

same conditions *p*-iodophenyl phenyl ether is metalated in reactions with *n*-butyllithium and phenyllithium.

p-Fluoro-, *p*-chloro- and *p*-bromoanisoles are metalated by methyllithium. Under the same conditions *o*- and *m*-bromo- and *o*- and *p*-iodo-

anisoles undergo some halogen-metal interconversion followed by coupling, which results in appreciable yields of methyl tolyl ethers.

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[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Products of the Hydrogenation of Lignin¹

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The first paper of this series described experimental work in which lignin, extracted from freshly cut aspen, was converted by hydrogenation over copper chromite to a mixture of saturated, colorless compounds.^{2,3} At least 75% of the lignin was converted to water, methanol and derivatives of propylcyclohexane. The predominance of hydroxy derivatives of propylcyclohexane among the products of the hydrogenation supported the hypothesis that lignin is a polymer in which the primary unit contains nine carbon atoms. However, the isolation of compounds of such low molecular weight does not show how they were joined together in the lignin molecule. It therefore seemed of importance to study the products of the hydrogenation of types of lignin which gave larger proportions of compounds containing more than nine carbon atoms to the molecule.

A survey in this Laboratory of the behavior of different types of lignin has shown that lignins obtained from either hard or soft woods, by either the soda or sulfite process, give a much lower yield of nine carbon atom compounds than did the lignin extracted with methanol from freshly cut aspen. Attention has therefore been concentrated upon a sample of lignin produced by the Meade Company of Chillicothe, Ohio, from a mixture of hard woods, using the soda process.⁴

(1) This investigation was supported in part by funds given by the Wisconsin Alumni Research Foundation.

(2) Harris, D'Ianni and Adkins, *THIS JOURNAL*, **60**, 1467 (1938).

(3) Credit should have been given in the first paper to Dr. Harold Hibbert of McGill University, who supplied the sample of lignin on which the first successful hydrogenation of lignin over copper chromite was accomplished. The mixture of products resulting from the hydrogenation was returned to him. The method and process used by me on the sample of lignin submitted by Dr. Hibbert was the same as that used almost a year later on a sample prepared by Dr. Harris. A patent has been obtained by Messrs. Earl C. Sherrard and Elwin E. Harris (application May 10, 1938, issued February 7, 1939, number 2,146,655) which attempts to cover the process of hydrogenating lignin over copper chromite.—H. A.

(4) We are indebted to Mr. Gaston DuBois of the Monsanto Chemical Company for our supply of Meade lignin.

The Meade lignin is a cocoa-like reddish-brown powder which according to an analysis by Dr. Carl Tiedcke of New York City contains 23.3% methoxyl, 65.65% carbon, 6.37% hydrogen, and so corresponds to the formula $(C_{48}H_{37}O_9(OCH_3)_7)_n$. These values were calculated after making allowance for the fact that the sample contained 3.1% ash.

About 80% of the lignin is soluble in cold dry dioxane to give a solution which, when saturated, contains about 15% lignin. Solution takes place rather slowly but may be accomplished by stirring the lignin (25 g.) with dioxane (150 ml.) for eight hours at room temperature. The portion of the lignin insoluble in cold dry dioxane may be readily suspended in the solution, but it is thrown out when centrifuged at 2500 r. p. m. in a no. 2 International Centrifuge.

Hydrogenation of Meade Soda Lignin.—There is a good deal of variation in the rate and extent of hydrogenation of a sample of lignin, depending upon the concentration of lignin in the solution and the temperature of hydrogenation. A few typical experiments carried out in reaction vessels of various sizes will be described below. The pressure of hydrogen during reaction was from two hundred to three hundred and fifty atmospheres.

(a) A solution (125 ml.) of lignin (15 g.) in dioxane with 6 g. of copper chromite in a steel reaction vessel of 270 ml. capacity required twelve hours at 260° or four and one-half hours at 290° for complete hydrogenation. In each case the solution of the product was colorless and one mole of hydrogen was absorbed by 27 to 28 g. of lignin.

(b) A solution (900 ml.) of lignin (85 g.) in dioxane with 30 g. of copper chromite in a steel reaction vessel of 1880 ml. capacity required twelve hours at 290° for complete hydrogenation.

