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The Reaction of Propane Sultone with Macromolecules. I. Cellulose and Starch

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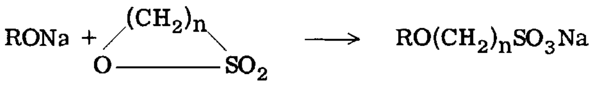
SUMMARY

Propane sultone reacts with alkali cellulose or alkali starch yielding sodium sulfopropyl derivatives. The highest degree of substitution (D.S.) is obtained when 2 moles of sodium hydroxide and 2 moles of sultone are reacted with 1 mole of cellulose or starch in a water-miscible organic solvent such as isopropanol or acetone at 45°C. Under these conditions cellulose yields a product with a D.S. of 0.68 and starch a product with a D.S. of 1.13. Celluloses of different molecular weights do not show marked differences in reactivity. Sodium sulfopropyl cellulose is water-soluble when the D.S. exceeds 0.20. Sodium sulfopropyl starch is always water-soluble, giving extremely viscous solutions. The free acids are made by treatment of the sodium salts with hydrogen chloride in methanol. They are, however, degraded to low molecular weight products. This is not the case with derivatives cross-linked by means of epichlorohydrine. These cross-linked derivatives swell but do not dissolve in water, and they can be used as ion-exchange resins.

INTRODUCTION

Sulfoalkyl ethers of cellulose and starch have been relatively little investigated. The lower sulfoalkyl ethers have been prepared by reaction of alkali cellulose or alkali starch with appropriate halogenated alkanesulfonates such as sodium chloromethane sulfonate [1, 2] or 2-chloroethane sulfonate [3-7]. Sulfoethyl cellulose has also been obtained by reaction of alkali cellulose with sodium ethene sulfonate [8].

Higher sulfoalkyl ethers could also be made by reaction of alkali cellulose or alkali starch with the corresponding chloroalkane sulfonates. However, these are more difficult to obtain and a better way consists in using sultones which are known to react nearly quantitatively with alcoholates [9-13] to form the corresponding sulfoalkyl ethers.



(I) n = 3
(II) n = 4

The reaction of alkali cellulose with butane sultone (II) was reported by Helberger et al. in 1954 [9], and in 1962 Husemann and Kafka described the synthesis of sulfopropyl amylose by reaction of alkali amylose with propane sultone (I) [14].

In a preliminary communication we reported the synthesis of sulfopropyl cellulose by reaction of propane sultone with alkali cellulose [15]. In the present paper the influence of several variables on the reaction between propane sultone and cellulose or starch are studied and the properties of the obtained sulfopropyl derivatives are described.

During the course of this work some articles and patents describing the reaction of propane sultone with alkali cellulose [16, 17] and with wheat flour [18] and the reaction of butane sultone with alkali starch [19] have appeared. The results mentioned in these publications sometimes differ markedly from our results.

SYNTHESIS OF THE SULFOPROPYL DERIVATIVES

Sulfopropyl Cellulose

Cellulose as such did not react with propane sultone but sulfoalkylation occurred readily with alkali cellulose. As shown with the data of Table 1, the best results were obtained when alkali cellulose was suspended in a water-miscible solvent such as dioxane, acetone, or isopropanol. When ethanol was used, no reaction occurred. The best results were obtained with isopropanol, so the reaction was studied in more detail in this medium. By measuring the decrease of sodium hydroxide concentration in the reaction mixture, it was found that the reaction was practically finished after 6 hr at room temperature. At 45°C the yields were higher but further increase of temperature did not affect the yield. At 60°C important degradation of the cellulose chain occurred. Experiments 8 to 11 (Table 1) show that excess sodium hydroxide gave lower yields and

Table 1. Synthesis of Sodium Sulfopropyl Cellulose: Influence of Several Variables on the D.S. of the Reaction Product[a]

Expt. No.	Solvent	Molar ratio[b]	Temp., °C	D. S.
1	Ethanol	1:2:2	45	0.02
2	Acetone	1:2:2	45	0.63
3	Dioxane	1:2:2	45	0.65
4	i-PrOH	1:2:2	45	0.68
5	i-PrOH	1:1:1	45	0.37
6	i-PrOH	1:3:3	45	0.57
7	i-PrOH	1:4:4	45	0.51
8	i-PrOH	1:2:2	20	0.48
9	i-PrOH	1:4:2	20	0.22
10	i-PrOH	1:6:2	20	0.11
11	i-PrOH	1:2:4	45	0.68

[a] Reaction time, 6 hr; water, 10-15%.

