Studies on the Cooking Mechanism of Wood. XI.[1] *On the Amount of B-group, and the Reactivity with Thioglycolic Acid*

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(Received June 22, 1955)

Sulphonatable groups of lignin consist of different functional groups, namely, X, Z and B[2]. X and Z groups are sulphonatable even at neutral pH; B group is, however, only at low pH. B group, or at least a part of it, is thought to be a group of lignin, which is connected with carbohydrate of wood, or with another part of lignin by ether-linkage, or glycosidic linkage, or by other types of hydrolyzable linkages. The hydrolyzed B group is termed B' group[3].

Reactivity of the B Group with Thioglycolic Acid.—In the previous communication[4], it was shown that X and Z groups react with thioglycolic acid. It will, therefore, be very interesting to see if B group reacts also with thioglycolic acid or not. If one lets the low sulphonated lignosulphonic acid, and the acids obtained by further sulphonation of it, react with thioglycolic acid in homogeneous phase, and sees if the sulphonic acid group introduced to B group interferes with the reaction with thioglycolic acid or not, one can expect to obtain a definite conclusion of this question.

In order to be sure that the sulphonic acid group originally present in lignosulphonic acid is not split off by the treatment with thioglycolic acid–a condition which must be fulfilled in our case–it is necessary to know the content of sulphonic acid group of lignosulphonic acid treated with thioglycolic acid. Sulphonic acid group will be very easily estimated by conductometric titration. The estimation of the amount of the thioglycolic acid residue combined is, however, not so simple, because one can not calculate it from the difference of the total sulphur content and the sulphonic acid sulphur, as reportedly the sulphur atom of the lignosulphonic acid consists not only of acidic, but also non-acidic, so-called "excess sulphur"[5] the existence of which is also expected in the lignosulphonic acid treated with thioglycolic acid.

Hachihama, Shinra and Kyogoku[6] titrated conductometrically not only lignosulphonic acid, but also a mixture of lignosulphonic acid and acetic acid, and observed a distinct "break" in the titration curve of acetic acid, and the so-called weak acidic group of lignosulphonic acid itself. This fact suggests a possibility of estimating thioglycolic acid re-

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[1] Part X, H. Mikawa, This Bulletin, **24**, 53 (1954); Part IX, ibid., 50; Part VIII, H. Mikawa and K. Sato, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, **57**, 639 (1954).

[2] H. Erdtman, *Tech. Assoc. Pulp Paper Ind.*, 32, 71, 75 (1949); H. Mikawa, K. Sato, C. Takasaki and H. Okada, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, **54**, 299 (1951); B. Lindgren, *Acta Chem. Scand.*, 5, 603 (1951); E. Nokihara, *J. Agr. Chem. Soc. Japan*, **26**, 207, 236 (1952).

[3] H. Erdtman, *Research*, 3, 83 (1950).

[4] H. Mikawa and K. Sato, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, **57**, 605 (1954).

[5] O. Samuelson and A. Westlin, *Svensk Papperstidn.*, **50**, 141 (1947); **51**, 179 (1948).

[6] Y. Hachihama, H. Shinra and Y. Kyogoku, *J. Soc. Chem. Ind. Japan*, **47**, 209, 212 (1944).

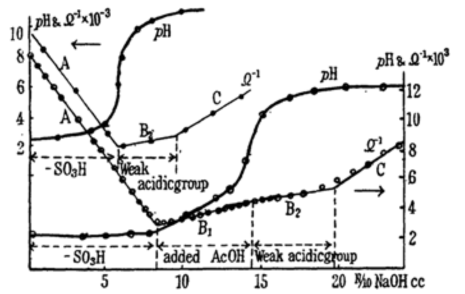

Fig. 1. Conductometric and potentiometric titrations of lignosulphonic acid (•) and a mixture of lignosulphonic acid and acetic acid (∘).