(c) A more concentrated solution containing 125 g. of lignin made up to 900 ml. with dioxane could not be hydrogenated to a mixture of colorless products without a retreatment with fresh catalyst. In practice it was found best to allow the first hydrogenation to proceed at 290° for only five hours, during which period about 70% of the required amount of hydrogen was absorbed. The copper chromite was then removed by centrifuging and the solution concentrated to 600 ml., thus distilling out the methanol and water produced by hydrogenation of lignin. This solution was hydrogenated with 20 g. of copper chromite in a steel vessel having a capacity of 1300 ml., at 290° for four to six hours until hydrogen was no longer absorbed and the solution was colorless.

(d) The simplest method for hydrogenating the soda lignin to colorless products proved to be as follows. Dry lignin (90 g.), copper chromite (30 g.) and dioxane (850 ml.) were placed in a steel reaction vessel of 1880 ml. capacity and the hydrogenation carried out at 290° for about twelve hours. The lignin presumably went into solution during the period (three hours) while the vessel was being rocked and heated to 290°.

Separation of Products by Fractional Distillation.—The reaction mixtures were centrifuged and the solutions combined until an amount containing the products from 500 to 600 g. of lignin had been accumulated. The solution was then concentrated under a Widmer column at atmospheric pressure, methanol, water and dioxane being distilled out. The concentrated solution was then placed under a modified Widmer column. The column carried a spiral 15 cm. in length with one turn of the helix per cm. A wide fraction was taken off at 55–150° (7 mm.). Two fractions were then taken off through a short still head at 125–150° (0.2 mm.) and 150–200° (0.2 mm.), respectively. The products were then refractionated once or twice. In the refractionations the modified Widmer column referred to above was used for the fractions boiling up to about 125° (0.2 mm.), while one with a spiral having eight turns of the helix on a spiral 15 cm. in length was used for the products boiling 125° (0.2 mm.) to 200° (0.3 mm.), while the short still head was used for higher boiling products.

In a typical fractionation there was obtained from 594 g. of lignin, 24 g. 55–85° (7 mm.), 24 g. 85–112° (7 mm.), 39 g. 76–145° (0.3 mm.), 45 g. 145–190° (0.3 mm.), 40 g. 190–235° (0.2 mm.),

and 147 g. residue boiling above 235° (0.2 mm.).

A total of approximately 10 kg. of lignin was hydrogenated and the products fractionated as above. In order to be sure that the products were completely saturated, the larger share of these various fractions was then submitted to rehydrogenation over copper chromite at 290° in dioxane solution. The products were distilled through the modified Widmer columns and fractions cut having boiling ranges of from 2 to 10°. This and subsequent papers will deal with the properties of the various mixtures so obtained.

The products from the lignin under consideration boil rather evenly over the range from 55° (7 mm.) to temperatures of the order of 400° (0.3 mm.). The proportion of these products may be summarized as follows. Fifty-eight g. of products boiling above dioxane are obtained by the hydrogenation of 100 g. of lignin. About 10 g. of this mixture boils in the range 55° (7 mm.) to 130° (1 mm.), while about 11 g. boils 130–200° (1 mm.). The remaining 37 g. boils above 200° (1 mm.).

The great difference in the yield of low boiling products from "methanol lignin," reported in the earlier paper, as compared with "soda lignin," is indicated by the fact that a 100-g. sample of the former would give about 45 g. of a fraction, 55° (7 mm.) to 130° (1 mm.), as compared with about 10 g. from soda lignin. There is a qualitative as well as a quantitative difference in the products from the two types of lignin. More than 25% of the weight of the "methanol lignin" appeared as 3-(4-hydroxycyclohexyl)-propanol-1, b. p. 125–127° (1 mm.). There was very little of this glycol produced by the hydrogenation of soda lignin.⁵

