On the Mechanism of Pulp Bleaching. III*. Some Properties of Lignosulfonic Acid Treated with Chlorine Water

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In part I of this series[1], the present authors reported that when lignosulfonic acid is brought into reaction with chlorine water at 0°C, at least 50% of the sulfonic acid group is split off as sulfuric acid, while the methoxyl group is cleaved as methanol in a yield ca. 80% of the theoretical, when about 4 mol. of chlorine are consumed per methoxyl. As that paper was published in Japanese, the main results of the chlorination of spruce (*Picea jezoensis*) and birch (*Betula Platyphylla*) lignosulfonic acids are cited here again in Figs. 1, 2 and 3. As shown in Figs. 1 and 2, the yield of methanol reaches a maximum at the consumption of about 4 mol. of chlorine and thereafter decreases, probably because of the decomposition of methanol from excess chlorine. The methoxyl content of the residue obtained by evaporation of the solution to dryness after the distillation of methanol decreases very rapidly, as expected, until the yield of methanol reaches a maximum. As is evident from Fig. 2, in which the formation of methanol from birch lignosulfonic acid is shown, the yield of methanol based on the total methoxyl of the lignosulfonic acid is very high, suggesting the formation of methanol not only from guaiacyl but also from syringyl type structural units in a high yield. The amount of sulfuric acid formed during the chlorination is shown in Fig. 3. When about 4 mol. of chlorine are consumed, about 0.5 mol. of SO_4^{2-} are formed per sulfonic acid group in lignin.

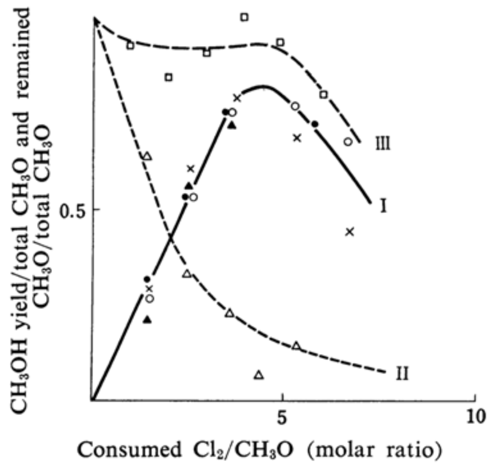

Fig. 1. Formation of methanol from spruce lignosulfonic acid by chlorination. I, mol. ratio of methanol formed to total methoxyl in lignin. II, mol. ratio of methoxyl remaining in the residue after distillation of methanol to total methoxyl in lignin. III, II+I.
[4 g. of Ba-lignosulfonate prepared from spruce (Anal. CH_3O, 11.95%; S in SO_3H form, 4.73%) were dissolved in water, passed through ion exchanger, made up to 100 ml., 20 ml. of this solution were mixed with an appropriate amount of saturated chlorine water at 0°C and analyzed after 16 hr.]

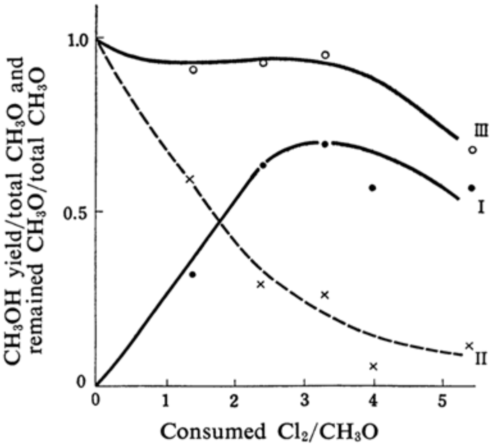

Fig. 2. Formation of methanol from birch lignosulfonic acid by chlorination. I, II and III, same as in Fig. 1. (Experimental conditions are also the same as the case of spruce lignosulfonic acid. Birch lignosulfonic acid, $C_9H_{9.65}O_{2.87}(CH_3O)_{1.40}(SO_3Ba/2)_{0.53}S_{0.36}^{neut}\cdot Ba_{0.04}^{excess}$).

Hibbert[2] assumed that when lignin was treated with chlorine, chlorine atoms were introduced at positions 5 or 6 of the benzene nucleus, the methoxyl group became unstable and the orthoquinone structure was perhaps formed after the cleavage of the methoxyl

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* Presented in part at the Second Lignin Symposium of Japan, Tokyo, November, 1957.

