The difference between the reducing powers of the epimers are: D-glucose, 4.41 − D-mannose, 4.19 = 0.22 (0.15), D-xylose, 3.68 − D-lyxose, 3.57 = 0.11 (> 0.06) and D-arabinose, 2.99 − D-ribose, 3.12 = −0.13 (> 0.05). The difference between sugars whose hydroxyl groups on C atoms 3 and 4 are *trans vs. cis* is: D-glucose, 3,4 *trans*, 2,3 *trans*, 4.41 − D-galactose, 3,4 *cis*, 2,3 *trans*, 3.51 = 0.90 (0.90). The last two sugars have opposite configurations on C atom 4. These results show that sugars whose neighboring hydroxyl groups are *trans* give higher yields of oxide under corresponding conditions than when these groups are *cis*.

The difference between the reducing powers of corresponding aldohexoses and aldopentoses is: D-glucose, 4.41 − D-xylose, 3.68 = 0.73 (0.69) and D-mannose, 4.19 − D-lyxose, 3.57 = 0.62 (0.62). The difference is about the same as when the hydroxyl group on C atom 6 is replaced by hydrogen, *i. e.*, D-mannose, 4.19 − D-rhamnose, 3.61 (same as L-rhamnose in the *d*-tartrate) = 0.65 (0.69) and D-galactose, 3.51 − D-fucose, 2.81 (same as L-fucose in the *d*-tartrate) = 0.70 (0.70).

The reducing power is only slightly lower, 0.11, when the hydroxyl group on C atom 2 of D-glucose is replaced by the NH_2 group in D-glucosamine. The reducing power is increased, 0.35, when the hydroxyl group on C atom 4 of D-glucose forms either the galactoside, lactose, or the glucoside, cellobiose, and it is increased by 0.55 when the hydroxyl group on C atom 6 of D-glucose forms the glucoside, melibiose. Only the glucose unit serving as the aglycone in these disaccharides reduces the copper reagent because the sugar residue of glycosides is non-reducing in the form of the hemi-acetal.

We are pleased to acknowledge generous financial support from the Sugar Research Foundation and the encouragement and patience of their Scientific Director, Dr. Robert C. Hockett.

Summary

1. The method devised by Shaffer and coworkers for estimating reducing sugars has been modified to give yields of cuprous oxide that are more easily reproduced and are up to 10% larger than formerly. The average reproducibility in each analysis is 1.2×10^{-7} mole of cuprous oxide which corresponds to an uncertainty of 0.048 ml. of 0.005 *N* thio in the difference between the thio titers for the blanks and sugar solutions.

2. A procedure is given for estimating the yields of cuprous oxide which automatically corrects for the oxide lost.

3. The yields of cuprous oxide produced by fourteen aldoses and two ketoses have been measured under equivalent conditions and the differences are compared with the differences in the configuration and structure of the sugars.

RECEIVED NOVEMBER 19, 1948

[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY]

Studies on Lignin and Related Products. I. The Oxidation of Basic Calcium Lignosulfonate with Mercuric Oxide and with Silver Oxide[1,2]

BY IRWIN A. PEARL

Lautch, Plankenhorn and Klink[3] treated isolated "cuproxam" lignin with alkali and oxides of copper, silver, mercury and lead and found that the oxides of these metals did not increase the yields of vanillin obtainable from lignin by the use of alkali alone.

Other work in this laboratory on the oxidation of vanillin to vanillic acid by means of silver oxide[4,5] and mercuric oxide[6] indicated that oxidation of lignin materials in the presence of metal oxides might yield vanillic acid instead of vanillin as the principal oxidation product. Therefore, the reaction of lignin materials with a large number of metallic oxides was reinvestigated. This paper deals with the reaction of basic calcium lignosulfonate (BCLS) with mercuric oxide and with silver oxide.

In preliminary experiments, BCLS was treated at the boiling point with a suspension of a freshly prepared mercuric oxide in alkaline solution, and the reaction product was acidified with sulfuric acid, extracted with ether and fractionated to bisulfite, bicarbonate, and alkali solubles and neutrals. These extracts yielded a total of approximately 60% of mercury-containing, ether-soluble products based on the original lignin. No attempt was made to isolate pure compounds from these mercury-containing fractions.

