The writers wish to thank Dr. Douglas G. Hill for suggestions on the kinetics of these reactions.

Summary

1. The rates of decomposition of the sodium salts of a series of substituted bromobenzamides have been measured at 30°.

2. The rates of decomposition of the sodium salts of bromobenzamide and of *m*-chloro- and *p*-methylbromobenzamides have been measured at two or three temperatures and their heats of activation calculated.

3. It has been found that the relative rates of decomposition of certain meta and para substituted bromobenzamides at 30°, and presumably their relative ease of rearrangement in the presence of alkali, are inversely related to the dissociation constants of the corresponding carboxylic acids.

4. These results are considered to be in agreement with the hypothesis that the ease of rearrangement of a bromoamide in the presence of alkali is dependent upon the ease of release of bromide ion from the negative ion of the alkali salt.

5. It has been found that in the presence of excess alkali at 30°, *p*-nitrobromobenzamide gives approximately as much *p*-nitrobenzoic acid by hydrolysis as *p*-nitroaniline by rearrangement; at 96–100°, however, a 90% yield of *p*-nitroaniline is obtained.

DURHAM, N. C. RECEIVED AUGUST 12, 1936

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY]

Studies on Lignin and Related Compounds. XXVI. The Properties of Spruce Lignin Extracted with Formic Acid

BY GEORGE F. WRIGHT AND HAROLD HIBBERT

The recent publications by Freudenberg and co-workers[1] and by Staudinger and Dreher,[2] in which they describe the extraction of spruce wood meal with formic acid, anticipate a current investigation in this Laboratory. Although this study is not yet complete it seems advisable to present a preliminary account of the work.

Considerable doubt exists as to the reliability of any known extraction process for isolating *unchanged* lignin from wood, and it seems preferable to consider an extractant as the first reagent in a series of reactions intended to prove structure. As one of a series of such extractants, so regarded, it has been found that boiling formic acid removes from resin- and soluble-carbohydrate-free spruce wood meal 17% of its weight in the form of methoxyl-containing material. Because of partial demethoxylation this process yields lignins of comparatively low methoxyl content (12–14%) but it possesses the advantages of: (a) rapidity and convenience of extraction, and (b) isolation of extracts readily soluble in many organic solvents. Thanks to this ease of solubility, it has been found possible to effect a separation of the isolated lignin into five fractions by precipitation of chloroform, acetone and aqueous acetone solutions into ether and also petroleum ether (Table I). This fractionation is undoubtedly incomplete; indeed, subsequent experiments show that the fractions are still complex. Nevertheless, examination of these partially separated products shows a definite trend in chemical and physical properties undoubtedly characteristic of the individual substances that comprise the isolated mixture called lignin.

The behavior of two functional groups has been examined in this study, namely, (a) reactions of the hydroxyl and (b) reactions of the carbonyl group. The suitable solubility of formic acid lignin has permitted the use of the Grignard machine[3] for simultaneous determination of both groups. These analyses have been supplemented by appropriate methoxylations and tosylations. The results (Table I) show two interesting facts: (i) the native lignins contain small amounts of non-enolizable carbonyl groups; (ii) the more soluble, and therefore simplest, fractions, have *higher hydroxyl* and *lower methoxyl* values than their more complex, insoluble analogs. This decrease in hydroxyl value with decreasing solubility suggests that increasing aggregation of

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(1) Freudenberg, Janson, Knopf and Haag, *Ber.*, **69**, 1415 (1936).

(2) Staudinger and Dreher, *ibid.*, **69**, 1729 (1936).

(3) Kohler, Stone and Fuson, THIS JOURNAL, **49**, 3181 (1927); Kohler and Richtmyer, *ibid.*, **52**, 3736 (1930).