[1] K. Sato and H. Mikawa, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **61**, 1090 (1958).

[2] H. Schwarz, J. McCarthy and H. Hibbert, *Papar Trade J.*, **113**, 115 (1941).

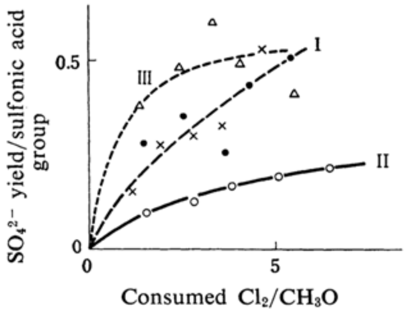

Fig. 3. Formation of SO_4^{2-} from various lignosulfonic acids by chlorination (The conditions of chlorination are the same as those of Figs. 1 and 2).
Curve I, Spruce lignosulfonic acid
Curve II, Methylated spruce lignosulfonic acid
Curve III, Birch lignosulfonic acid

group. Giertz[3] reports that substitution and oxidation reactions may occur when lignin is treated with chlorine water. During the first fifteen minutes the former reaction predominates almost exclusively, while thereafter the latter reaction increases, both reactions being about the same after one hour; after four hours, more than half of the consumed chlorine had been used for the oxidation reaction. Adler[4] has reported recently that the methoxyl groups of the lignin model compounds of the guaiacyl type cleave to give methanol in a good yield when treated with periodate and that guaiacol gives orthobenzoquinone by the same reaction.

It may therefore be expected that carboxyl, carbonyl and/or orthoquinone structures would be formed in the residual lignosulfonic acid in unbleached sulfite pulp when it is treated with chlorine water during the bleaching process. In the present paper, some properties of lignosulfonic acid treated with chlorine water at 0°C were investigated: — 1) the amount of sodium borohydride consumed by the chlorinated lignosulfonic acid, 2) the nature of the weakly acidic group formed by the chlorination, and 3) the change in the ultraviolet and infrared absorption spectra during the chlorination. The main object in the present investigation is, therefore, to see preliminarily the mode of the chemical change of the lignosulfonic acid during its chlorination in aqueous solution at 0°C.

Chlorination of Lignosulfonic Acid

The results obtained when 70, 100, 130 and 160% (by weight) of chlorine were reacted with lignosulfonic acid are shown in Figs. 4, 5, 6 and 7, in which curve I represents the amount of chlorine added, curve II, the chlorine reacted with the lignin, curve III, the amount of carbonyl group estimated from the sodium

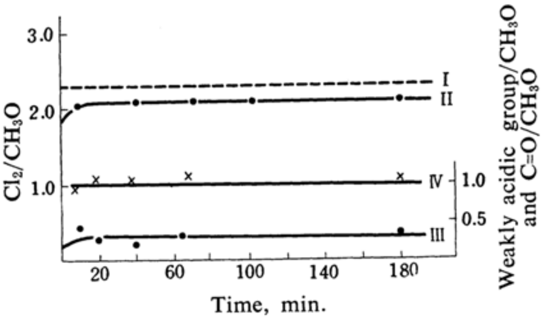

Fig. 4. Chlorination of lignosulfonic acid. 70% of chlorine was added.
I, Chlorine added II Chlorine consumed III, Carbonyl groups produced IV, Weakly acidic group.

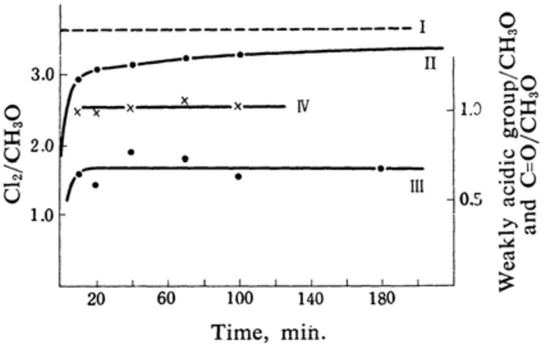

Fig. 5. Chlorination of lignosulfonic acid. 100% of chlorine was added (I, II, III and IV are the same as in Fig. 4).