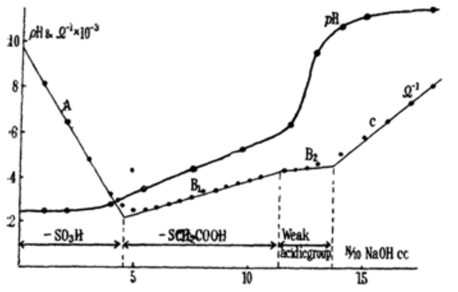

Fig. 2. Conductometric and potentiometric titration of lignosulphonic acid after reaction with thioglycolic acid.

sidue by conductometric titration, in spite of the presence of a weak acidic group of lignosulphonic acid itself. Examples of the conductometric and potentiometric titration curves of lignosulphonic acid, a mixture of lignosulphonic acid and acetic acid, as well as lignosulphonic acid treated with thioglycolic acid are shown in Figs. 1 and 2. The experiments of Fig. 1 were performed only in order to compare the curves with those of Fig. 2. As was reported by Hachihama, Shinra and Kyogoku, A-part of Fig. 1 corresponds to SO_3H group, B_2-part to the weakly acidic group, and the acetic acid added was titrated at B_1-part. The titration curve of the lignosulphonic acid treated with thioglycolic acid showed completely the same shape as the titration curve of a mixture of lignosulphonic acid and acetic acid, in this case B_1-part being due to carboxyl group of thioglycolic acid residue attached to lignin. In this case, the separation of the carboxyl group of thioglycolic acid residue from the "weakly acidic group" is not very distinct, but is possible.

Low sulphonated lignosulphonic acids with $S/CH_3O = 0.25–0.3$, prepared in the usual manner, were sulphonated further at pH 1.8, for various periods of hours. Total sulphur content, and the sulphonic acid group content of the lignosulphonic acids obtained, are shown by curves I and II of Fig. 3, and the data are summarized in Table I. The difference

TABLE I

FURTHER SULPHONATION OF LIGNOSULPHONIC ACIDS

	Condition of further sulphonation		Analyses of Ba-LSA after further sulphonation					
	pH	hrs.	Total S	S in the form of SO_3H	CH_3O	weak acidic group equiv./CH_3O	Total S/CH_3O	SO_3H/CH_3O
$LSLSA_a$	—	—	3.19	2.97	12.8	0.21	0.24	0.23
	1.8	3	5.80	5.49	11.6	0.27	0.48	0.45
		8	6.46	—	11.2	—	—	—
		16	8.16	6.98	10.5	0.30	0.75	—
		24	7.76	5.73	10.2	0.32	0.74	0.55
$LSLSA_b$	—	—	3.00	2.98	12.8	0.18	0.23	0.23
	1.8	3	5.31 A	4.87	10.8	0.25	0.48	0.44 A
		8	6.10 B	5.72	10.1	0.26	0.59	0.57 B
		24	8.21 C	6.68	10.4	0.30	0.77	0.63 C
		10+10*	6.70	6.12	10.2	0.26	0.64	0.58
		10+10+16	7.65	6.09	9.9	0.28	0.75	0.60
$LSLSA_c$	—	—	3.54	3.04	11.6	0.20	0.29	0.25
	5.8	20	5.73	4.99	9.8	0.20	0.57	0.49
		20+20	6.20	4.76	11.2	0.24	0.54	0.41
	8.5	10	4.25	3.94	11.4	0.22	0.36	0.34
		10+30	4.84	4.63	10.9	0.27	0.43	0.41
		10+30+20	5.01	4.27	11.0	0.28	0.44	0.38
LSA (from indust. waste liquor)	—	—	6.80	6.00	10.5	0.24	0.63	0.56
	1.8	3	6.24 D	5.71	10.8	0.24	0.56	0.52 D
		8	6.32 E	5.82	10.5	0.25	0.58	0.54 E
		16	6.78 F	6.15	11.4	0.24	0.58	0.52 F
		24	7.12 G	6.42	10.3	0.24	0.67	0.60 G

LSLSA=low sulphonated lignosulphonic acid, LSA=lignosulphonic acid *10+10 means that the sulphonation was continued another 10 hr. with fresh liquor after isolating and purifying LSA after the first 10 hr. of sulphonation.

