

During the present work the following new DL-1-acetyl-2-thiohydantoin (III) were prepared from the appropriate α -amino acids according to the usual procedure⁶.

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Studies on Lignin. XII. * Alkaline Desulphonation of Radioactive Lignin Sulphonic Acid

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When lignin sulphonic acids are heated with aqueous alkali, they gradually undergo desulphonation^{1,2}, with the formation of sulphite. Under suitable

conditions this process can be effected stepwise³, and it was considered that a detailed study of the reaction might throw much light on the problem of the nature of the sulphonatable groups in lignin.

This preliminary communication describes some desulphonation experiments with a spruce "Kullgren acid" (S = 5.5 %, Ba/S = 0.50, S/OCH₃ = 0.49) which was further sulphonated with sulphite containing S³⁵, and then analyzed as follows: S = 6.8 %, Ba/S = 0.53, S/OCH₃ = 0.68. The data obtained during desulphonation are listed in Table 1.

Table 1. Alkaline desulphonation of lignin sulphonic acid.

Time of alkali treatment minutes	Sulphur removed as SO ₂ (c), % of total	Specific S ³⁵ activity (relative values)
15	26.1	100 ± 0.5
30	30.2	97.7 ± 0.9
50	32.0	95.0 ± 0.7
110	36.7	91.3 ± 0.7
170	39.9	89.0 ± 0.4

The figures of the last column are averages of 4 measurements.

The statistical error is 0.4–0.5 %.

Initially, sulphite is formed rapidly, but subsequently much more slowly as is evident from Fig. 1, in which ln (100-c) is plotted against time.

The graph shows clearly that the desulphonation involves two reactions, one relatively fast and one relatively slow. In the rapid reaction about 30 % of the total sulphur is liberated. (This figure, obtained by extrapolation, changes only little if it be assumed that only e.g. 75 % of the total sulphur may be liberated.)

The specific activity of the liberated SO₂ decreases regularly with time, showing that the sulphur introduced in the second phase of the sulphonation is most readily

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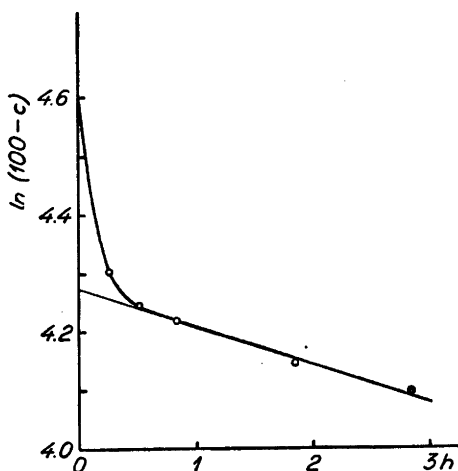


Fig. 1. $\ln(100-c)$ as a function of time.

removed. In theory it is possible to calculate the specific activities of the sulphur liberated in the two stages of the desulphonation, but to do so on the basis of the present incomplete data would be premature.

Experimental. Active BaS (from Oak Ridge) was diluted with inactive sulphide and the sulphide ions were precipitated as CdS. Hydrogen sulphide, liberated by treatment with conc. orthophosphoric acid, was combusted to sulphur dioxide which was absorbed in 2 N sodium hydroxide. The active sulphite solution was acidified to pH 1.5 with inactive sulphur dioxide and then used for the sulphonation of the Kullgren acid⁴. (Temperature 135°, time 6 hours.) The product was isolated in the usual manner⁴. Sulphur was determined by the method of Salvesen and Hogan⁵.

For desulphonation, the active barium lignin sulphonate (0.8 g) was dissolved in water and the solution was heated to 100°. Sodium hydroxide solution (0.2 mol), preheated to 100°, was then added (final volume 80 ml, nitrogen atmosphere). The reaction was stopped by the addition of conc. hydrochloric acid. The sulphur dioxide was expelled by a current of nitrogen and absorbed in a Grote-Krekeler apparatus containing dilute hydrogen peroxide solution. The sulphuric acid formed was determined by precipitation with barium

chloride, and the barium sulphate precipitate prepared for the measurement of the S^{35} activity by centrifugation in tubes with removable bottoms, using a refined procedure developed by G. Aniansson and A. Edhborg (cf. Larson *et al.*⁶).

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Studies on the Chemistry of Oil Tanning. I. Formation of Peroxide Groups in the Oils

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The very old method of tanning, oil tanning, is, in this country, carried out in the following way. After the skins, mostly from sheep or deer, have been split, the flesh layers are impregnated with oil which is squeezed into the skins with heavy beaters in a stamping mill. This milling is repeated about ten times. Between every treatment the skins are exposed to the sun for about one hour and then packed close together until the next milling, new oil being sometimes added. Between the last millings the skins are hung in heated rooms where the tanning process proceeds rapidly with the liberation of heat and the skins assuming a yellowish colour. When heat ceases to be evolved the tanning process has finished.

The oils used in the tanning are highly unsaturated, usually marine oils, such as