More than 10% of the weight of the methanol lignin appeared as 4-*n*-propylcyclohexanol-1. This alcohol has also been isolated from the hydrogenation products of soda lignin, but it was produced to the extent of only a few tenths of a per cent. Cyclohexanol, 4-methylcyclohexanol and 4-ethylcyclohexanol were also isolated and characterized by their boiling points and the melting points of their solid phenylurethans. A ten carbon alcohol was isolated as its phenylurethan, but its structure has not yet been ascertained. There

(5) A product of similar boiling and melting points was obtained in a yield of a few tenths of 1%, but all attempts to characterize this product by means of solid derivatives failed. Harris, Saeman and Sherrard (*Ind. Eng. Chem.*, **32**, 440 (1940)) claim that they obtained 3-(4-hydroxycyclohexyl)-propanol-1 by the hydrogenation of soda and other types of lignin. However, they did not report solid derivatives and gave no other substantial evidence that they had isolated or characterized the glycol among the products of their hydrogenations of soda lignin.

TABLE I
 ANALYTICAL VALUES FOR HIGH MOLECULAR WEIGHT PRODUCTS

Designation	B. p., °C. (mm.)	Hydroxyl, %	Methoxyl, %	Carbon, %	Hydrogen, %	Mol. wt.	G. fraction	Av. mol. formula parent hydrocarbon		Carbons per cycle
								C	H	
R ^a	Above 200° (1)	7.5	1.7	79.9	11.4	538	..	35	59	5.5
R'	1.0	0.4	86.6	11.6	...	47
R' ₁	70-110 (0.2)	0.4	.1	87.7	12.3	352	6	26	43	4.9
R' ₂	110-190 (0.2)	.5	.1	88.2	11.9	417	9	30	49	4.5
R' ₃	190-260 (0.2)	.8	.3	87.4	11.4	527	9	38	39	4.0
R' ₄	260-285 (0.2)	.8	.3	88.2	11.6	535	9	39	61	4.2
R''	3.0	.4	86.1	12.4	727				
R'' ₁	120-150 (0.1)	2.6	.7	85.0	12.5	357	4.8	25	44	6.1
R'' ₂	155-240 (0.1)	2.5	.8	85.8	12.3	533	6.6	38	65	5.7
R'' ₃	Above 240 (0.1)	3.1	.9	85.5	12.1	979	23.7	70	117	5.6
F	180-190 (1.0)	10.5
F ₁	106-112 (0.5)	0.4	.4	86.6	13.0	303	3.5	22	39	6.6
F ₂	130-150 (0.5)	.4	.4	85.4	12.6	355	2.0	25	44	6.2
F ₃	150-220 (0.5)	.6	.6	85.7	12.3	386	2.0	27	47	5.5

^a R is a mixture of products b. p. above 200° (1 mm.) from the hydrogenations of soda lignin. R' and R'' were obtained from R through the use of zinc and oxalic acid, respectively. Various fractions obtained from R' and R'' are indicated by subscripts. A 14-g. residue from the distillation of R' was not analyzed since it had been somewhat decomposed in the process of distilling R'₄. F is a fraction, boiling below R, from which F₁, F₂ and F₃ were obtained after applying the oxalic treatment to F. The boiling ranges and pressures given were observed in fractionating columns so that not much significance can be attached to the precise values.

is reason to believe that other alcohols are present in the mixture from which the five alcohols noted just above have been separated. However, the yield of all of them taken together represents less than 1% of the weight of lignin submitted to hydrogenation.

No pure compound has as yet been isolated from the mixture of products of soda lignin boiling above the nine carbon atom glycols (130° (1 mm.)),⁶ which contained about half of the weight of the lignin submitted to hydrogenation and over 80% of the products if water and methanol are disregarded. However certain facts have been ascertained with regard to the nature of the components of the mixture which are significant in connection with their structure.

Attempts are being made to isolate and characterize some of the compounds which make up the products boiling above the nine carbon atom glycols and below 200° (1 mm.). But for the present it can only be said that the fractions boiling within this range show by analysis approximately 10% hydroxyl, 2% methoxyl, and are made up of mixtures of alcohols and glycols along with small proportions of hydrocarbons.