[b] Molar ratio of anhydroglucose units/sodium hydroxide/sultone.

that excess propane sultone gave no increase of the degree of substitution (D.S.). Figure 1 (curve a) shows the relation between the amount of sodium hydroxide and propane sultone (equimolar quantities) which was allowed to react with cellulose and the D.S. of the obtained sulfopropyl cellulose. From this figure it follows that the maximum D.S. was obtained with 2 moles of sodium hydroxide and 2 moles of sultone for 1 mole of anhydroglucose units.

The concentration of water was of great importance. As shown in Fig. 2 (curve a), no substitution occurred in the absence of water. Under the conditions mentioned the optimal water concentration was between 10 and 20%.

To obtain products with higher D.S. two methods were used. The first one consisted of reacting propane sultone with sulfopropyl cellulose instead of cellulose. The second method, which is the best, consisted in adding equimolar amounts of sodium hydroxide and propane sultone at regular intervals. Sulfopropyl cellulose having a D.S. of 1.14 was obtained by adding three times 2 moles of sodium hydroxide and 2 moles of propane sultone every 4 hr. Between the addition of sodium hydroxide and propane sultone the mixture was stirred for ½ hr.

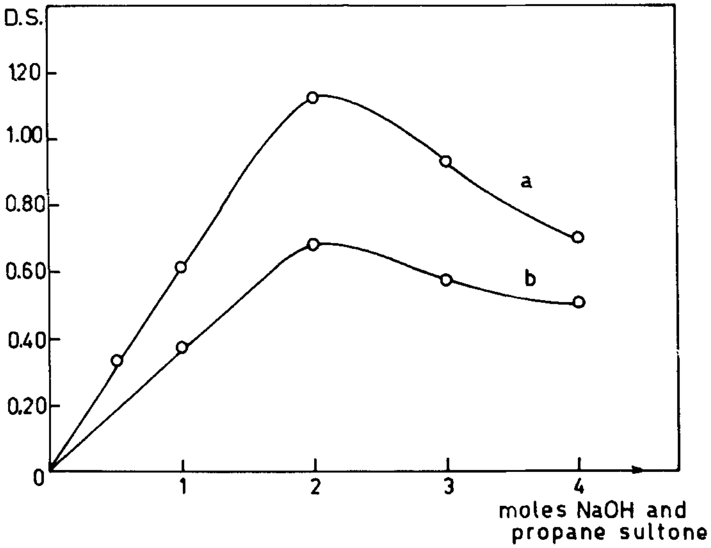


Fig. 1. Influence of the molar ratio (sodium hydroxide and propane sultone) to (anhydroglucose units) on the D.S. of the obtained sulfopropyl derivatives. a, starch (solvent: acetone); b, cellulose (solvent: isopropanol); temperature, 45°.

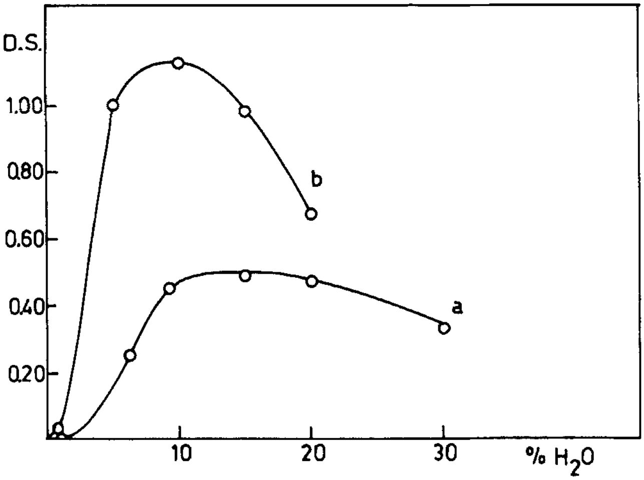


Fig. 2. Influence of the water concentration on the D. S. of the sulfopropyl derivatives. a, cellulose (solvent: isopropanol); b, starch (solvent: acetone); molar ratio anhydroglucose units/sodium hydroxide propane sultone, 1 : 2 : 2.