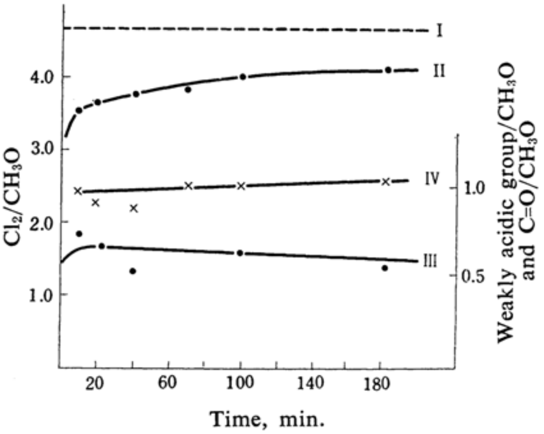

Fig. 6. Chlorination of lignosulfonic acid. 130% of chlorine was added (I, II, III and IV are the same as in Fig. 4).

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[3] H. W. Giertz, *TAPPI*, 35, 209 (1951).

[4] E. Adler, S. Hernestam and I. Walldén, *Svensk Papperstidn.*, 61, 641 (1958); E. Adler and R. Magnusson, *Acta, Chem. Scand.*, 13, 505 (1959).

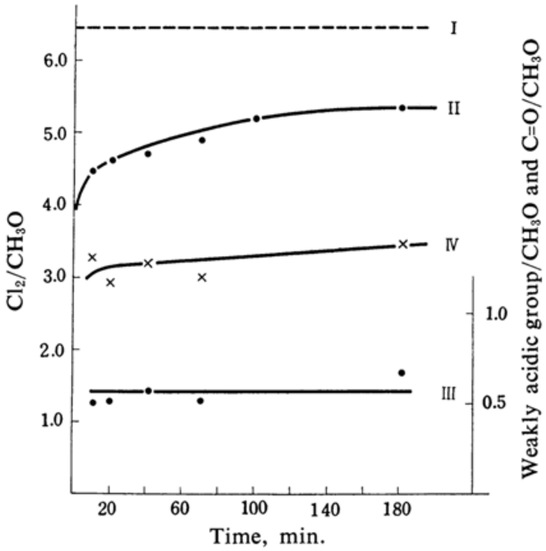

Fig. 7. Chlorination of lignosulfonic acid. 160% of chlorine was added (I, II, III and IV are the same as in Fig. 4).

borohydride consumption, and curve IV, the amount of the weakly acidic group estimated by conductometric titration.

When 70 and 100% of chlorine were used, the amounts of chlorine consumed after twenty minutes were 90 and 85% of the chlorine added respectively. The amount of the consumed chlorine did not exceed 90%, however, even after completion of the reaction.

Curve III in Figs. 4, 5, 6 and 7 shows the amounts of sodium borohydride consumed in the reduction of the reaction mixture with sodium borohydride for various lengths of time, the amounts being expressed for the sake of simplicity as mol. of carbonyl groups equivalent to the sodium borohydride consumed per methoxyl. It must, therefore, be remarked that the carbonyl groups of quinoidal structure, if any, are not calculated as two, because an ordinary carbonyl group consumes two atoms of hydrogen, but quinoidal structure with two carbonyl groups consumes the same amount. Curve IV indicates the amounts of the weakly acidic group. When the amounts of the carbonyl group and of the weakly acidic group of all these figures are plotted against the amount of chlorine consumed, Fig. 8 is obtained. It clearly shows that when the consumed chlorine is lower than 4 mol. per methoxyl, the amount of the weakly acidic group is about 1 equiv./CH_3O, which is distinctly higher than the value of ca. 0.3 equiv./CH_3O of ordinary lignosulfonic acid. After the consumption of about 4 ml. Cl_2/CH_3O, the amount of the weakly acidic group begins to increase, and at the same time the amount of the carbonyl group decreases. This fact might suggest that carbonyl groups, once formed, are oxidized further to give carboxyl groups after the consumption of about 4 mol. of Cl_2/CH_3O.