During the separation of the bisulfite-soluble fraction from the original ether extract, a white crystalline precipitate separated. Upon warming with dilute sulfuric acid, this crystalline precipi-

---

(1) Presented before the Division of Cellulose Chemistry at the 114th meeting of the American Chemical Society, Western Session, Portland, Oregon, September 13-17, 1948.

(2) This paper represents a portion of the results obtained in the research program sponsored by the Sulphite Pulp Manufacturers' Research League and conducted for the League by The Institute of Paper Chemistry. Acknowledgment is made by the Institute for permission on the part of the League to publish these results. Some of the data reported in this paper have been disclosed in U. S. Patent 2,433,227 (Dec. 23, 1947).

(3) Lautch, Plankenhorn and Klink, *Angew. Chem.*, **53**, 450 (1940).

(4) Pearl, THIS JOURNAL, **68**, 429 (1946).

(5) Pearl, *ibid.*, **68**, 1100 (1946).

(6) Pearl *ibid.*, **70**, 2008 (1947).

tate decomposed into free mercury and vanillin. Thus, the crystalline product appeared to be the sodium bisulfite addition product of a mercurated vanillin, which was decomposed by the sulfur dioxide liberated upon sulfuric acid treatment. This result suggested that sulfur dioxide might be used advantageously as the initial acidifying agent and, thus, decompose all mercurated organic compounds before subsequent fractionation.

Accordingly, BCLS was oxidized with alkali and 6 moles of mercuric oxide (freshly prepared by mixing hot solutions of mercuric chloride and sodium hydroxide), but this time the entire reaction mixture was acidified with sulfur dioxide and extracted directly with ether. The sulfur dioxide-acidified aqueous solution was further acidified with sulfuric acid and re-extracted with ether. Both ether extracts were fractionated into bisulfite-soluble, bicarbonate-soluble, alkali-soluble, and neutral fractions; these did not contain mercury and amounted to approximately 50% of the original lignin.

In exactly the same manner, BCLS was treated with dry yellow mercuric oxide and with cold freshly prepared mercuric oxide (prepared by mixing cold solutions of mercuric acetate and sodium hydroxide). The nature of the fractions obtained with the various forms of mercuric oxide was essentially the same, but the distribution of the fractions varied considerably with the particular oxide employed. The yields of these fractions from the three types of mercuric oxide oxidations are given in Table I.

TABLE I

OXIDATIONS OF BCLS WITH THREE TYPES OF MERCURIC OXIDE

	% after acidification					
	Hot freshly prepared HgO		Cold freshly prepared HgO		Dry HgO	
Fraction	SO_2	H_2SO_4	SO_2	H_2SO_4	SO_2	H_2SO_4
Bisulfite soluble	24.5		15.0		12.2	
Bicarbonate soluble	14.4	7.9	32.6	4.8	31.5	3.5
Alkali soluble	2.7	4.1	4.8	1.5	2.0	1.5
Neutral	0.9	0.2	0.7	0.6	3.5	1.7
Total	18.0	36.7	38.1	21.9	37.0	18.9
Grand total	54.7		60.0		55.9	

The bicarbonate-soluble material of the sulfur dioxide-acidified solution was the principal fraction in all experiments except those in which hot freshly prepared mercuric oxide was employed. This fraction always appeared as a very light yellow, powdery solid and was considered to be impure vanillic acid. Tiemann,[7] in a study of the solubility of salts of vanillic acid, found that the lead salt was insoluble. However, in an attempt to purify vanillic acid by means of its lead salt, it was found that, of all the acidic materials present in this fraction, only vanillic acid did not give an insoluble product on treatment with neutral lead acetate. Thus pure vanillic acid was isolated in yields up to 90% of the bicarbonate-soluble fraction.

The non-vanillic acid portion of the bicarbonate-soluble fraction isolated from the lead precipitate was a methoxyl-containing acid which has not been identified. The bicarbonate-soluble fraction from the sulfuric acid-acidified solution as isolated was usually darker in color than the corresponding fraction from the sulfur dioxide-acidified solution. In addition, the vanillic acid content was usually somewhat lower.