The material boiling above 200° (1 mm.) is a

(6) Octadecyl alcohol was isolated and characterized by Lawrence Richards from the fractions boiling in the vicinity of 140° (1 mm.). The presence of this straight chain alcohol among the products is presumably not significant in connection with the chemistry of lignin, since it was probably produced by the hydrogenation of a stearate originating in the fat of the wood.

clear rosin-like solid. It showed an average molecular weight of about 538 by the Rast camphor method. The analytical data on this mixture are given in Table I. The "average molecule" in this mixture contains 35.4 carbon atoms, 57.4 hydrogens, 2.36 hydroxyls and 0.29 methoxyl. The "average parent hydrocarbon" would be approximately C₃₅H₅₉. Since the open chain saturated hydrocarbon of thirty-five carbon atoms would contain seventy-two hydrogens in the molecule, more than six rings per molecule are indicated.

In order to obtain more precise information as to the size and degree of cyclization of the molecules in the residue (R) boiling above 200° (1 mm.) attempts were made to remove as completely as possible the hydroxyl and methoxyl groups. Two methods to this end were utilized. In the first, the mixture of compounds was reduced with amalgamated zinc and hydrochloric acid, as in the Clemmensen method. In the second method, the mixture was partially dehydrated by heating with oxalic acid. The products of both methods were then hydrogenated over Raney nickel at 275° to give mixtures of products that will be referred to as R' and R'', respectively. The analytical figures on these products as well as for various fractions obtained from each by distillation are given in Table I.

A fraction boiling 180-190° (1 mm.) was also partially dehydrated with oxalic acid, and the

residual alcohols in large part removed as the acid phthalate. The resulting mixture of compounds contained only about 0.4% hydroxyl instead of the 10.5% present in the original fraction b. p. 180–190° (1 mm.). After saturation with hydrogen over Raney nickel the mixture was roughly fractionated. The average molecular weights and the analytical figures for the various fractions are also given in Table I.

In none of the products listed in Table I were oxygen-free mixtures obtained. The zinc reduction method gives a product that has a considerably lower oxygen content than that obtained by the oxalic acid method, but for the reasons given below the former method is not considered so satisfactory as the latter. However, it is possible to calculate the approximate molecular formulas of the parent hydrocarbons in the various fractions. Such approximate molecular formulas are given in the ninth and tenth columns of Table I. They are useful because they show the number of carbon atoms in a molecule of the observed molecular weight, and also the carbon to hydrogen ratio in the parent compounds in which all methoxyl and hydroxyl groups have been replaced by hydrogen.

The parent hydrocarbons derived from the 180–190° (1 mm.) fraction contain from 22 to 27 carbons per molecule. This conclusion is in accord not only with the observed molecular weights but is also in harmony with the boiling range of the mixture of alcohols and glycols in the 180–190° (1 mm.) fraction and also with the boiling ranges of the hydrocarbons themselves. These facts are significant for they suggest that the oxalic method of dehydration of the alcohols and glycols does not bring about the formation of compounds of higher molecular weight than the original alcohols and glycols. The fact that a hydrocarbon boiling as low as 106–112° (0.5 mm.) is obtained from a hydroxylated compound boiling 180–190° (1 mm.) shows that the hydroxylated compound was a di- or trihydric alcohol. Other work has indicated that alcohols of higher molecular weights than the glycol were also present, but that there was little if any non-oxygenated compound present.

The fractions from the dehydration of the residue b. p. above 200° (1 mm.) show a carbon content of more than 25 carbon atoms per molecule. In fact a consideration of the weight of the various fractions as given in Table I taken in connec-

tion with their average molecular weights, shows that a majority of the molecules contain more than 38 carbon atoms per molecule. The average molecular weight of the residue from the oxalic treatment corresponds to about seventy carbon atoms. This residue weighs more than twice as much as the combined weights of the two fractions distilled, which show average molecular weights corresponding to 25 to 38 carbon atoms per molecule, respectively.

It should be kept in mind that the portion of the hydrogenation products from soda lignin now shown to contain more than 22 carbon atoms per molecule constitutes about two-thirds of the weight of the products, disregarding water and methanol. In fact it seems safe to say that more than half of the products boiling above 100° contain more than about 35 carbon atoms per molecule, with a very considerable portion consisting of compounds having at least twice this molecular size.

