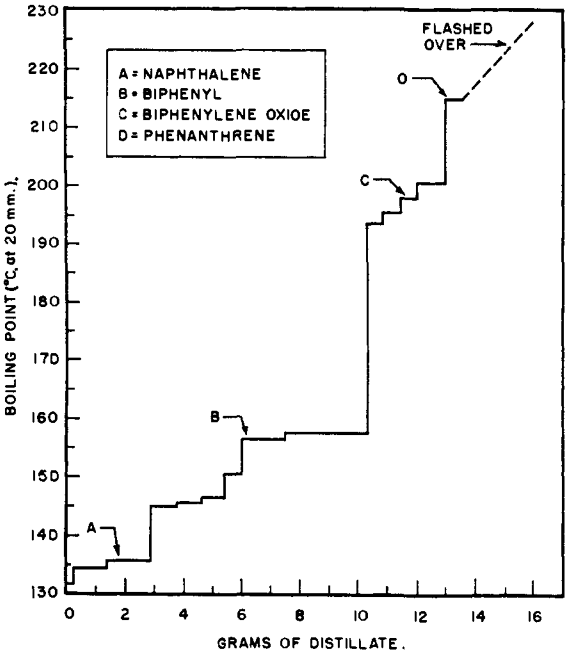

Fig. 1.—Fractionation of "A-1-R-I."

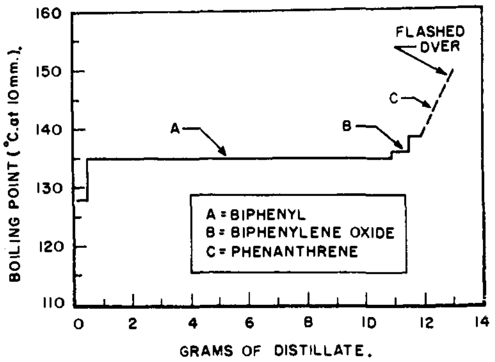

Fig. 2.—Fractionation of "A-1-R-II."

Approximately 1.5 g. of a light yellow, crystalline material was isolated and identified as fluorenone; m.p. and mixed m.p. 81–83° (literature 83°)[8]; 2,4-DNP, m.p. 300–301° (literature 299–301°)[9]; *p*-nitrophenylhydrazone, m.p. 267–268° (literature, 269°)[8]; oxime, m.p. 192–193° (literature 192–193°).[8] The infrared spectra of this material and its 2,4-DNP derivative were identical with those of fluorenone and the 2,4-DNP of fluorenone.

Fraction A-1-R-IV: Benzophenone, 6 g. and fluorenone, 4.5 g., were isolated and identified by the methods described above.

Fraction A-2: This material was distilled *in vacuo* in a Piros–Glover spinning band column. The plot of this distillation is shown in Fig. 3, with all boiling points corrected to atmospheric pressure. A fraction, 0.2 g., collected at 108–123° (760 mm.) consisted essentially of pyridine contaminated with quinoline, as shown by its ultraviolet spectrum. The picrate of this material was recrystallized several times from ethanol, m.p. and mixed m.p. with pyridine picrate 166–168° (literature 167°).[10]

Quinoline, 2 g., was isolated and identified; b.p. 239° (760 mm.), n^{25}_{D} 1.62^{20}; picrate, m.p. 201–203° (literature 203°).[10] The infrared and ultraviolet spectra of this material and that of quinoline were identical.

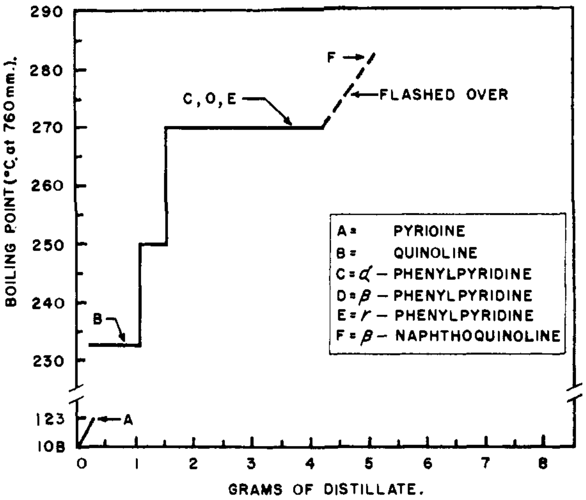

Fig. 3.—Fractionation of steam-volatile nitrogen bases.