TABLE I

EXTRACTION OF WOOD MEAL (40 GRAMS)[a]

	Extracting medium						Grignard machine analysis	
	Formic acid (95%) for 13 hr.		Formic acid (95%) for 6 hr.		Formic acid (80%) for 6 hr.			
Solubilities of product	Wt., g.	OCH_3, %	Wt., g.	OCH_3, %	Wt., g.	OCH_3, %	Active H per kg.	RMgX added per kg.
Chloroform–acetone–pet. ether soluble	0.16	...	..	...	..	...	...	...
Chloroform–acetone–ether soluble	.35	...	..	...	0.40	12.17	4.4	0.7
Chloroform soluble	.81	13.13	..	...	.64	13.38	4.6	.7
Acetone soluble	1.37	12.81	..	...	.92	13.42	3.5	.5
Soluble only in acetone–water	4.40	13.45	..	...	.19	14.15	3.0	.6
Total lignin	7.09	...	5.85	12.05	2.15	13.50	4.0	.6
Acetone–water insoluble	0.01	2.5	1.79	3.0	0.96	2.5		
Total water insoluble extract	7.10	...	7.64	...	3.11	...	...	...

[a] It should be noted that complete extraction of the lignin is favored by increased strength of formic acid and by longer heating; on the other hand, the amount of acetone–water insoluble extract decreases during the course of the extraction. An absolutely anhydrous medium should be avoided because of secondary reactions (presumably formylation) occurring during the extraction.

the lignin complex is associated with loss of hydroxyl. The question as to whether these more complex molecules exist pre-formed in the wood[1] or, alternatively, arise from some simpler type during the extraction process[4] would, at this time, seem to be of secondary importance as compared with elucidation of the structure of lignin as it comes to hand.

The small but consistent amount of Grignard reagent added by both native and substituted formic acid lignins confirms the previous claim[5] that lignin contains a carbonyl linkage. That this small value (about one-half carbonyl group per kilogram) is real is shown by treatment of the lignin with phenylmagnesium bromide; the phenylated lignin, thus produced, is no longer capable of adding methyl-magnesium iodide (Table II, expt. 8).

Analyses in the Grignard machine indicate that the *unfractionated* formic acid lignin contains about four hydroxyl groups per kilogram (Table I). This was confirmed by tosylation of the same material, four tosyl groups per kilogram being introduced. These four have been differentiated into phenolic and non-phenolic hydroxyl groups by methoxylation of the unfractionated lignin with diazomethane. Both the gas evolution and the final methoxyl value indicate that two out of the four hydroxyl groups per kilogram are phenolic in character. While the reaction with diazomethane provides inconclusive evidence for distinguishing phenolic, enolic and carboxylic hydroxyls, the presence of labile enol is considered improbable because of the constancy of the carbonyl value found in all of the formic acid lignin derivatives; a keto-enolic equilibrium undoubtedly would be disturbed in the several methoxylation processes which were employed. With regard to a carboxylic linkage, methoxylation would increase the carbonyl value, since methyl esters usually react with two equivalents of Grignard reagent. Since no change in the carbonyl value was found (Table II, expt. 7) it would seem that the hydroxyl groups, reactive toward diazomethane, are phenolic in character.[6]

This amount of phenolic hydroxyl is rather larger than that observed with other lignins.[7] It is, however, significant that this increase corresponds closely with the difference in methoxyl value between the spruce lignin isolated by the Klason method[8] (17%) and the formic acid method (14%). This evidence indicates that the labile methoxyl (which is liberated as methyl formate) is attached in the lignin to phenolic hydroxyl.

It was somewhat surprising to find that native formic acid lignin contained only four hydroxyl groups per kilogram, since complete methoxylation should yield, correspondingly, a lignin containing only 24.6% methoxyl, while it has been found by many investigators[7,8] that "completely methoxylated lignin" contains about 32% OCH_3. Actually a single methoxylation of the formic acid lignin with dimethyl sulfate and sodium hydroxide gave a product containing 24–27% OCH_3 (Table II, expts. 3, 4, 5, 6). Furthermore,

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(4) Hilpert and co-workers, *Ber.*, **67**, 1551 (1934); **68**, 16, 371, 380 (1935).

(5) (a) Cross and Bevan "Researches on Cellulose. III (1905–1910)," Longmans, Green and Co., London, 1912; (b) Schrauth, *Z. angew. Chem.*, **36**, 149 (1923); (c) Klason, *Ber.*, **56**, 200 (1923); (d) Friedrich, *Monatsh.*, **46**, 31 (1925).