It is interesting to note that F. E. Brauns of the Paper Institute has presented convincing evidence that the minimum size of "native lignin" corresponds to a 41 or 42 carbon atom unit.⁷ Since hydrogenolysis or cleavage occurs in the reaction of hydrogen with lignin, the products of this reaction will have a lesser number of carbon atoms per molecule than did the original lignin. The fact that a large portion of the molecules in the products of the hydrogenation of soda lignin contain from 35 to 70 or more carbon atoms, is thus in complete accord with the concept of a unit of 42 carbon atoms or its dimer.

There has been little evidence as to whether or not the "lignin building unit" of 42 carbon atoms is held together in part by ether linkages. According to the formulation of Freudenberg in 1930 lignin is made up of phenylpropane units in ether union with each other, but in view of the work of Hibbert this concept has been revised to include benzofuran and benzopyran structures. The analyses of the mixtures of compounds reported herewith show conclusively that quite large carbon units are present among the hydrogenation products of soda lignin. For example, the sum of the analyses for carbon, hydrogen and hydroxyl and methoxyl oxygen, of the residue b. p. above 200° (1 mm.), leaves less than 0.9% that might be accounted for as ether oxygen. The dis-

(7) F. E. Brauns, *THIS JOURNAL*, **61**, 2120 (1939). Reference should be made to the current papers of Hibbert for the present status of the problem of the structure of lignin.

crepancy between 100% and the sum of the analyses for carbon, hydrogen and hydroxyl and methoxyl oxygen is even less in the case of the various fractions R' , R'_1 , R'_2 , R'_3 , R'_4 , R'' , R''_1 , R''_2 and R''_3 where the ether oxygen (other than methoxyl) is negligible.

The conclusion must be drawn that in soda lignin there are units, containing at least 40 carbon atoms, in which carbon atoms are joined in chains and cycles without the aid of oxygen atoms. There is of course no question but that in the original lignin there are ether linkages other than methoxyl, but they must be so situated in cycles that the hydrogenolysis of the ether linkage does not result in fragmentation of the molecule.

The degree of cyclization in the products is perhaps best brought out by a consideration of the number of "carbon atoms per cycle" as given in the last column of Table I for the various products. These figures are arrived at in the following way. The molecular formula of the average molecule in R''_1 is $C_{25}H_{44}$. The corresponding saturated open chain compound would be $C_{25}H_{52}$. There are thus 4 cycles in the $C_{25}H_{44}$ compound and the number of carbon atoms per cycle is $25/4$ or 6.2. The figures given in the table for "carbon atoms per cycle" were calculated from the original data so that they do not correspond precisely with the "rounded off" figures for the molecular formulas given in columns 9 and 10.

In the derivatives of propylcyclohexane there are 9 carbon atoms per cycle, while in the hydrocarbons (F_1 and F_2) boiling 106–150° (0.5 mm.) there are only 6.2 to 6.6 carbon atoms per cycle. The lowest molecular weight fraction (R''_1) from the residue boiling above 200° (1 mm.) is cyclic to a similar degree for it has 6.1 carbon atoms per cycle.

The residue, R , b. p. above 200° (1 mm.), and the two higher molecular weight fractions, R''_2 and R''_3 , obtained from it by the oxalic method, show between 5.5 and 5.7 carbon atoms per cycle. This means that in R''_3 , for example, there are at least 12 cycles in the average molecule. The products of the zinc method of deoxygenation are even more cyclic than those from the oxalic method, the carbon atoms per cycle being 4.0 to 4.5 for R'_2 , R'_3 and R'_4 . However, since these values are lower than for the original material, R , it seems probable that cyclization occurred during the application of the zinc method so that not so much significance is attached to the values.