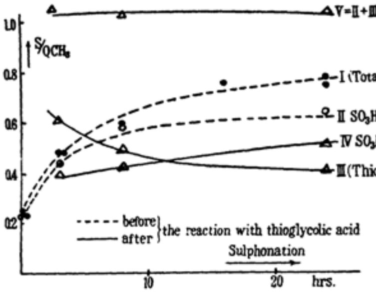

Fig. 3. Further sulphonation of low sulphonated lignosulphonic acid (LSLSA) and reaction of further sulphonated $LSLSA_b$ with thioglycolic acid.

of these two curves corresponds to the so-called "excess sulphur", which is not acidic in nature. Lignosulphonic acids with various degrees of sulphonation thus obtained, were heated with aqueous thioglycolic acid solution in 1 N hydrochloric acid, for ten hours at 100°C–the condition confirmed by the preliminary experiment, to be sufficient to complete the reaction. Because of the low solubility of the "low sulphonated lignosulphonic acid" in aqueous acidic solution of thioglycolic acid, this acid was not suitable for our purpose. Curves III and IV of Fig. 3 are the conductometrically obtained (Thio S)/CH_3O and SO_3H/CH_3O, after the reaction with thioglycolic acid, where "Thio S" means the sulphur due to the thioglycolic acid residue in the sample.

From the results shown in Fig. 3, it is evident that the sulphonic acid group originally present in the lignosulphonic acid is split off by the treatment with thioglycolic acid, by the amount of the difference of curves II and IV. This amount is however not so large as to invalidate the following discussion. As the content of the total sulphur and the sulphonic acid group increases along with the curves I and II, the amount of the thioglycolic acid group introduced drops rapidly to about 0.4 Thio. S/CH_3O. Thus, the sulphonic acid group introduced to B′-group interferes with the reaction with thioglycolic acid, from which it may be concluded that thioglycolic acid is able to combine with the B′-group too. Thioglycolic acid reacts with some another group, however, even after the complete sulphonation of lignin. This fact is most clearly shown by the lignosulphonic acid isolated from industrial waste liquor. As is known the lignosulphonic acid obtained from the waste liquor of industrial cooking can not be sulphonated, which is also clear from the lowest part of the table. Such lignosulphonic acid is, therefore, completely sulphonated, but does react with thioglycolic acid to some extent as is shown in the third column from the right side of Table II.

TABLE II

ANALYSES OF Ba-SALT A-G AFTER REACTION WITH THIOGLYCOLIC ACID

LSA	Total S	SO_3H	Thio S	CH_3O	SO_3H/CH_3O	Thio S/CH_3O	Total S/CH_3O	Thio S+SO_3H per CH_3O
A	8.47	3.37	5.11	8.20	0.40	0.61	1.00	1.01
B	8.56	3.90	4.55	8.95	0.42	0.49	0.93	0.91
C	8.22	4.59	3.57	8.73	0.51	0.40	0.91	0.91
D	7.34	4.20	3.34	8.98	0.45	0.36	0.79	0.81
E	7.61	4.33	3.02	8.89	0.47	0.33	0.83	0.80
F	7.48	4.56	3.02	8.95	0.50	0.33	0.81	0.83
G	7.42	4.56	2.82	8.88	0.50	0.31	0.81	0.81

The fact that the values of the last two columns of the table, i.e. those for analytically obtained (Total S)/CH_3O and (ThioS $+SO_3H$)/CH_3O, coincide well after the reaction with thioglycolic acid, indicates that "excess sulphur" which had been contained in the original lignosulphonic acid was eliminated during the reaction with thioglycolic acid.

On the Amount of the B-group.—Among the three different sulphonatable groups, the amount of X and Z groups are found to be about 0.12–0.14/CH_3O²⁾. The structure of these two groups are now almost clear, but that of B group is not so certain. The amount of this group was estimated by Lindgren⁷⁾ to be as much as 0.7/CH_3O. If this figure is correct, the sulphonatable groups with known structure, i.e. X and Z groups, are not more than one third of the total sulphonatable groups.