The alkali-soluble materials from the sulfur dioxide-acidified solution were chiefly acetovanillone and guaiacol. The alkali-soluble fraction from the sulfuric acid-acidified solution consisted essentially of vanillin. The occurrence of vanillin in the alkali-soluble fraction after an original sodium bisulfite extraction was discussed previously.[6]

The bisulfite-soluble materials were identified as a mixture of acetovanillone and vanillin. The neutral fractions consisted of a mixture of a waxy substance and a clear, colorless, viscous oil which has not been positively identified.

If the original mercuric oxide-BCLS reaction mixture was filtered free of inorganic mercury compounds and acidified with a non-reducing acid, such as sulfuric acid or hydrochloric acid, a heavy precipitate of mercurated vanillin and lignin derivatives separated. 5-Hydroxymercurivanillin has been isolated from the bisulfite-soluble fraction. Both the isolated mercurated lignin derivatives and the original filtered alkaline reaction mixture are effective bactericides and fungicides. The toxicities of these products toward micro-organisms and toward fish are very similar to those of 5-hydroxymercurivanillin reported earlier.[6] In addition, these products were found to possess prophylactic properties when employed on diseased test fish. This property of pyridylmercuric acetate was noted by Van Horn and Katz.[8]

For studying the oxidation of BCLS with silver oxide, the ratio of silver oxide to a unit lignin weight of 180 was arbitrarily set at 3:1. When BCLS was added to a stirred suspension of freshly prepared silver oxide (dry silver oxide may be used) at temperatures above 50°, an immediate reaction took place—the silver oxide was reduced to metallic silver and the temperature rose to the boiling point. This reaction mixture, when worked up in accordance with the general procedure noted under mercuric oxide oxidations, yielded fractions very similar to those obtained with mercuric oxide. The fractions were free of silver and over 99% of the original silver was recovered as silver metal. In this oxidation, the bicarbonate-soluble materials comprised the largest percentage of the ether extractives; these contained from 70–90% vanillic acid. Very little vanillin was obtained in silver oxide oxida-

---

(7) Tiemann, *Ber.*, **8**, 511 (1875).

(8) Van Horn and Katz, *Science*, **104**, 557 (1946).

tions—the bisulfite- and alkali-soluble materials were essentially acetovanillone. This is easily understood in view of the fact that vanillin undergoes oxidation in the presence of silver oxide and alkali,[4] whereas acetovanillone is stable toward silver oxide under these conditions.

Instead of the two-step acidification treatment employed with the mercuric oxide oxidations, a single sulfuric acid acidification yielded essentially the same results with silver oxide oxidations. However, if BCLS is treated with silver oxide generated *in situ* by addition of silver nitrate to a warm alkaline solution of the sulfonate, the resulting filtered reaction mixture must be treated with sulfur dioxide before the use of other acids in order to prevent the formation of nitro derivatives. Thus, 4-nitroguaiacol was isolated as light yellow needles melting at 97–98° from such a reaction without prior sulfur dioxide treatment.

Furthermore, such acidified reaction mixtures should be extracted with benzene rather than ether. In several experiments in which ether extracts of nitrite- or nitrate-containing reaction mixtures were concentrated, vigorous nitration reactions took place during the concentration.

4-Nitroguaiacol was identified in the following manner: Analysis indicated a mononitroguaiacol. Two nitroguaiacols are known with melting points in this range—4-nitroguaiacol (4-nitro-2-methoxyphenol), melting at 99–100°,[9] and 5-nitroguaiacol (5-nitro-2-methoxyphenol), melting at 103–104°.[10] The crystals were nitrated to 4,6-dinitroguaiacol. Inasmuch as 4,6-dinitroguaiacol could have been formed only from 4-nitroguaiacol or 6-nitroguaiacol and since 6-nitroguaiacol melts at 62°,[11] the compound in question must be 4-nitroguaiacol. Its formation in this reaction mixture is probably caused by the nitration of guaiacol in the same manner that vanillic acid is nitrated to 5-nitrovanillic acid during oxidations of vanillin with silver nitrate and alkali.[5]

Experimental

All melting points are uncorrected.

Starting Material.—The BCLS of spruce origin was kindly furnished by the Marathon Corporation of Rothschild, Wisconsin. The powdered product had the following percentage analysis on the "as received" basis: moisture, 5.45; CH_3O, 9.20; ash, 21.93; total sulfur, 5.00; sulfite sulfur, 0.45. Inasmuch as all the methoxyl in this product belonged to lignin, and assuming lignin to contain 14.5% methoxyl, the lignin value of this product becomes 60.0%.