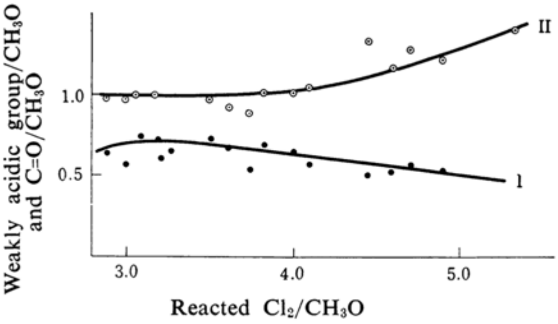

Fig. 8. Formation of weakly acidic groups and carbonyl groups during chlorination.
Curve I, Carbonyl group
Curve II, Weakly acidic group

It must be remarked here that, if no carboxyl groups were formed, the amount of the conductometrically estimated weakly acidic group existing in the solution of chlorination would not exceed one per methoxyl group, insofar as no C_9-building units with more than one phenolic hydroxyl group in a unit—eq. pyrocatechol structure—are formed by chlorination, and only one of the two phenolic hydroxyl groups of the pyrocatechol type structure thus formed is conductometrically titratable.

As shown in Fig. 9, the introduction of chlorine atoms into the nucleus seems to have no influence on the titratability of the carboxyl and phenolic hydroxyl groups (cf. 6-chlorovanillic acid and 5,6-dichlorovanillin), and only one phenolic hydroxyl group of the two phenolic hydroxyl groups of the pyrocatechol structure is conductometrically titratable (cf. protocatechualdehyde and propiocatechon). Moreover, as is evident from Fig. 10, where some hydrochloric acid is added first to the solution of the model compounds almost all of the excess hydrochloric acid was neutralized by adding 3~4 ml. of a 0.1 N sodium hydroxide solution and the remaining excess hydrochloric acid and the phenolic hydroxyl groups were titrated conductometrically, although only one of the two phenolic hydroxyl groups of the pyrocatechol structure is conductometrically titratable, even in the presence of a salt of a strong acid and a base in excess.

The authors will report in a forthcoming paper that some of the pyrocatechol structure may be formed in the chlorination of lignin. As stated above, the maximum amount of the conductometrically estimated weakly acidic group existing in the reaction mixture of chlorination can not exceed one per methoxyl

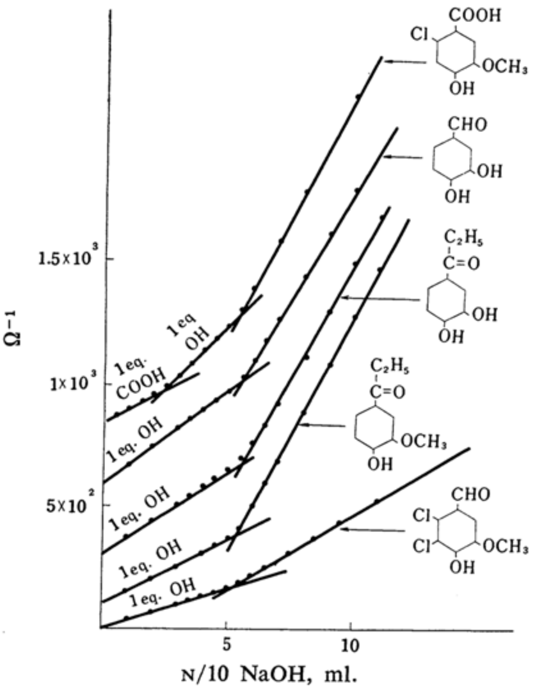

Fig. 9. Conductometric titration curves of some model compounds related to the chlorination of lignosulfonic acid.

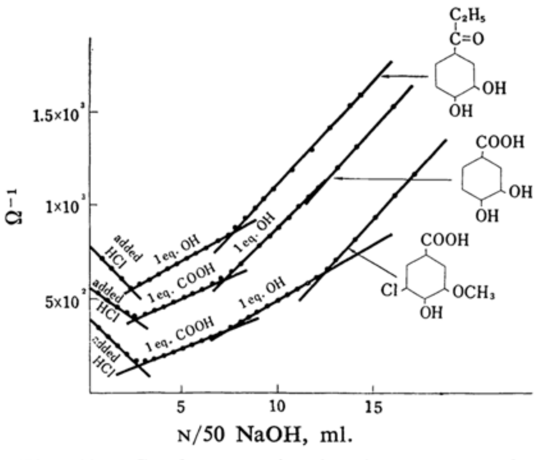

Fig. 10. Conductometric titration curves of some model compounds, titration being performed in the presence of excess hydrochloric acid.