There can be little question that lignin is made up in considerable part of six carbon atom cycles. However the degree of cyclization in the products of soda lignin are too high to be accounted for by assuming that such cycles are united in long chains. There is ample evidence that there are some carbon atoms not in cycles and thus the number of carbon atoms actually forming the cycles is considerably less than 5.5. The conclusion must be drawn that the higher boiling products of the hydrogenation of soda lignin contain fused or condensed rings. It seems useless to discuss whether these fused ring systems are of the indene, naphthalene, phenanthrene or other type until such a time as dehydrogenation and oxidation studies have yielded more definitive results.⁸

Experimental Part

Reduction with Zinc.—One hundred and fifty grams of amalgamated zinc was placed in a 1-liter three necked flask to which were attached by ground glass joints a reflux condenser, a stirrer, and a tube for passing in gas. Sixty-two grams of the fraction b. p. above 200° (1 mm.) dissolved in 40 ml. of dioxane, 400 ml. of glacial acetic acid, and 200 ml. of concentrated hydrochloric acid were added. After one day of refluxing, with stirring, gaseous hydrogen chloride was passed in until the fifth day, after which time most of the zinc had reacted. An additional 150 g. of amalgamated zinc was then added and the reaction continued until on the ninth day nearly all the zinc had disappeared. The reaction mixture was diluted with water and extracted with methylcyclohexane. The extract was washed thoroughly with water, concentrated to a volume of 130 ml., and hydrogenated at 200° over 5 g. of Raney nickel for seven hours. The pressure of hydrogen in this and other hydrogenations described below was approximately 300 atm. The resulting solution was centrifuged and rehydrogenated at 275° with 12 g. of Raney nickel for six hours.

Dehydration with Oxalic Acid.—One hundred and eleven grams of the fraction b. p. above 200° (1 mm.) dissolved in 70 ml. of dioxane was placed in a 500-ml. round-bottomed flask equipped with a side arm and two necks with ground glass joints. Nitrogen was passed in through the side arm and the necks were equipped with a stirrer and a reflux condenser. The temperature was raised to 150° and 50 g. of oxalic acid was added in small portions. The temperature was then raised slowly to 220° while formic acid, water, and dioxane distilled out of the mixture. The operation was repeated with five additional portions of oxalic acid (300 g. in all) and the mixture then heated to 300° until all foaming ceased. Dioxane in small amounts was used to wash the last traces of sublimed oxalic acid back into the liquid so that complete decomposition might take place.

(8) Willstätter and Kalb (*Ber.*, **55**, 2637 (1922)) obtained from lignin products having a carbon to hydrogen ratio similar to those reported above. They reduced lignin with hydriodic acid and red phosphorus at 250°. However not much significance has been attached to their work in recent years.

The product dissolved in 100 ml. of methylcyclohexane was hydrogenated at 200° for two hours over 12 g. of Raney nickel. The hydrogenation was repeated with 5 g. of Raney nickel at 275° for five hours. The dehydration with oxalic acid was then repeated using 150 g. of oxalic acid in three portions. The product was twice hydrogenated as described above. After removal of the catalyst and solvent from the last hydrogenation the product weighed 23.7 g. In order to ensure complete saturation of the product the treatment with hydrogen and Raney nickel at 275° was again repeated. The product was analyzed and fractionated to give R'_1 , R'_2 , and R'_3 .

Thirty grams of the fraction, F_1 , b. p. 180–190° (1 mm.), was dehydrated with 150 g. of oxalic acid in three portions, by essentially the same procedure described above. The product after hydrogenation was heated with 21.8 g. of phthalic anhydride at 120–130° for twenty-four hours. The reaction mixture was leached with petroleum ether (b. p. 60–68°) and about 100 ml. of ethanol added to the petroleum ether. The mixture was neutralized with sodium hydroxide in 100 ml. of water. The petroleum ether phase was washed with water, and the solvent evaporated. The residue was hydrogenated in methylcyclohexane over Raney nickel at 250°. After removing the catalyst and solvent the weight of the product was 10 to 12 g. It was again treated with phthalic anhydride, extracted and hydrogenated as before. The product was then fractionated to give F_1 , F_2 and F_3 referred to in Table I.