Reaction of BCLS with Hot Freshly Prepared Mercuric Oxide.—In a 3-neck, 12-liter flask equipped with a mercury-sealed stirrer and a reflux condenser were placed 1400 g. (5 moles) of mercuric chloride and 5 liters of water. The mixture was heated with stirring until the mercuric chloride dissolved and was then treated with vigorous stirring with a hot solution of 1000 g. (25 moles) of sodium hydroxide in 1250 cc. of water. The hot orange-colored mixture was treated directly with 250 g. (0.83 mole of lignin having a unit weight of 180) of BCLS, boiled under reflux with stirring for 17 hours, and allowed to cool. The bright orange color changed to olive green during the heating period. With continued stirring, the reaction mixture was saturated with sulfur dioxide and heated to boiling with continued sulfur dioxide introduction. A gray sludge in a brown solution separated. The entire mixture was transferred to a gas-agitated, liquid-liquid extractor[12] and was continually extracted with ether, using air and sulfur dioxide alternately as agitating gases. The ether was separated and extracted successively with 8% sodium bicarbonate and 5% sodium hydroxide solutions. The extracted ether solution was dried with sodium sulfate and distilled to leave the neutral fraction. The bicarbonate extract was acidified with 1:1 sulfuric acid, saturated with sodium chloride, and extracted with ether. The ether solution was dried with sodium sulfate and distilled to yield the bicarbonate-soluble materials as a light yellow solid. Similar treatment of the sodium hydroxide extract yielded the alkali-soluble material as a light yellow oil which solidified on cooling to yellow crystals with the odor of guaiacol.

The sulfur dioxide-saturated aqueous mixture left after ether extraction was filtered, and the mercury-containing precipitate was washed with hot water. The clear filtrate and washings were combined, acidified with 1:1 sulfuric acid, aspirated with air to remove the dissolved sulfur dioxide, and extracted continuously with ether in the liquid-liquid extractor, using air as the agitating gas. This ether extract was extracted successively with 21% sodium bisulfite solution, 8% sodium bicarbonate solution, and 5% sodium hydroxide solution. The residual ether, the bicarbonate extract, and the alkali extract were worked up as described above. The sodium bisulfite extract, which contained a little crystalline material in suspension, was acidified with 1:1 sulfuric acid and aspirated to remove sulfur dioxide. Considerable precipitate separated. The mixture of precipitate and acid solution was saturated with sodium chloride and extracted with ether. The yellow ether solution was dried and distilled, leaving the bisulfite-soluble fraction as a brown oil which crystallized upon cooling. The yields of fractions for this experiment are those listed in Table I.

Oxidation of BCLS with Cold Freshly Prepared Mercuric Oxide.—To a solution of 1595 g. (5 moles) of mercuric acetate in 5 liters of cold water was added, with stirring, a cold solution of 405 g. (10+ moles) of sodium hydroxide in 2 liters of water. The light yellow-orange mixture was stirred for a short period and allowed to settle. The mercuric oxide was washed by decantation several times and was then transferred to the 12-liter reaction flask, covered with a solution of 600 g. (15 moles) of sodium hydroxide in 5 liters of water, and treated as described above.

Oxidation of BCLS with Dry Mercuric Oxide.—In this reaction, 1080 g. (5 moles) of dry mercuric oxide (C. P. yellow) was employed instead of the cold freshly prepared mercuric oxide described directly above.

Analysis of Fractions.—The following examples are for the fractions isolated from the individual, hot, freshly prepared mercuric oxide oxidation detailed above. The actual percentages of pure identified compounds isolated from other experiments vary considerably.

Bicarbonate-soluble Material from Sulfur Dioxide-acidified Solution.—Five grams of the light yellow powder was boiled with 1500 cc. of water, filtered from the little tarry residue, and treated with an excess of saturated neutral lead acetate solution. The small amount of yellow precipitate was allowed to settle, filtered, and washed thoroughly with water. The combined filtrate and washings were saturated with hydrogen sulfide and finally boiled to remove excess hydrogen sulfide. The precipitated lead sulfide was filtered and washed with boiling water. The filtrate and washings were concentrated to a small volume and allowed to cool. Vanillic acid separated as white needles melting at 207–208°. The yield was 3.5 g. An additional 0.8 g. of crude vanillic acid

---

[9] Wegscheider and Klemenc, *Monatsh.*, **31**, 737 (1910).