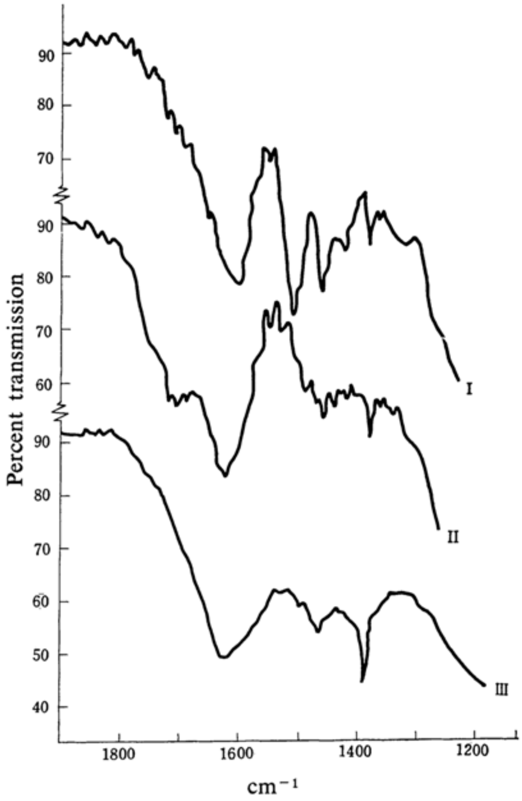

Fig. 11. Infrared absorption spectra of various barium-lignosulfonates. Curve I, Original sulfonate, Curve II, Chlorinated sulfonate; Curve III, Chlorinated sulfonate reduced with $NaBH_4$.

group if no carboxyl group is formed, since it has been proved that only one phenolic hydroxyl of the pyrocatechol structure is conductometrically titratable. Hence it may safely be concluded that at least that part of the weakly acidic group of Fig. 8 exceeding the one-per-methoxyl level may be due to the newly-formed carboxyl group.

The infrared absorption spectra of isolated chlorinated barium lignosulfonate also seem to support the theory of the presence of carboxyl groups in it. Figure 11 shows the infrared absorption spectra of ordinary α-lignosulfonic acid (curve I), chlorinated α-lignosulfonic acid (curve II), and chlorinated lignosulfonic acid reduced with sodium borohydride (curve III). Curve II, the absorption spectrum of chlorinated α-lignosulfonic acid, has two absorptions, at 1700 and 1750 cm^{-1}, which do not exist in the case of ordinary α-lignosulfonic acid (curve I). The absorption band at 1700 cm^{-1} disappears after reduction with sodium borohydride, suggesting that this band is due to the carbonyl group. The wave number of this band is somewhat higher than that of the ordinary carbonyl absorption of usual lignin, 1660 cm^{-1} 5). The wave number of the carbonyl group of lignosulfonic acid seems therefore to shift to the vicinity of 1700 cm^{-1} when chlorine is introduced; similarly, it is known that carbonyl groups of aldehyde, ketone and orthoquinone generally have absorption near 1660 cm^{-1} and

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5) H. Sofuye and S. Fukuhara, *J. Chem. Soc. Japan, Ind. Chem. Soc.* (*Kogyo Kagaku Zasshi*), **61**, 1070 (1958).

that this absorption shifts to the 1690 cm^{-1} region when chlorine is introduced into the molecule[6,7].

The absorption at 1751 cm^{-1} seems to be due to the carboxyl group influenced by chlorine, which group is, however, not clear in curve III. There exists, however, anothor, broad absorption at the vicinity of 2610 cm^{-1} which seems to be due to the carboxyl group[7]. It can, therefore, safely be concluded that there exist carbonyl groups and carboxyl groups in chlorinated lignosulfonic acid.

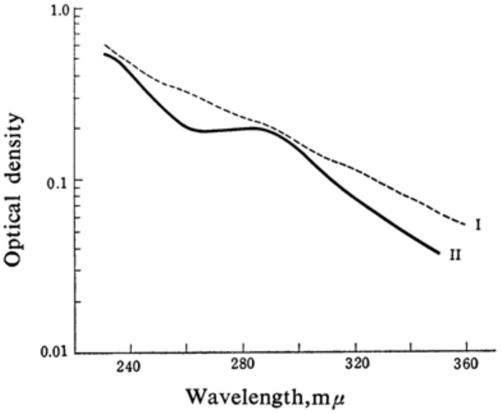

Fig. 12. Ultraviolet absorption curves of the solution of lignosulfonic acid after treatment with chlorine water. Curve I, Reaction mixture not reduced; Curve II, Reaction mixture reduced with sodium borohydride.