Determination of Hydroxyl Values.—The method was that of Marks and Morrell⁹ with some modifications in procedure in view of the paper of Smith and Bryant.¹⁰ Between 0.15 and 0.30 g. of the substance was weighed in a glass stoppered tube (11 × 1.5 cm.). Two ml. of a mixture of one part of acetic anhydride and seven parts of pyridine was added from a pipet. The stoppered tube was placed in an electrically heated oil-bath maintained at 90 to 100°. The stopper was removed after thirty seconds. The upper third of the ground surface was greased and the stopper firmly replaced. The tube containing the mixture was heated four hours, or overnight, then cooled and the contents washed out with cold water which had been previously boiled. The mixture was titrated with 0.2 *N* sodium hydroxide solution, using phenolphthalein as an indicator. The amount of acetic acid used in acetylating the hydroxyl groups of the sample was calculated from the difference between the titration value as determined above and the titration value of 2 ml. of the acetic anhydride-pyridine mixture.

The procedure given above has been shown to give the hydroxyl value with an error of less than 1% for an alcohol such as 4-(*n*-propyl)-cyclohexanol-1, *i. e.*, 12.1% as compared with a calculated value of 12.0%. However, for a mixture having a very low hydroxyl value the percentage error is much larger. For example a mixture of cholesterol and phenanthrene known to have an hydroxyl value of 0.86% was found on analysis to show 1.02%.

Methoxyl values were determined by the Zeisel method using the adaptation of Johnson, Barnes and McElvain.¹¹

Molecular weight determinations were made by the Rast camphor method. Approximately 0.3 g. of Japanese camphor was weighed accurately into test-tubes 7.5 cm. in length along with 0.03 to 0.05 g. of sample. The tube was held in an oil-bath at 200° for a moment until fusion took place, the contents being stirred. The tube was cooled immediately in cold water. Several observations on the melting point of the mixture were made by suspending the test-tube in an oil-bath and observing the temperature with an Anschütz thermometer. For a typical high molecular weight alcohol, values of 298 were observed for cholesterol, which has a molecular weight of 292.

Cyclohexanol, b. p. 58–61° (8 mm.), n_D^{25} 1.4599; 4-methylcyclohexanol, b. p. 62–65° (8 mm.), n_D^{25} 1.4582; 4-ethylcyclohexanol, b. p. 80–85° (8 mm.), n_D^{25} 1.4604; and 4-*n*-propylcyclohexanol, b. p. 94–94.5° (8 mm.), n_D^{25} 1.4645, were isolated from the products of hydrogenation of soda lignin. Cyclohexanol and methylcyclohexanol gave 3,5-dinitrobenzoates, m. p.'s 111–112°, and 138–141°, respectively. The phenyl urethans of the third and fourth alcohols listed above showed m. p.'s of 115–116° and 130–130.5°, respectively. All of these derivatives were compared by mixed melting points with derivatives of cyclohexanols prepared by hydrogenation of the corresponding phenols.

Conclusions and Summary

Lignin, separated from hard wood by the soda process, undergoes hydrogenation over copper chromite in dioxane solution at 250 to 300°, to give saturated colorless products. The amount of hydrogen absorbed per gram of lignin and the general behavior on hydrogenation was very similar to that previously observed for lignin extracted with methanol from the hardwood aspen. However, the products from soda lignin differed in several respects from those obtained from methanol lignin.

There was no predominance of nine carbon atom compounds produced from soda lignin, and in fact cyclic compounds containing from 6 to at least 70 carbon atoms were found among the products. Cyclohexanol and at least four different alkylcyclohexanols were produced by hydrogenation but by far the greater part of the soda lignin was converted to alcohols and glycols related to polycyclic hydrocarbons having 20 to 70 or more carbon atoms in the molecule.

High molecular weight compounds were also obtained from methanol lignin but they were much less in amount and were more oxygenated than were the products of similar physical properties obtained from soda lignin. The high boiling products from methanol lignin carry one oxygen for each six carbon atoms while the products from soda lignin have one oxygen for an average of 13.5 carbon atoms.

(9) Marks and Morrell, *Analyst*, **56**, 428 (1931).

(10) Smith and Bryant, *THIS JOURNAL*, **57**, 61 (1935).

(11) Johnson, Barnes and McElvain, *ibid.*, **62**, 964 (1940).