[10] Cardwell and Robinson, *J. Chem. Soc.*, **107**, 258 (1915).

[11] Klemenc, *Monatsh.*, **33**, 704 (1912).

[12] Pearl, *Ind. Eng. Chem., Anal. Ed.*, **16**, 62 (1944).

melting at 190-200° was obtained by evaporation to dryness. Recrystallization of both fractions from water or ethanol yielded pure vanillic acid melting at 209-210° and not depressing a mixed melting point with authentic vanillic acid.

The original lead precipitate was treated with dilute sulfuric acid and the resulting mixture was extracted with ether. The ether solution was dried and distilled to yield a yellow solid containing 18.0% methoxyl. This fraction has not yet been identified.

Alkali-soluble Material from Sulfur Dioxide Solution.—This fraction solidified, on standing, to light brown crystals with the odor of guaiacol. The product (4.1 g.) was distilled with steam. The steam distillate was extracted with ether, and the ether was dried and distilled, leaving 1.3 g. of guaiacol as a brown oil. The oil was shaken with benzoyl chloride and sodium hydroxide and the resulting precipitate was recrystallized from ethanol to give crystals melting at 57° and not depressing a mixed melting point with authentic guaiacol benzoate.

The residue from the steam distillation crystallized. The crude crystals melted at 108-109° and weighed 2.7 g. Recrystallization from high-boiling petroleum ether in the presence of decolorizing carbon raised the melting point to 114-115°. A mixed melting point with authentic acetovanillone was not depressed.

Alkali Solubles from Sulfuric Acid Solution.—This fraction (4.2 g.), smelling of guaiacol, was distilled with steam and treated to recover 0.1 g. of guaiacol as described above. The residue from the steam distillation solidified on cooling to crystals melting at 65-70°. Recrystallization from low-boiling petroleum ether yielded colorless needles melting at 80-81° and not depressing a mixed melting point with authentic vanillin. The semicarbazone, nitrophenylhydrazone and 2,4-dinitrophenylhydrazone were identical with those prepared from authentic vanillin.

Bisulfite-soluble Material from Sulfuric Acid Solution.—This fraction crystallized on cooling, yielding a heavy crop of sublimed needles of pure acetovanillone melting at 114-115°. Long extraction of the main bulk of the crystallized solid with low-boiling petroleum ether yielded a small amount of vanillin. Sublimation of the residue gave white crystals of acetovanillone, which did not depress a mixed melting point with authentic acetovanillone.

Oxidation of BCLS with Silver Oxide.—A solution of 540 g. (3.0 moles) of silver nitrate in 2000 ml. of water was treated with stirring with a solution of 125 g. (3.1 moles) of sodium hydroxide in 1000 ml. of water. The precipitate which separated was stirred for a short time, filtered, and washed with water until free of nitrates. The washed silver oxide was transferred to a 3-liter, 3-neck flask fitted with a reflux condenser and oil-sealed stirrer and supported by a hemispherical mantle. The silver oxide was covered with 1500 ml. of water and, with rapid stirring, 450 g. of sodium hydroxide was added. The temperature of the mixture rose to 65°. With continued stirring, 150 g. (0.5 mole of lignin) of BCLS was added and the flask was closed with a stopper carrying a thermometer reaching below the surface of the reaction mixture. Reaction set in immediately and the temperature began to rise. At 100° a violent reaction took place and the temperature rose to 105°. Stirring under reflux was continued until the mixture became cool. No outside heat was applied in this reaction. All the silver oxide appeared to be reduced after several minutes. The cooled reaction mixture was filtered through a sintered funnel, and the granular silver metal was thoroughly washed with hot water. The combined filtrate and washings were acidified with sulfur dioxide and worked up as described under mercuric oxide oxidations. The yields of fractions are shown in Table II.

The fractions were analyzed in accordance with the methods employed for the mercuric oxide oxidations and the results were very similar. Two exceptions should be noted. In the present instance the alkali-soluble fraction from the sulfuric acid-acidified solution is almost pure acetovanillone, whereas in the case of the mercuric oxide oxidation the corresponding fraction consisted essentially of vanillin. Furthermore, the bisulfite-soluble fractions in the case of silver oxide oxidations contain much less vanillin than do the corresponding fractions obtained in the mercuric oxide oxidations.