Celluloses of different molecular weights (between 100, 000 and 450, 000) showed only little difference in reactivity (see Table 5).

As shown in Table 2, when low ratios of cellulose/sodium hydroxide/propane sultone were used, the yields were somewhat higher when less solvent was used. This effect was not observed at higher ratios.

Table 2. Influence of Dilution on the D.S. of Sodium Sulfopropyl Cellulose[a]

Expt. No.	Concn. of cellulose, wt./vol. %	Molar ratio[b]	D.S.
12	5	1 : 1 : 1	0. 30
5	10	1 : 1 : 1	0. 37
13	5	1 : 2 : 2	0. 67
4	10	1 : 2 : 2	0. 68

[a] Solvent, isopropanol; t, 45°C; reaction time, 6 hr; H_2O, 15%.
[b] Molar ratio of anhydroglucose units/sodium hydroxide/sultone.

Sulfopropyl Starch

Pure starch dissolved in dimethylsulfoxide reacted with propane sultone in the presence of potassium carbonate, but the yields were low (maximum 8%). Sulfopropylation occurred readily with alkali starch, suspended in a water-miscible organic solvent. The data of Table 3 clearly show the greater reactivity of starch compared to cellulose. The highest yields were obtained when isopropanol or acetone was used as the reaction medium, and, as with cellulose, practically no reaction occurred in ethanol. Also water had to be present. As shown in Fig. 2 (curve b), the highest yields were obtained at water concentrations between 5 and 15%. The important decrease of the yield at higher concentrations was principally due to the fact that the formed sulfopropyl starch was very water-soluble and clotted to a sticky or rubbery mass, which made further reaction difficult. This clotting did not occur when products with a low D.S. were prepared. Acetone caused less clotting than isopropanol.

When equimolar amounts of sodium hydroxide and propane sultone were allowed to react with starch, a maximum D.S. was obtained when the ratio anhydroglucose units/sodium hydroxide/sultone was 1 : 2 : 2 (Fig. 1, curve b). Excess of sodium hydroxide gave a lower D.S. (expt. 22).

Table 3. Synthesis of Sodium Sulfopropyl Starch: Influence of Several Variables on the D.S. of the Reaction product[a]

Expt. No.	Solvent	Molar ratio[b]	D.S.
14	Ethanol	1 : 2 : 2	0. 10
15	Acetone	1 : 2 : 2	1. 13
16	Dioxane	1 : 2 : 2	0. 69
17	i-PrOH	1 : 2 : 2	1. 08
18	i-PrOH	1 : 0. 5 : 0. 5	0. 33
19	i-PrOH	1 : 1 : 1	0. 61
20	Acetone	1 : 3 : 3	0. 93
21	Acetone	1 : 4 : 4	0. 70
22	Acetone	1 : 3 : 2	0. 64

[a] Reaction time, 6 hr; t, 45°C; water, 10-15%.
[b] Molar ratio of anhydroglucose units/sodium hydroxide/sultone.

PROPERTIES OF THE SULFOPROPYL DERIVATIVES

Solubility

From Table 4 it can be seen that the solubility of sulfopropyl cellulose increased with higher D.S. However, the conditions during the preparation also played an important role. Higher water concentrations gave more soluble products and clearer solutions. Products obtained in isopropanol generally were more soluble than those prepared in other solvents.

All sulfopropyl starches gave clear, extremely viscous, and stable water solutions.

Table 4. Solubility of Sodium Sulfopropyl Cellulose in Water

D.S.	Solubility
0-0. 10	Insoluble
0. 10-0. 40	Swells or partially soluble
0. 30-0. 50	Turbid solutions
0. 40 or higher	Clear solutions

All starch and cellulose products were insoluble in methanol, ethanol, or other organic solvents. Fe^{3+}, Pb^{2+}, and Th^{4+} ions formed insoluble salts with sulfopropyl cellulose and with sulfopropyl starch.