All of these facts are in harmony with the concept that in methanol lignin units related to propylbenzene are joined in chains, while in soda lignin cyclization has taken place during the process of isolation. Hydrogen over copper chromite cleaves the bond between successive C_9 units in

methanol lignin, while with soda lignin the action of hydrogen is largely limited to hydrogenation of unsaturated rings and the hydrogenolysis of hydroxyl, methoxyl and cyclic ether linkages, since the rings are stable toward hydrogenolysis.

MADISON, WISCONSIN

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[CONTRIBUTION FROM THE GEOCHEMICAL SECTION OF THE ILLINOIS STATE GEOLOGICAL SURVEY]

The Oxidizing Power of Illinois Coal. I. The Reaction with Titanous Chloride¹

BY G. R. YOHE AND C. A. HARMAN²

High volatile bituminous coals such as those found in Illinois are known to deteriorate rather rapidly upon exposure to air. This deterioration is particularly evident in the loss of coking properties³ and in the diminution of calorific value.⁴ The purpose of the present work was to investigate the initial stages of this atmospheric oxidation.

It has been shown that finely divided lignite possesses oxidizing power,⁵ and the observations of Francis⁶ upon spontaneous combustion suggest that weathered coal contains an active oxidizing agent. It has been postulated that organic peroxides play an important role in the mechanism of spontaneous ignition of coals.^{7,8}

Although charcoals have been shown to possess oxidizing ability,⁹ it does not necessarily follow that similar activity exhibited by coal is of the same nature, since bituminous coals contain little, if any, free carbon.^{10,11}

Preparation of Samples.—Samples were collected by chipping coal from a freshly exposed face directly into a special stainless-steel ball mill. The cylindrical portion of this mill was 7.6 cm. i. d. and 20.3 cm. long; conical ends carrying needle valves were provided to facilitate the replacement of air by an inert gas. Flint pebbles were used. The pulverized coal was removed from the mill, passed through a 100-mesh sieve and portions placed in

ground glass capped weighing bottles in an air-tight handling box containing a carbon dioxide atmosphere. Determinations of oxidizing power were made upon unexposed samples and upon samples exposed to air or oxygen at room temperature for various lengths of time.

Determination of Oxidizing Power.—A weighed sample of approximately 1 g. of coal, 150 ml. of boiled distilled water, 5 ml. of concentrated hydrochloric acid and a few drops of 2% aqueous Aerosol-OT¹² were placed in a titration bottle swept with a stream of oxygen-free nitrogen. A measured quantity of 0.02 to 0.03 *N* titanous chloride was added, and the excess titrated with standardized ferric chloride,¹³ approximately 0.01 *N*. The end-point was detected potentiometrically. A blank determination was run, and the difference between the amounts of ferric chloride used in the two titrations gave the oxidizing power of the coal used. The results are shown graphically in Fig. 1; all but two points (second point for C-2102 and third point for C-2094) were obtained by averaging two or more duplicate determinations. The results of duplicate determinations showed an average deviation from the mean of 0.0023 milliequivalent per gram.

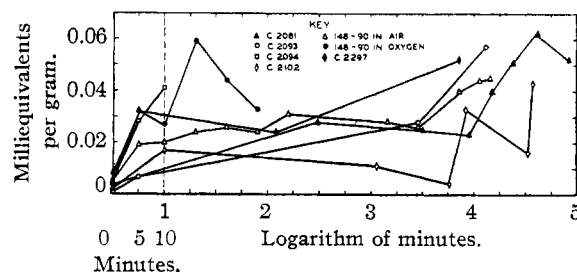


Fig. 1.—Change of oxidizing power of coals with increased time of exposure to air.

Effect of Mechanically Entrained Air.—Determinations made using powdered silica in place of coal indicated that mechanically entrained oxygen had a negligible oxidizing action upon the titanous chloride.

Effect of Soluble Ferric Compounds.^{9,14}—The determinations of the oxidizing power of coal C-2297 were

(1) Presented before the Division of Gas and Fuel Chemistry at the Detroit meeting of the American Chemical Society, Sept. 12, 1940. Published with the permission of the Chief of the Illinois Geological Survey.

(2) Associate Chemist and Research Assistant, respectively.

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(12) Kindly provided by the American Cyanamid and Chemical Corporation.

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