TABLE II

OXIDATION OF BCLS WITH THREE MOLES OF SILVER OXIDE

Fractions	SO_2– Acidified solution, %	H_2SO_4– Acidified solution, %	Total, %
Bisulfite soluble		11.0	11.0
Bicarbonate soluble	19.3	8.7	28.0
Alkali soluble	1.0	0.9	1.9
Neutral	0.5	0.3	0.8
Total	20.8	20.9	41.7

The neutral fractions were obtained as waxy residues. These were combined and repeatedly recrystallized from acetone to yield white platelets melting at 61-62°. The compound appeared to be identical with eicosanol, CH_3-$(CH_2)_{18}CH_2OH$, which has been found in beech bark and in the acetone extract of plantation rubber.[13]

Anal. Calcd. for $C_{20}H_{42}O$: C, 80.46; H, 14.18. Found: C, 80.67, 80.57; H, 13.80, 14.07.

Oxidation of BCLS with Alkali and Silver Nitrate.—A solution of 575 g. of sodium hydroxide in 1500 ml. of water was placed in a 5-liter, 3-neck flask fitted with a reflux condenser and oil-sealed stirrer. With stirring, the alkaline solution was treated with 150 g. of BCLS and the mixture was heated to 60°. With continued stirring, this mixture was treated at one time with a warm (60°) solution of 540 g. of silver nitrate in 500 cc. of water, and the flask was stoppered. A vigorous reaction took place, raising the temperature to 104°. Boiling was maintained for one hour and the mixture was allowed to cool with stirring. This reaction mixture (when worked up in the same manner as that described in the above experiment except that benzene was substituted for ether) gave yields of fractions almost identical with those in the above experiment.

4-Nitroguaiacol.—The above original reaction mixture was filtered and the silver was washed thoroughly with hot water. The combined filtrate and washings were acidified with dilute sulfuric acid and extracted continuously with benzene, employing air agitation. The benzene extract was extracted successively with sodium bisulfite, sodium bicarbonate, and sodium hydroxide solutions. The sodium hydroxide extract was acidified with dilute sulfuric acid and distilled with steam. A light yellow distillate was obtained; distillation was continued until the distillate became colorless. The yellow distillate was saturated with sodium chloride and extracted with ether. The ether was dried and distilled, leaving a light yellow oil which solidified to long yellow needles on cooling. The yield was 1.5 g. Recrystallization from petroleum ether yielded light yellow needles melting at 97-98°.

Anal. Calcd. for $C_7H_7O_4N$: C, 49.71; H, 4.17; CH_3O, 18.35. Found: C, 50.60; H, 4.40; CH_3O, 18.35.

Some of the crystals were dissolved in concentrated nitric acid at 20° and allowed to stand for two hours. The yellow solution was poured into an excess of ice water and the yellow crystals which separated were filtered. Recrystallization from ligroin yielded yellow crystals melting at 120-122° which did not depress a mixed melting point with authentic 4,6-dinitroguaiacol.[5] Pollecoff and Robinson[14] have reported the nitration of 4-nitroguaiacol to give 4,6-dinitroguaiacol.

Further work on the silver oxide oxidation of non-carbohydrate-containing lignin preparations such as fermented

---

[13] Heilbron, Jones, Roberts and Wilkinson, *J. Chem. Soc.*, 347 (1941).

[14] Pollecoff and Robinson, *ibid.*, **113**, 647 (1918).

sulfite waste liquor, other calcium lignosulfonates, and isolated lignins including studies of reactant ratios, temperatures and pressures of reaction, type of silver oxide, etc., will be the subjects of future papers.

Summary

Basic calcium lignosulfonate has been treated with mercuric oxide in the presence of excess alkali at atmospheric pressure to give increased yields of ether-soluble materials, which have been separated to bisulfite-, bicarbonate- and alkali-soluble and neutral fractions. Vanillic acid has been obtained in high yield. Other compounds isolated were vanillin, guaiacol, acetovanillone and 5-hydroxymercurivanillin. A new procedure for the isolation of pure vanillic acid from bicarbonate-soluble fractions obtained upon oxidation of lignin is described.