(6) The term phenolic refers to the non-labile enolic hydroxy grouping such as exists in phenol.

(7) Brauns and Hibbert, THIS JOURNAL, **55**, 4720 (1933).

(8) Harris, *ibid.*, **58**, 894 (1936).

TABLE II

REACTIONS AND ANALYSES OF LIGNINS

					Machine analyses before reaction						Machine analyses ol product		
No.	Wt. ol lignin used, g.	Type of lignin used in reaction	% OCH_3 before reaction	Solvent	Active H per kg.	RMgX added per kg.	Description of reaction	Solubilities of product	Yield of product, g.	% OCH_3 in product	Solvent	Active H per kg.	RMgX added per kg.
1	1	Unfractionated formic acid	13.50	Quinoline	4.0	0.6	Methn. with $(CH_3)_2SO_4$ and $NaHCO_3$	Soluble, alkali, chloroform	0.84	15.8			
1a	1	Product No. 1	15.8				Solution in 2% NaOH for 48 hr. acidification	Insoluble, chloroform, acetone Soluble, water–acetone					
2	1	Unfractionated formic acid	13.50	Quinoline	4.0	.6	Methn. with $(CH_3)_2SO_4$ and Na_2CO_3 Wash with 1% NaOH	Insoluble, alkali Partly sol. benzene, ethyl alcohol Soluble, chloroform, acetone	.83	20.72	Dioxane	3.3	0.8
3	1	Unfractionated formic acid	13.50	Quinoline	4.0	.6	Methn. with $(CH_3)_2SO_4$ and 20% NaOH in air	Partly sol. benzene, ethyl alcohol Sol. chloroform, acetone	.88	24.30			
3a	0.88	Product No. 3	24.30				Methn. with diazomethane	Partly sol. benzene	.44	24.30	Dioxane	4.2	0.3
3b	.2	Product No. 3a	24.30	Dioxane	4.2	.3	Treatment with CH_3MgI, shaken with aq. acetone and $(CH_3)_2SO_4$		.15				
4	1	Unfractionated formic acid	13.50	Quinoline	4.0	.6	Methn. with $(CH_3)_2SO_4$ and 20% NaOH under N_2	Partly sol. benzene	.97	23.22			
4a		Product No. 4	23.22				Separation by benzene solubility	Fract. 1, benzene-sol. Fract. 2, benzene-insol.	 .88	23.85 22.91			
4b	0.90	Product No. 4	23.22				Methn. with $(CH_3)_2SO_4$ and 30% NaOH under N_2	Sol. benzene, chloroform, acetic acid Insol. ethyl alcohol, ether, carbon disulfide	.85	25.28			
4c	0.85	Product No. 4b	25.28				Methn. with $(CH_3)_2SO_4$ and 30% NaOH under N_2		.65	28.44			
4d	.65	Product No. 4c	28.44				Methn. with diazomethane	Partly sol. xylene	.55	30.0	1:1 xylene dioxane	2.3	0.7
5	1	Chloroform soluble formic acid	13.13	Dioxane	4.6	.7	Acetylation with C_5H_5N + Ac_2O: methn. with $(CH_3)_2SO_4$ and 30% NaOH under N_2	Sol. benzene	.92	25.82			
6	1	Acetone soluble formic acid	12.81	Dioxane	3.5	.5	Acetylation with C_5H_5N + Ac_2O: methn. with $(CH_3)_2SO_4$ and 30% NaOH under N_2	Partly sol. benzene Sol. chloroform	.87				
6a	0.87	Product No. 6					Separation by solubility in hot benzene	Fract. 1, benzene-sol. Fract. 2, benzene-insol.	.28 .48	26.83 23.30	Dioxane	3.0	0.5
7	1	Unfractionated formic acid	13.50	Quinoline	4.0	.6	Methn. with diazomethane	Partly sol. benzene, ethyl alcohol Sol. chloroform	.97	18.55	Dioxane	2.0	0.6
8	1	Formic acid chloroform–acetone–ether soluble	12.17	Quinoline	4.4	.7	Reaction with C_6H_5MgBr and $(CH_3)_2SO_4$	Fract. 1, sol. chloroform–ether, sodium bicarbonate Fract. 2, sol. chloroform–ether, 1% sodium hydroxide	.05 .56	14.71 18.31	 Dioxane	 4.9	 0.0
9		Methanol–H_2SO_4	21.0				Methn. with diazomethane			24.7	Dioxane	3.0	0.4
10	5	CH_3OH–HCl on methylated wood	33.2				Methn. with diazomethane		3.5	35.42	Xylene	0.9	0.6
11	3	Unfractionated formic acid	12.86	Quinoline	4.0	.6	Reaction with tosyl chloride and pyridine	Insol. alkali Partly sol. dioxane Sol. chloroform, pyridine	4.47	7.79	Quinoline	4.0	2.
12		Chloroform soluble glycol–HCl	16.08	Dioxane	4.1	.0	Repeated acetylation–methn. with $(CH_3)_2SO_4$ + NaOH			31.76	Dioxane	2.0	0.3
13		Unfractionated formic acid	12.86	Quinoline	4.0	.6	Solution 45 days in 1% NaOH–acidification	Insol. acetone Partly sol. dioxane Sol. acetone–water		11.98	Dioxane	12.5	0.0