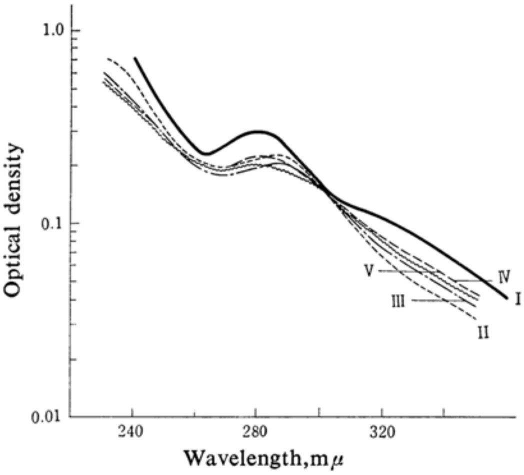

Fig. 13. Ultraviolet absorption curves of lignosulfonic acid at various stages of chlorination. (Spectra were taken after reduction with sodium borohydride.) Curve I, Original; Curve II, Cl$_2$/CH$_3$O=2.09; Curve III, 3.25; Curve IV, 4.1; Curve V, 5.35.

Figure 12 shows an example of the ultraviolet absorption spectra of lignosulfonic acid both immediately after chlorination and when reduced with sodium borohydride after the chlorination. The former has no minimum and maximum; these reappear only after the reduction. Figure 13 shows the ultraviolet absorption spectra of lignosulfonic acid reduced with sodium borohydride after chlorination to various stages. The minimum and maximum at 263 and 280 mμ in the spectrum of the original lignosulfonic acid shift to 270 and 285 mμ respectively. The fact that the optical density at 285 mμ maximum remains approximately constant might suggest that not very profound structural changes occur when 2 to 5 mol. of chlorine are consumed; i. e., the main part of the benzene ring structure seems not to be destroyed by the chlorination.

Experimental

Barium Lignosulfonate.—Barium lignosulfonate was prepared as usual from spruce (*Picea jezoensis*) sulfite waste liquor by 1-(*N*-piperidinoacetylamino)-naphthalene (PAN)[8], and was analyzed as follows: CH$_3$O, 11.95; S, 8.07%.

Chlorinated Barium Lignosulfonate. — Barium lignosulfonate (20 g.) was dissolved in a small portion of water and passed through ion-exchange resin in hydrogen form, and an aqueous chlorine solution was added (Cl$_2$/CH$_3$=2.48). After having been kept at 0°C for 5 min., this was diluted with water, and the chlorinated barium lignosulfonate was precipitated as usual from the above solution by PAN. As it is well known that the chlorine atoms in chlorinated lignin are at least partly unstable to alkali, the separation of the chlorinated lignosulfonic acid from the PAN salt thus obtained was performed as follows: The PAN salt of the chlorinated lignosulfonic acid was suspended in a small amount of water, mixed with ion exchange resin Amberlite IR-120 in hydrogen form, and shaken for about one hour, and then the solution of the chlorinated lignosulfonic acid thus obtained was again passed through ion-exchange resin Amberlite IR-120 in hydrogen form. The solution thus obtained was neutralized with barium carbonate, and the barium salt of the chlorinated lignosulfonic acid was isolated as usual.

Anal. CH$_3$O, 2.82; Cl, 12.45; Ba, 24.21%.

Chlorination.—Barium lignosulfonate containing 5 mmol. of the methoxyl group was dissolved in a small amount of water, passed through ion exchange resin in hydrogen form, and increased to 30 ml. To the lignin solution thus obtained were added, at 0°C, 190 ml. of an aqueous chlorine solution containing 23.2 mmol. of chlorine (the weight of chlorine is approximately 130% of that of lignin), and the whole was maintained at 0°C while being stirred. At definite periods, 1 ml. of the solution

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6) Marie-Louise Josién, N. Fuson and Jeanne-Marie Lebas, *J. Chem. Phys.*, **21**, 331 (1953).

7) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", Methuen & Co., London (1954).