A mixture of α-, β- and γ-phenylpyridine, 3 g., was isolated. This mixture was added to a hot alcoholic picric acid solution and the resulting mixture of picrates fractionally crystallized from acetone. Three crystalline picrates were isolated: (1) large, yellow, rhombic, m.p. 174–176°; (2) fluffy, yellow, m.p. 162°; (3) yellow, indeterminate, m.p. 195–196°. The literature values for the picrates of α-, β- and γ-phenylpyridine are 175–176, 162–164 and 195–196°.[11] None of these picrates showed mixed melting point depressions with the picrates of these phenylpyridines prepared by the method of Haworth[11] and their infrared spectra were identical with those of authentic samples. Each of the picrates of the phenylpyridines obtained from fraction A-2 was dissociated by steam distillation from aqueous alkali and the phenylpyridine was recovered. The infrared spectra of these phenylpyridines were identical with those of authentic samples.

Part of the "flashed over" material of fraction A-2 was converted to the picrate and fractionally crystallized from acetone. The only identifiable material was the picrate of β-naphthoquinoline, m.p. 252–253° (literature 251–252°).[12] A mixed melting point of this picrate and picrate of the material crystallized from acetone showed no depression and the two picrates gave identical infrared spectra. Approximately 0.3 g. of β-naphthoquinoline was estimated to be present.

A summary of the compounds and quantities isolated from the decarboxylation of 2000 g. of these acids is shown in Table I. For quantitative purposes it is pointed out that

TABLE I

COMPOUNDS ISOLATED FROM THE PRODUCTS OF DECARBOXYLATION OF 2000 G. OF ACIDS OBTAINED FROM OXIDATION OF BITUMINOUS COAL

Compound	Wt., g.	Compound	Wt., g.
Benzene	15	Benzoic acid	91
Naphthalene	6	Lactone of 2-hydroxybiphenyl-2'-carboxylic acid	49
Biphenyl	20	Pyridine	0.1
Biphenylene oxide	4	Quinoline	2
Phenanthrene	4	α-Phenylpyridine	3
Benzophenone	10	β-Phenylpyridine	
Fluorenone	6	γ-Phenylpyridine	
Phenol	15	β-Naphthoquinoline	0.3

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[9] An incorrect melting point for the 2,4-DNP of fluorenone, 283°, is given in ref. 8, page 610. N. Campbell and H. Wang, *J. Chem. Soc.*, 2186 (1949), report the melting point of this derivative as 299–301°. The derivative prepared in this Laboratory from authentic fluorenone (Eastman Kodak Co.) melted at 300–301°.

[10] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

[11] J. W. Haworth, I. M. Heilbron and D. H. Hey, *J. Chem. Soc.*, 349 (1940).

[12] S. P. Mulliken, "A Method for the Identification of Pure Organic Compounds," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1916, p. 98.

approximately 1075 g. of this charge of acids consisted of carbon dioxide in the form of carboxyl groups.

The results of the investigation of fractions B and E will be reported at a later date. Preliminary data show fraction B to consist essentially of ketones and aromatic hydrocarbons. Fraction E consists of the residual copper catalyst with some adsorbed organic material.

Discussion

The compounds isolated and identified in this work have a twofold significance: (1) they reveal the nature of some of the nuclei of these aromatic acids produced by the oxidation of coal and (2) they reveal the nature of some of the fundamental units which together comprise the coal structure.

Since benzoic acid has been shown not to be one of the benzenecarboxylic acids present in the mixture of these acids,[13] the benzoic acid obtained in this work must be the result of partial decarboxylation of other benzenecarboxylic acids.

The presence of hydroxybenzenecarboxylic acid in these aromatic acids is indicated by the isolation of phenol from the decarboxylation products. In order to investigate the possibility that a phenol could be produced during decarboxylation by the cleavage of an ether linkage, 100 g. of benzofurancarboxylic acid (coumarilic acid) was decarboxylated under conditions identical with those used for the decarboxylation of the aromatic acids from coal. There was recovered 41 g. (58%) of benzofuran, a considerable amount of benzofuran polymer, but no detectable amount of a phenol.