analyses of these methoxylated products in the Grignard machine showed that the lignin still contained from 4 to 3 free hydroxyl groups per kg. (Table II, expts. 3, 4, 6). Calculations from these figures indicate that complete methoxylation should yield lignin containing 34.6–35.2% OCH_3. Accordingly, two further methoxylations were effected with dimethyl sulfate followed by treatment with diazomethane (Table II, expt. 4), the final methoxyl value being 30%. Further attempts are being made to increase the methoxyl content of this product containing 30% OCH_3 and 2.3 hydroxyl groups per kg. However, the futility of alkaline methoxylation as a criterion for the detection and estimation of hydroxyl groups can be seen from the fact that this lignin (OCH_3 30%) still contains sufficient free hydroxyl groups to yield methoxylated lignin containing 36% methoxyl, assuming these groups to be capable of methoxylation. It is thus apparent that repeated methoxylation increases the *potential* methoxyl number by about 1% (34.6–35.2 to 36%). An explanation of this peculiar behavior is furnished in the analysis of the native lignin which had been allowed to stand for forty-five days in 1% sodium hydroxide solution (Table II, expt. 13), during which period there was no absorption of atmospheric oxygen. The original hydroxyl number increased from 4 to 12.5 per kg. with an accompanying decrease of methoxyl from 12.86 to 11.98%. The calculated methoxyl value, upon addition of 4.25 moles of water per kilogram of lignin, is 11.96%, *viz.* $12.86\,(10)/[1000 + (12.5-4)18/2]$. In short, hydroxyl groups appear *de novo* upon treatment of the native lignin with alkali.[8a] It is noteworthy that if the entire non-methoxyl oxygen content of the formic acid lignin were converted to hydroxyl (by ring opening) the hydroxyl number as deduced from ultimate analysis[2] would likewise be 12.5 per kg.

In view of these surprising results, other lignins were examined for their hydroxyl content. The chloroform soluble fraction of glycol lignin[9] (OCH_3, 16.68%) was found to contain 4.1 hydroxyl groups per kg. (Table II, expt. 12) corresponding to a fully methoxylated value of 27.3%. Repeated treatment of this with diazomethane, followed by subsequent acetylation and dimethyl sulfate methoxylation gave a product containing *31.7%* OCH_3 and this "completely methoxylated" derivative still contained two free hydroxyl groups. On the other hand, a methanol lignin (OCH_3, 24.7%) which had been methoxylated only with diazomethane and, therefore, had not been subjected to an alkaline treatment was found to contain three free hydroxyl groups per kilogram (Table II, expt. 9). A sample of the fully methoxylated methanol lignin (OCH_3, 32%) was not available but a methoxylated methanol lignin prepared from methoxylated wood meal[10] and further methoxylated with dimethyl sulfate and sodium hydroxide, followed by treatment with diazomethane, gave a product with 35.4% OCH_3 but still containing 0.9 free hydroxyl group per kilogram (Table II, expt. 10). All of these methoxylated lignins were free from sulfur.