Further sulphonation of the low sulphonated lignosulphonic acid was studied by Leopold⁸⁾, and by his experiments it was made clear that the amount of sulphur introduced to lignin increased nearly up to one per methoxyl. Assuming the amount of the sum of X and Z groups as 0.3/CH_3O the amount

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7) B. Lindgren, *Svensk Papperstidn.*, **55**, 78 (1952).

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

of B group was estimated as 1–0.3=0.7. This conclusion was drawn from the analytically obtained total sulphur content of the lignosulphonic acid. As stated before, it was however made clear by Samuelson that not all of the sulphur of lignosulphonic acid consisted of acidic sulphonic acid group, being partly non-acidic sulphur, which he called "excess sulphur". If this excess sulphur combines with B-group, the amount of this group must be estimated from the total sulphur of the completely sulphonated lignosulphonic acid. If, on the other hand, the excess sulphur does not combine with B group, the amount of this group must be estimated from the amount of the sulphonic acid group of the carefully and completely sulphonated lignosulphonic acid.

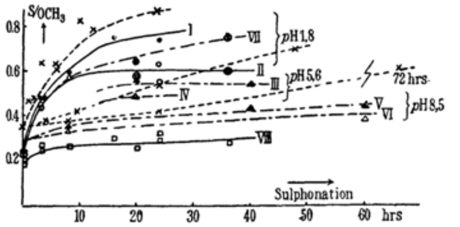

Fig. 4. Further sulphonation of low sulphonated lignosulphonic acid at three pH's.

pH	1.8	5.8	8.5
Total S	●I ⊙VII	▲III	▲V
SO_3H	○II ◎II	△IV	△VI

Curves I ● and II ○ are the same with I and II of Fig. 3.

Curves VII ⊙ and II ◎ were obtained at pH 1.8 changing cooking acid repeatedly with fresh one and purifying lignosulphonic acid.

Curve VIII is the amount of weak acidic group of lignosulphonic acids obtained at pH 1.8 in (equiv.)/OCH_3 scale.

…×… are the data reported by Erdtman and Leopold for (Total S)/OCH_3 at pH 1.8, 3.4 and 5.8.

For this purpose the low sulphonated lignosulphonic acid was sulphonated further at pH 1.8, 5.8 and 8.5, and the data obtained are shown in Table I and in Fig. 4. Curves I and II are (Total S)/CH_3O, and SO_3H/CH_3O of the lignosulphonic acids, obtained at pH 1.8. As the amount of sulphonic acid group is, however, considerably less than the total sulphur, and reaches its saturation value much earlier; the total amount of the sulphonatable group seems to be only about 0.6 per methoxyl, although it might not be impossible that some part of B' group had been changed to unsulphonatable structure during the reaction. Even if one carries out the sulphonation carefuly (curves VII and II), i.e. changing the cooking acid frequently with fresh acid and at the same time, isolating and purifying the lignosulphonic acid, the amount of the sulphonic acid group never exceeds 0.6– the value, obtained by ordinary one-step sulphonation. The difference between the total sulphur and the sulphonic sulphur is much smaller in this case, and consequently, the curve for the total sulphur (VII) approaches that of the sulphonic sulphur (II). If such were the case, many high values of the analytically obtained sulphur content of lignosulphonic acid reported in the literature might be due to the nonacidic "excess sulphur", which was introduced to some non-sulphonatable group, probably by thiosulphate formed during the sulphonation. From this point of view, the total amount of B group may be estimated, as only about 0.6–(X+Z)=0.3∼0.35 per methoxyl. The low sulphonated lignosulphonic acid, obtained from the sulphonated wood by Kullgren process can not represent the total lignin, contained in the wood. Lignosulphonic acid prepared from industrial waste liquor has, however, also about 0.6 SO_3H/CH_3O.