The isolation of phenol indicates that the original coal structure either contained phenolic hydroxyl groups *per se*, protected from oxidation by surrounding large groups, or that these hydroxyl groups result from the cleavage of an ether linkage and were protected from further oxidative degradation by surrounding groups.

Carboxylic acids of the lactone of 2-hydroxybiphenyl-2′-carboxylic acid are now shown to be part of the complex mixture of the aromatic acids from coal. There are several possibilities concerning the relationship of this lactone to those units comprising the coal structure.

It is very probable that this lactone resulted from the oxidation of a phenanthrene type unit in the coal structure. Brooks[7] and Fieser[14] have shown the preparation of this lactone by the oxidation of phenanthrene. This will be discussed in detail when the significance of the isolation of phenanthrene from the decarboxylation products is presented.

However, it is possible that in the original coal structure a linear link of the biphenyl type existed between large condensed nuclei. Alkaline oxidation failed to rupture this biphenyl link, but did oxidize the condensed nuclei with the resulting formation of the sodium salt of a polycarboxylic 2-hydroxybiphenyl-2′-carboxylic acid. Lactonization occurred during recovery of these acids by acidification since this type of acid lactonizes spontaneously in an acidic medium. This speculation assumes that a phenolic hydroxy group was present in the coal structure or resulted from ether cleavage during oxidation.

The benzene isolated in this work was derived from the complete decarboxylation of the benzene carboxylic acids present in these acids from coal.

The isolation of naphthalene confirms the presence of naphthalenecarboxylic acids in these acids derived from coal. The naphthalene nucleus could neither be synthesized under the conditions prevailing during the alkaline oxidation of coal, nor could it be synthesized during the decarboxylation of the resulting acids. Therefore, a condensed bicyclic nucleus must be one of the units which comprised the coal structure.

The presence of acids with a heterocyclic oxygen ring in these aromatic acids from coal is shown by the isolation of biphenylene oxide. Since the biphenylene oxide nucleus could not be synthesized under the relatively mild decarboxylation conditions, it is apparent that biphenylene oxide carboxylic acids were present in these aromatic acids, and since it is highly improbable that the biphenylene oxide nucleus could have been synthesized during the oxidation of the coal structure, it is evident that a part of this coal structure consisted of oxygen heterocycles. The isolation of biphenylene oxide in this work confirms the hypothesis that a part of the oxygen in coal is in the form of cyclic ethers.

The presence of phenanthrenecarboxylic acids in the mixture of the acids from coal is shown by the isolation of phenanthrene from these decarboxylation products. This indicates that the phenanthrene nucleus is part of the original coal structure. This is confirmed by the isolation of the lactone of 2-hydroxybiphenyl-2′-carboxylic acid (V), fluorenone (VI) and biphenyl (VII), all products of the normal oxidation of phenanthrene and subsequent decarboxylation of the diphenic acid formed.

The unstable intermediates, 2-(2′-hydroxyphenyl)-benzoylformic acid and 9-hydroxyfluorene-9-carboxylic acid would not be expected to survive oxidation. Phenanthraquinone has not been isolated to date; however, the decarboxylation fraction wherein this compound would be found has not been investigated as yet. It is not probable that a phenanthraquinone nucleus would survive alkaline oxidation because of the ease with which it undergoes the benzilic acid rearrangement to a fluorenone type nucleus, and the ease of oxidation to biphenyl type acids as well as to lactones of the 2-hydroxybiphenyl-2′-carboxylic acid type.

It is possible that the biphenyl which was isolated in this decarboxylation work came from sources other than biphenylcarboxylic acids produced by the oxidation of a phenanthrene nucleus. For example, it is also possible that the biphenyl nucleus existed in the original coal structure as part of large condensed units which were linearly linked by biphenyl-type bonds. Upon oxidation a biphenyl polycarboxyllic acid would result which, upon decarboxylation, would produce biphenyl.