It thus appears that *alkaline methoxylation is unreliable both as a measure of the hydroxyl groups originally present in the lignin and of complete methoxylation.* A few attempts to methoxylate formic acid lignin with dimethyl sulfate at controlled *p*H (Table II, expts. 1, 2) resulted in incomplete reaction; the work is being continued. The possibility that the active hydrogen determination gives false values, either because of demethoxylation or enolization, is improbable. Firstly, no type of demethoxylation involving gas formation with Grignard reagent under these conditions is known, although what may be a typical compound, pentamethylquercetin, was examined (Table III, expt. 1). Secondly, the appearance of enolic methoxyl must necessarily be accompanied by a corresponding decrease in carbonyl value, while actually the carbonyl value is constant within experimental error. Consequently the Grignard analysis is considered reliable for the estimation of hydroxyl groups in lignin.

Extended speculation concerning these newly synthesized hydroxyl groups must await additional experimental evidence. Obviously they could be formed either by addition of the elements of water to double bonds, or by splitting of oxygen rings. It is improbable that all such oxygen rings could be pyrones because of the

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(8a) The authors find it necessary to point out that additional work has failed to confirm the *quantitative* values thus obtained. although *qualitatively* the evidence supports the conclusions drawn. They are likewise in harmony with previous experimental work carried out by Jack Compton in these laboratories and to appear in the *Canadian Journal of Research*, January, 1937.

(9) King, Brauns and Hibbert, *Can. J. Research*, **B13**, 35 (1935).

(10) Brauns and Hibbert, *ibid.*, **B13**, 78 (1935); Compton, Greig and Hibbert, *ibid.*, **B14**, 115 (1936).

TABLE III

ANALYSES OF RELATED COMPOUNDS

Expt. no.	Substance	Solvent	Active hydrogen	RMgX added
1	Pentamethylquercetin, m. p. 148°	Xylene	0.1 per mole	0.8 per mole
2	Cellulose prepared from wood meal (extracted twice with phenol containing 1% concd. HCl and dried at 60° (20 mm.) for 3 hr.	Quinoline (suspension)	1.2 per kg.	0.6 per kg.
3	Oleic acid	Xylene	1.1 per mole	1.0 per mole
4	Isosafrole	Xylene	0.1 per mole	0.0 per mole

low carbonyl value found in the lignin. This does not exclude the presence of the more probable chromanol grouping.[11] The experimental results are contradictory concerning this possibility. Since the splitting of a chromanol ring necessitates formation of a phenolic hydroxyl group, an attempt was made to determine this by treating the previously dimethyl sulfate-alkali methoxylated lignin with diazomethane (Table II, expt. 3a) but no phenolic group was detected. On the other hand, when the same lignin, thrice dimethyl sulfate-alkali methoxylated, was treated with diazomethane an increase of about 1.5% OCH_3 was observed (expt. 4d). The reason for this discrepancy is being investigated. It is certain that hydroxyl formation takes place under exceedingly mild conditions (1% sodium hydroxide) but ethylene oxide or lactone rings cannot be involved because they would have been detected in the Grignard analysis of the native lignin in amounts corresponding to the subsequent hydroxyl increase, resulting from ring fission.

Likewise from the evidence submitted here it is not possible to designate the type of carbonyl function found in this lignin except that it probably is not an acyl group (lignin-OCOR) which would have been removed during methoxylation. Also the carbonyl group is probably not of an enolizable type. The latter reservation follows from its constant value throughout the methoxylation experiments. The carbonyl function is, however, destroyed by prolonged treatment with alkali (Table II, expt. 13). Finally it must be emphasized that this is a preliminary report of work in progress, the methods of which are to be refined in the interest of accuracy.

The authors wish to thank Dr. Saul M. Trister for aid in the experimental work.