8) B. Leopold, *Acta Chem. Scand.*, **6**, 64 (1952).

was sucked out and the amount of the chlorine consumed was measured iodometrically as usual. Another 30 ml. of the reaction solution was also sucked out into a graduated flask of 40 ml. capacity, several drops of allyl alcohol were added, the pH adjusted by alkali to 7, and increased to just 40 ml. Half of this solution was used for the sodium borohydride reduction, and the other half for conductometric titration.

Amount of Chlorine Consumed. — The amount was determined iodometrically as usual. No correction is applied for the orthoquinone structure which might be formed during the chlorination and thus exist in the solution. As is known, the orthoquinone structure is able to isolate iodine⁹⁾ from the iodide solution.

Reduction with Sodium Borohydride.—The above-mentioned solution (20 ml.) from the chlorination was reduced with sodium borohydride for one hour according to the method of Lindberg¹⁰⁾. As a control experiment, vanillin, 5-chlorovanillin, acetoguaiacon, propioguaiacon, camphorquinone and β-naphthoquinone were reduced by this method. The amount of the consumed borohydride were 100, 102, 97, 104, 96.6 and 104% of the theoreticals respectively. The chlorinated lignosulfonic acid isolated from the chlorination solution was also reduced. As is evident from Fig. 14, one hour is sufficient for complete reduction.

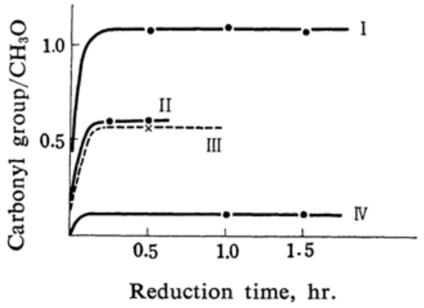

Fig. 14. $NaBH_4$ reduction of several lignin samples. Curve I, Chlorinated thiolignin ($Cl_2/CH_3O=4.58$); Curve II, Chlorinated hydrochloric acid lignin ($Cl_2/CHO_3=2.26$); Curve III, Chlorinated barium lignosulfonate; Curve IV, Thiolignin.

Conductometric Titration.—Four milliliters of the above-mentioned neutral solution (40 ml.) prepared from the chlorination solution were eluted through ion exchange resin in hydrogen form and were neutralized with 4∼5 ml. of a 0.1 N sodium hydroxide solution in order to neutralize a part of the hydrochloric acid. The solution thus obtained was titrated conductometrically with a 0.02 N sodium hydroxide solution. The amount of the weakly acidic group and/or weakly acidic substances were determined from the difference in the titers of the second and the first "breaks".

Ultraviolet Absorption Spectra. — The solution obtained after the above-mentioned reduction with sodium borohydride contains reaction products in reduced form. One milliliter of this solution was diluted to 50 ml. with water, and the ultraviolet absorption spectra were measured and shown directly as the optical density of the solution.

Infrared Absorption Spectra. — The infrared absorption spectra of barium lignosulfonate and chlorinated barium lignosulfonate were measured by the potassium bromide method using a Koken D 101 type infrared spectrophotometer (Japan).

Syntheses of the Model Compounds for the Conductometric Titration. — 5-Chlorovanillic acid was obtained by the oxidation of 5-chlorovanillin with silver oxide¹¹⁾; propiocatechon and propioguaiacon, by the condensation of propionic acid with catechol and guaiacol, according to the method of Nakazawa¹²⁾, and 5,6-dichlorovanillin, according to the method of Laiford¹³⁾.

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9) H. Meyer, "Analyse und Konstitutionsermittlung Organischer Verbindungen", 5. Aufl.), Verlag von Julius Springer, Berlin (1931), p. 628.

10) B. Lindberg and A. Misiorny, *Svensk Papperstidn.*, **55**, 13 (1952); B. Lindberg and J. Pajv. *Svensk Kem. Tidskr.*, **65**, 9 (1953).

11) I. A. Pearl, *J. Am. Chem. Soc.*, **68**, 1100 (1946).

12) K. Nakazawa, *J. Pharm. Soc. Japan* (*Yukagaku Zasshi*), **54**, 836 (1954).

13) L. C. Raiford and J. G. Lichty, *J. Am. Chem. Soc.*, **52**, 4576 (1930).