Oxidation of BCLS with silver oxide and excess alkali gives high yields of ether-soluble materials. The chief product is vanillic acid. Other products isolated and identified were vanillin, acetovanillone, guaiacol, eicosanol and 4-nitroguaiacol.

APPLETON, WISCONSIN RECEIVED OCTOBER 16, 1948

[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN]

Oxidation of D-Galactose and Cellulose with Nitric Acid, Nitrous Acid and Nitrogen Oxides

BY W. W. PIGMAN, B. L. BROWNING, W. H. MCPHERSON, C. R. CALKINS AND R. L. LEAF, JR.[1]

The marked specific oxidation by nitrogen dioxide (NO_2) of primary alcoholic groups as compared with secondary alcoholic groups in carbohydrates has stimulated considerable interest in this type of reaction.[2] Certain experimental work in this laboratory has indicated that the course of the oxidation by nitrogen dioxide is markedly influenced by the amount of water present in the system. A consideration of the method through which water might be effective led to the view that nitric acid with added nitrites or nitric oxide would be an effective oxidant. The present paper presents the results obtained in the oxidation of D-galactose. In addition, the probable course of the oxidation of galactose to mucic acid is described. The oxidation methods used were also applied to cellulose.

Results and Discussion

Oxidations with Nitrogen Dioxide.—When air-dry cotton linters were oxidized by gaseous nitrogen dioxide in an apparatus similar to that of Yackel and Kenyon,[2] it was found that the rate of oxidation was retarded by the presence of a desiccant (phosphorus pentoxide) in the system. The degree of oxidation was judged by application of the carbon dioxide-evolution method to the oxidized product. When no desiccant was present the carbon dioxide yield from the product obtained by ninety-six hours of oxidation was 25.5%, as compared with a theoretical value of 25.0%. When the reaction system was subjected to the action of the desiccant, the oxidized product yielded only 13% of carbon dioxide after ninety-six hours of oxidation and very slightly more after 120 hours of oxidation.

When solid D-galactose was subjected to oxidation by gaseous nitrogen dioxide, a similar inhibiting effect caused by desiccation was found. In this case, the extent of oxidation was judged by the amount of insoluble mucic acid formed. For periods of oxidation from twelve to ninety-six hours, the yields were from 60 to 80% of theoretical in the absence of added water, and from 80 to 86% when small amounts of water were added. The results were erratic because of the very heterogeneous nature of the reaction.

It is difficult to control the amount of water present during reactions of the kind described, because water is one of the products of the reaction and because the oxidation systems are heterogeneous. However, the results obtained indicate that oxidations by nitrogen dioxide are markedly influenced by the presence of moisture, which may be present in the original materials or formed as a product of the oxidation. Riebsomer[3] has indicated the importance of the maintenance of anhydrous conditions if nitrogen dioxide is to be considered the actual reactant.

Although the equilibria in the system nitrogen oxides–water undoubtedly are complex,[4] a possible explanation of the results obtained with nitrogen dioxide is that a mixture of nitrous and nitric acids are formed according to the known reaction

$$2NO_2 + H_2O \rightleftarrows HNO_3 + HNO_2$$

Since such a mixture would be provided by the addition of nitrites to concentrated nitric acid,

---

(1) Presented before the Division of Sugar Chemistry and Technology, American Chemical Society, New York, 1947. Taken in part from theses presented by W. H. McPherson and C. R. Calkins in partial fulfillment of the requirements of The Institute of Paper Chemistry for the degree of Master of Science from Lawrence College, Appleton, Wisconsin.

(2) E. C. Yackel and W. O. Kenyon, THIS JOURNAL, **64**, 121 (1942); C. C. Unruh and W. O. Kenyon, *ibid.*, **64**, 127 (1942); K. Maurer and G. Drefahl, *Ber.*, **75**, 1489 (1942).

(3) J. L. Riebsomer, *Chem. Rev.*, **36**, 157 (1945).

(4) See D. M. Yost and H. Russel, Jr., "Systematic Inorganic Chemistry of Fifth- and Sixth-group Non-metallic Elements," Prentice-Hall, New York, N. Y., 1944. The kinetics and equilibria involved have been studied particularly by E. Abel and associates, *Z. physik. Chem.*, **A132**, 55 (1928); **A148**, 337 (1930).