Experimental

Preparation of Formic Acid Lignin.—A suspension of 40 g. of spruce wood meal (75 mesh) (previously extracted successively with a 1:1 alcohol–benzene mixture, then with water, and dried at 55° (30 mm.))[12] in 300 cc. of formic acid of various concentrations (Table I) was refluxed in different experiments for six to thirteen hours. After cooling the mixture was filtered by suction and washed with 100 cc. of cold 90% formic acid. The residual moist wood meal (vacuum dried, wt. 23–15 g. depending on duration of boiling) was further extracted for twenty-four hours with 100 cc. of dioxane and another twenty-four hours with 100 cc. of dioxane containing 1% concd. hydrochloric acid. Although this latter treatment decreased the weight of wood meal from 23 g. (vacuum dried at 55°) to 14.6 g., the evaporated extracts yielded only 0.23 g. of lignin. Evidently a large part of the cellulose is hydrolyzed in the process. The reflux condenser was maintained at 40° during the extraction and the uncondensed gases from the condenser were conducted through a dry-ice trap. The condensate was identified as methyl formate (b. p. 31.5°) and by test for methanol following alkaline hydrolysis.

The original formic acid solution, obtained by filtration from the residual wood meal, was evaporated almost to dryness at 25 mm. pressure and the residue washed with water to remove soluble carbohydrates[13] and filtered by suction. After thorough washing with water on the filter and drying by prolonged suction under a rubber dam, the water-insoluble portion was dissolved in 300 cc. of a 3:17 water–acetone mixture leaving a residue[13] which was removed either by suction filtration or centrifuging. The solution was evaporated to dryness (25 mm.), the drying process being facilitated by addition of chloroform. The residue was extracted with three 100-cc. portions of chloroform and the extract concentrated to 40 cc. (30 mm.) (solution A). The chloroform-insoluble residue was further extracted with three 50-cc. portions of acetone and then concentrated to 50 cc. (30 mm.) (solution B). Finally the acetone insoluble residue was dissolved completely in 110 cc. of the 3:17 water–acetone mixture (solution C). These three solutions (A, B and C) were each precipitated into tenfold volumes of ether and the precipitates removed by centrifuging. The chloroform–ether and acetone–ether solutions, containing some lignin, were concentrated to 20 cc. and precipitated into 200 cc. of petroleum ether (b. p. 30–50°). Evaporation of the centrifuged chloroform–ether–petroleum ether solution left a slight residue of odoriferous material. The results of this separation are shown in Table I.

Methoxylation of Lignin with Diazomethane.—One gram of lignin was dissolved in 15 cc. of dry dioxane. To

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[11] Russell, *Chem. Rev.*, **17**, 155 (1935).

[12] As could have been predicted by King and Hibbert, *Can. J. Research*, **B14**, 12 (1936), a fourfold extraction of the wood meal with 5% alkali had no effect on methoxyl, active hydrogen or carbonyl content of the extracted lignin.

[13] At present undergoing investigation.

this solution at 25° was added, at one time, 4 cc. of an ether solution of diazomethane prepared from 0.5 cc. of nitrosomethylurethan. After five hours the gas evolution according to second order reaction rate ceased, about 48 cc. having been evolved. The solution was allowed to stand overnight, evaporated to dryness (30 mm.) and redissolved in benzene or acetone according to its solubility. The solution was centrifuged to remove diazomethane polymer and then precipitated into a tenfold volume of ether, the yield of centrifuged, ether-washed lignin dried at 60° (20 mm.) being 0.9–1.0 g.