Viscosities

Table 5 gives a summary of the viscosities of aqueous 0.5% solutions of various sulfopropyl celluloses having approximatively

Table 5. Preparation and Viscosity Properties of Sodium Sulfopropyl Cellulose Made from Cellulose of Different Molecular Weight[a]

Expt. No.	Type of cellulose	Mol. wt.[b]	D.S.	Viscosity,[c] cP
23	ES 5	102,000	0.68	10.8
24	ES 200	266,000	0.67	57.9
25	ES 2000	395,000	0.65	103.0
26	ES 4000	431,000	0.65	159.0

[a] Molar ratio of anhydroglucose units/sodium hydroxide/sultone, 1 : 2 : 2; t, 45°C; reaction medium, 80% isopropanol.

[b] Values kindly supplied by Hercules Powder Co.

[c] Viscosity of a 0.5% solution in water (t = 25°C).

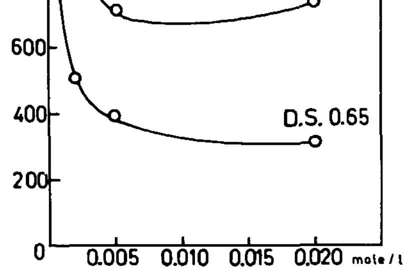


Fig. 3. Influence of the concentration of sodium sulfopropyl cellulose on the reduced viscosity of aqueous solutions at 25°.

the same D.S. made from celluloses of different molecular weight. Figure 3 shows the variation of the reduced viscosity of aqueous solutions of sulfopropyl cellulose as a function of the concentration. This behavior is typical for polyelectrolytes.

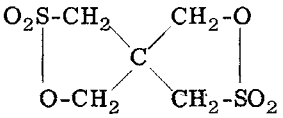
A 0.5% solution of sulfopropyl starch (D.S. 0.75) had a viscosity of 2250 cP.

Preparation of the Free Acids

Sodium sulfopropyl cellulose suspended in methanol was treated several times with dry hydrogen chloride. After each treatment the product was filtered off and finally washed with methanol until the filtrate was no longer acidic. In this way it was possible to obtain sulfopropyl cellulose in the acidic form. The number of acidic groups corresponding to the D.S. was found by titration. However, the cellulose molecules were considerably degraded. For example, the free acid obtained from a sodium salt which had a viscosity of 103 cP as a 0.5% solution had a viscosity of only 1.5 cP at the same concentration. When this acid was neutralized with sodium hydroxide, a sodium sulfopropyl cellulose formed again having a low viscosity of 1.4 cP. Sulfopropyl cellulose or starch in the acidic form were hydroscopic and swollen or even partially dissolved by methanol or ethanol.

Preparation of Insoluble Derivatives

A first attempt to make insoluble sulfopropyl cellulose consisted in reacting a mixture of propane sultone and 2,2-bis(hydroxymethyl)-propane-1,3-disulfonic acid disultone (III) with alkali cellulose, which was expected to lead to a cross-linked product. However, the disultone was not incorporated because of its low reactivity, which has also been observed in other reactions [20].


(III)

A better method to cross-link cellulose or its derivatives is reaction with epichlorohydrin in an alkaline medium. When this cross-linking was carried out on sulfopropyl cellulose or sulfopropyl starch, insoluble products were indeed obtained. Since the reaction conditions for sulfoalkylation and for cross-linking are about the same, both reactions can be carried out sequentially without isolation of the sulfopropyl derivative. Table 6 shows some examples of preparations and the ion-exchange capacities of the obtained products. Cross-linked sulfopropyl cellulose ob-

Table 6. Capacity of Insoluble Sulfopropyl Cellulose or Starch[a]

Expt. No.	Starting material (D.S.)	Molar ratio A[b]	molar ratio B[c]	Capacity, meq/g
27	SP cellulose (0.68)	—	1:2:2	2.26
28	Cellulose (—)	1:2:2	1:2:2	2.75
29	SP starch (1.00)	—	1:2:2	2.25
30	Starch (—)	1:2:2	1:2:2	2.50

[a] The reactions were carried out in 80% acetone at 45°C.