The amount of the weakly acidic group of lignosulphonic acid (curve VIII, Fig. 4) seems to remain nearly constant, irrespective of the further sulphonation. It is remarkable that even the so-called low sulphonated lignosulphonic acid contains nearly the same amount of weakly acidic group. The nature of this weak acidic group will be investigated in the next communication.

Experimental

Preparation of the low sulphonated lignosulphonic acid.—The method used is essentially the same with that of Erdtman[9]. Extractives free wood meal (100 mesh, 200 g.) was heated with neutral sulphite solution (pH 5.7, 1.5 l) to 135°C within 3 hrs. and kept at this temperature for 14 hrs. Sulphonated wood meal thus obtained was washed well with HCl (0.3%), and subsequently with distilled water, until free from Cl^-, heated twice with water for 4 hrs. each at 90°C, the combined extracts concentrated in vacuo, and the extracted low sulphonated lignosulphonic acid was precipitated by adding 1-(N-piperidinoacetylamino)-naphthalene sulphate[8]. The precipitate was washed with water until neutral pH, decomposed with 1% NaOH, and the free base separated, was filtered next day. The filtrate was passed through Amberlite IR 120 in hydrogen form, neutralized with $BaCO_3$, centrifuged, and the supernatant solution was poured into absolute

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[9] C. Kullgren, *Svensk Kem. Tid.*, **44**, 15 (1932); H. Erdtman, *Svensk Papperstidn.*, **48**, 75 (1945).

alcohol. The precipitated Ba-lignosulphonate was separated by centrifuge, washed well with alcohol, ether and petroleum ether successively.

Further sulphonation of Ba-lignosulphonate.—Ba-lignosulphonate (16 g.) to be sulphonated was dissolved in water, freed from barium by cation exchanger, sodium hydroxide (16 g.) added, and SO_2 was bubbled, until pH was lowered to the desired value (1.8–8.5), and the total volume was adjusted to 400 ml. by water. The solution was divided into four ampoules and heated at 135°C. After the sulphonation, the content was evacuated, passed through cation exchanger, evacuated again in order to expel SO_2, and the lignosulphonic acid was precipitated by 1-(N-piperidinoacetylamino)-naphthalene sulphate. The precipitate was treated as above.

Preparation of Ba-lignosulphonate from industrial waste liquor.—The waste liquor was dialyzed with cellophane membrane for 1–2 weeks, neutralized with $BaCO_3$, centrifuged, and the solution was poured into alcohol. The crude salt thus obtained was dissolved in water, passed through cation exchanger in hydrogen form, and the lignosulphonic acid was purified by the same precipitating agent as before.

Reaction of lignosulphonic acid with thioglycolic acid.—Ba-lignosulphonate (1 g.) was dissolved in water, passed through cation exchanger, thioglycolic acid (3 g.) and dil. HCl added, and the whole was made up to 30 ml. and adjusted to 1 N with respect to HCl. The solution was heated at 100°C for 10 hrs., extracted continuously with ether in order to remove excess thioglycolic acid, and the lignosulphonic acid was separated by the precipitating agent, and processed just the same as mentioned above.

Analyses.—Sulphur with micro Carius and CH_3O according to Viebök-Blecher and Gran[10]. Conductometric and potentiometric titrations were performed with a solution of lignosulphonic acid, which was prepared by passing a solution (20 ml.) of Ba salt (500 mg.) through cation exchanger, and making up to 50 ml. with water.

Summary

B-group of lignin reacts with thioglycolic acid. Total amount of the sulphonatable groups of lignin is about $0.6/CH_3O$, the amount of B-group being consequently $0.3–0.35/CH_3O$. Higher S/CH_3O values reported in the literature may be due to the presence of non-acidic "excess sulphur".

The authors are indebted to Dr. H. Okada, the head of our laboratory, and to Miss. S. Suehiro for their encouragement.

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[10] G. Gran, *Svensk Papperstidn.*, 55, 255 (1952).