Methoxylation of Lignin with Dimethyl Sulfate.—One gram of lignin was dissolved in a mixture of 40 cc. of acetone and 10 cc. of water. The solution was stirred under nitrogen while 3.8 cc. (0.09 mole) of dimethyl sulfate and 0.05 mole of the desired alkaline reagent were added simultaneously, the alkali being maintained constantly in excess during a period of ninety minutes and the solution stirred for a further thirty minutes. It was then diluted to 200 cc. with water, and acetic acid added until the suspension gave an acid reaction to litmus paper. At this point precipitation always occurred. The precipitated product was removed by extraction with chloroform, and the chloroform solution washed with 1% sodium hydroxide. In some cases it was found advisable to supplement this alkaline wash with an acid wash using 1% acetic or hydrochloric acid since chloroform soluble sodium lignates have been encountered. The washed chloroform solution was dried by evaporation at 25° (30 mm.) and the dried solution precipitated subsequently into a tenfold volume of ether or petroleum ether (b. p. 30–50°). The precipitated lignin was washed with a fresh portion of the precipitating reagent and dried at 60° (20 mm.). Yields were 0.9–1.0 g. as compared with yields of 0.8–0.9 for similar reactions carried out in air.

Tosylation of Lignin.—A solution of 3 g. of lignin and 5 g. of tosyl chloride in 50 cc. of dry pyridine was allowed to react for three days at room temperature and then added in a fine stream to 800 cc. of water containing 20 g. of potassium bicarbonate. After five hours' subsequent stirring, the precipitate was filtered by suction and dried (30 mm.). It was insoluble in alkali. A solution of the crude material in 100 cc. of chloroform was precipitated into 800 cc. of ether. The centrifuged, ether washed product was dried at 60° (20 mm.); weight, 4.47 g. The calculated yield, assuming esterification of four hydroxyl groups and addition of two molecules of water per kilogram is 4.96 g. The methoxyl content of this assumed compound would be 7.9% OCH_3. Found: OCH_3, 7.8%. One gram of the product when treated with phenylmagnesium bromide and subsequently oxidized with 1% potassium permanganate yielded 0.02 g. of sublimed benzoic acid.

Grignardization of Formic Acid Lignin.—A solution of 1 g. of chloroform–ether soluble lignin (containing 12.17% OCH_3 and 4.4 active hydrogen per kg.) in a mixture of 50 cc. ether and 50 cc. of dioxane was stirred under nitrogen while 20 cc. (0.021 mole) of phenylmagnesium bromide solution in ether was added over a ten-minute period. The reaction mixture was refluxed for two hours and allowed to stand overnight. Next day a solution of 4.75 cc. (0.05 mole) of dimethyl sulfate in 10 cc. of ether was added dropwise to the stirred reaction mixture in order to increase the lignin solubility by methoxylation. After three hours of refluxing the reaction was left overnight. Next morning the mixture was poured into 0.5% hydrochloric acid. The ether layer was diluted with chloroform, separated from the aqueous layer, and washed once with sodium bicarbonate solution and thrice with 1% sodium hydroxide in water. The acidified aqueous solutions were extracted thrice with chloroform. These solutions after drying by vacuum evaporation were precipitated into a tenfold volume of petroleum ether (b. p. 30–50°): yield of vacuum-dried product from the bicarbonate extract, 0.05 g.; OCH_3, 14.75%; yield of vacuum-dried product from the sodium hydroxide extract, 0.56 g.; OCH_3, 18.31%.

The reaction products so obtained were analyzed for methoxyl content (micro)[14] and for active hydrogen and carbonyl in the Grignard machine. The solution medium for this latter determination was either xylene, quinoline or dioxane (5 cc. in quantity), the latter two being conveniently purified by distillation from methylmagnesium chloride or sodium–benzophenone. Because of the volatility of dioxane on the boiling water-bath it was necessary to cool the outlet of the reaction flask during the heating period of fifteen minutes. The analyses together with yield and differentiating solubilities of the reaction products are summarized in Tables II and III.

Summary

1. The extraction of spruce wood meal with boiling formic acid is described.

2. A comparison of active hydrogen determinations with the results of alkaline methoxylation throws doubt on the hitherto assumed reliability of the latter as an agent for the proof of lignin structure.

3. The presence of carbonyl in lignin is confirmed.

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[14] The micromethoxyl method is admirably suited for the methoxyl determination of lignin because the divergence of duplicate analyses informs the experienced analyst as to the homogeneity of his sample. One-tenth of the amount of phenol recommended by Clark [THIS JOURNAL, 51, 1979 (1929)] for the semi-micromethoxyl determination is employed.