[b] Molar ratio of anhydroglucose units/sodium hydroxide/propane sultone.

[c] Molar ratio of anhydroglucose units/sodium hydroxide/epichlorohydrin.

tained in the described manner is a slightly yellow colored granular substance; cross-linked sulfopropyl starch is a colorless powder. Both swell in water but remain insoluble; hence they can easily be packed in a column and be used as an ion-exchange resin. They do not degrade when kept in the acidic form, as was found for the non-cross-linked products.

EXPERIMENTAL

Commercial propane sultone was distilled under reduced pressure, b.p.$_{8mm}$ 140°C. Cellulose of the "chemical cotton" type (cotton linters) in the form of sheets was supplied by Hercules Powder Co. The types used were ES 5, ES 200, ES 2000, and ES 4000. Most experiments were performed with ES 2000. The cellulose sheets were passed several times under heavy pressure between two rollers driven at a different speed and transformed into a fine powder by means of a hammer mill. This treatment does not degrade the cellulose [21]. Pure starch, derived from rice, was used as supplied. Solvents were distilled before use. Viscosity measurements were carried out with a Hoeppler viscosimeter.

General Procedure for the Preparation of Sodium Sulfopropyl Cellulose

To a well-stirred suspension of 17 g of cellulose (with a water content of 5%) in 125 ml of isopropanol and 15 ml of water was added 20.5 ml of a 30% sodium hydroxide solution. The mixture was stirred at room temperature for 1 hr, then 24.4 g of propane sultone dissolved in 20 ml of acetone was added and the mixture vigorously stirred at 45°C for 6 hr and left overnight at room temperature. The mixture was poured into 500 ml of methanol and the obtained suspension was neutralized with acetic acid. The precipitate was filtered off, washed with 90% methanol until the filtrate was salt-free, and dried in vacuum at room temperature. The product contained 5.98% sodium and 8.11% sulfur, which corresponds to sulfopropyl cellulose with a D.S. of 0.65-0.68. (Yield: 32.5-34% calculated on propane sultone.)

Sodium Sulfopropyl Starch

This was prepared in the same way as sodium sulfopropyl cellulose except that the reaction was preferably carried out under nitrogen. When the same quantities were used as described for the preparation of sulfopropyl cellulose, sulfopropyl starch containing 7.83% sodium, corresponding to a D.S. of 1.08, was obtained (Yield: 54%, calculated on propane sultone.)

Preparation of Insoluble Sulfopropyl Cellulose

By vigorous stirring, 17 g of cellulose was suspended in 125 ml of acetone and 20.5 ml of a 30% sodium hydroxide solution for 1 hr at room temperature. Added was 24.4 g of propane sultone dissolved in 20 ml of acetone, and the mixture was stirred for 6 hr at 45°C. Then 20.5 ml of a 30% sodium hydroxide solution was added again, together with 50 ml of acetone to reduce the water concentration to 20%. After 1 hr of stirring, 18.5 g of epichlorohydrin was added, and the reaction mixture was stirred for 6 hr at 45°C. The reaction mixture was poured into 500 ml of methanol and neutralized with acetic acid. The precipitate was filtered off, washed with 50% methanol until the filtrate was free of salt, and dried in vacuum at room temperature. The exchange capacity of the product was determined as follows: 2.5 g of the substance was suspended in 50 ml of 1 N aqueous hydrogen chloride. After 1 hr the product was allowed to precipitate and the acid solution was decanted. This procedure was repeated three times. The acidified ion exchanger was packed in a column and washed with twice-distilled water until the eluate was acid-free. Aqueous sodium hydroxide (250 ml of 0.1 N) was passed through the column, and the column was washed again with twice-distilled water until neutral. By titration of the excess sodium hydroxide in the eluate, it was found that 6.87 meq of sodium hydroxide had been neutralized on the column, corresponding to an ion-exchange capacity of 2.75 meq/g.

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