Previously reported work[15] has shown that compounds with the properties of polymethylbiphenyls have been obtained by the hydrogenolysis of the butyl esters of the acids obtained by the oxi-

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[13] A. N. Roy and H. C. Howard, This Journal, **74**, 3239 (1952).

[14] L. H. Fieser, *ibid.*, **51**, 2471 (1929).

[15] J. Entel, *ibid.*, **76**, 3646 (1954).

dation of coal. Since the biphenyl nucleus could not be synthesized in this hydrogenolysis reaction, it is apparent that this nucleus must have originally been present in the esters of these acids.

It has been reported[4] that small quantities of biphenyl have been isolated from the decarboxylation of an aqueous solution of the sodium salts of benzenecarboxylic acids at 450°. However, decarboxylation of the copper salts of one mole of benzoic acid, under identical conditions used for the decarboxylation of the acids from coal, produced less than 0.5 g. of benzophenone and no detectable amount of biphenyl.

The formation of fluorenone and benzophenone, respectively, from 2,2′-biphenyldicarboxylic acid and the benzenecarboxylic acids as a result of ketonization during decarboxylation is unlikely. One mole of CO_2 results per mole of carboxyl group removed, if a hydrocarbon results. However, one mole of CO_2 results per 2 moles of carboxyl group removed if a ketone results. Within experimental limits, the quantity of CO_2 produced in each of the 20 decarboxylation runs described here corresponded to the theoretical amount of CO_2 which would be produced by the conversion of one mole of carboxyl group to one mole of CO_2. This indicates that very little ketonization occurred during the decarboxylation of these acids.

Too large quantities of fluorenone and benzophenone have been isolated to allow ketonization during decarboxylation to be the sole source of these ketones. The previously cited isolation of less than 0.5 g. of benzophenone from 1 mole of benzoic acid is indicative of the very small amount of ketonization which might have occurred during this method of decarboxylation.

This suggests that benzophenonecarboxylic acids were present in the mixture of the acids from coal and, since oxidation of diphenylmethane will produce benzophenone, it is possible that part of the fundamental units in the coal structure may consist of condensed cyclics linked by methylene groups.

There is a striking similarity between the nuclear structure of the nitrogen bases and the hydrocarbons isolated in this work. Pyridine, quinoline, the phenylpyridines and β-naphthoquinoline are the nitrogen base analogs of benzene, naphthalene, biphenyl and phenanthrene.

A naphthoquinoline upon oxidation gives products analogous to those produced by the oxidation of phenanthrene. Although no specific ketonic material was isolated and identified in this nitrogen base material, a fraction was isolated which contained 2.57% oxygen and which showed significant adsorption in the carbonyl region of the infrared spectrum. A few drops of this material gave a positive test for carbonyl groups with 2,4-dinitrophenylhydrazine.

It is, therefore, probable that these nitrogen bases play an identical role as described previously for the analogous hydrocarbons in establishing the relationship of the compounds isolated in this work to some of the nuclei of the aromatic acids produced by the oxidation of bituminous coal, and to some of the fundamental units which comprise the coal structure.

It now appears evident that some of the nuclei of the aromatic acids produced by the alkaline oxidation of coal are: benzene, naphthalene biphenyl, biphenylene oxide, phenanthrene, hydroxybenzene, lactone of 2-hydroxybiphenyl-2′-carboxylic acid, pyridine, quinoline, α-, β-, γ-phenylpyridine and β-naphthoquinoline. It is highly probable that fluorenone polycarboxylic acids are present, and it is likely that benzophenone polycarboxylic acids are also present.

From a knowledge of the nuclear structure of some of the acids now known to be present in the mixture of aromatic acids from coal it appears evident that some of the units, which were all part of larger units and which together comprised the coal "molecule," consisted of single rings (benzene and pyridine), carbo- and heterocycles (naphthalene, phenanthrene, quinoline and naphthoquinoline) and cyclic ethers (biphenylene oxide). It is indicated that some units in this coal structure were linked linearly by a biphenyl type bond (biphenyl and phenylpyridine) and some by methylene groups.

From this work it cannot be stated with certainty whether hydroxyl groups exist *per se* as part of the coal "molecule" or whether they result from the cleavage of ether linkages during oxidation.

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