

## Reversible Crosslinking in Cellulose. VI. Formation of Sulfonium Derivatives by the Reaction of Cellulose $\beta$ -Mercaptoethylaminocarboxylate with Methyl Iodide

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### Synopsis

The reaction of methyl iodide with cellulose  $\beta$ -mercaptoethylaminocarboxylate (RDTC) made from cotton was investigated. The product was found to contain dimethyl sulfonium groups in addition to S-methyl groups, with accompanying hydrolytic cleavage of some of urethane linkages. The iodide counterions could be easily exchanged with hydroxide and chloride ions. The dyeability of RDTC and its sulfonium derivatives toward Direct Sky Blue A was studied. The equilibrium uptake of the dye by RDTC decreased with increasing sulfur content, while the uptake by the sulfonium derivatives was higher than that of control cotton and increased with increasing sulfonium content. The counterions did not affect the dyeability. The dye adsorbed onto the sulfonium derivatives was very fast against solvent extraction, and could be extracted only with Cadoxen containing 0.5% sodium hydroxide. The equilibrium uptake of the dye was much more than the amount calculated on basis of the 1:1 ionic bonding between the sulfonic acid group in the dye molecule and the sulfonium group in the modified cotton. The spatial effect in the dye-sulfonium bonding is discussed.

### INTRODUCTION

A recent publication<sup>1</sup> has demonstrated that the reaction of cotton with bis- $\beta$ -isocyanatoethyl disulfide yields disulfide-crosslinked cotton (DTC), which can be converted to the uncrosslinked form, cellulose  $\beta$ -mercaptoethylaminocarboxylate (RDTC), by reduction with tri-*n*-butylphosphine. In a preliminary stage of the work<sup>2</sup> on the effect of crosslinks on the dyeability of cotton, the direct dye adsorption behaviors of DTC and RDTC were compared to show that both DTC and RDTC uptook only very limited amounts of the dye. It has often been observed that crosslinked cotton exhibited a reduced dyeability<sup>3</sup> so that the reduced dye uptake of DTC was not unexpected. RDTC would possibly undergo oxidation during dyeing to form a crosslinked product which would result in the reduced dyeability. It became necessary to investigate the dyeing behavior

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of mercaptan-blocked RDTC. It was found that the RDTC blocked with acrylonitrile adsorbed as small an amount of a direct dye as the unmodified RDTC. The RDTC treated with methyl iodide adsorbed ten times as much dye as did control cotton. The dyestuff on the RDTC treated with methyl iodide (MRDTC<sub>i</sub>) could not be extracted with aqueous pyridine. The anomaly of this derivative in the dyeing seemed to be explained by the formation of a sulfonium derivative from RDTC during the treatment with methyl iodide.

In this report, the reaction of RDTC with methyl iodide will be discussed, and some additional data on the dyeability of the MRDTC<sub>i</sub> will be given to confirm the early observations.

## EXPERIMENTAL

### Material and Reagents

All samples were prepared from 140 × 70, bleached, scoured, and unmercerized cotton printcloth kindly provided by Fuji Spinning Co. Ltd., Japan.

Cellulose  $\beta$ -mercaptoethylaminocarboxylate (RDTC) was prepared by treating cotton fabrics with bis- $\beta$ -isocyanatoethyl disulfide in dimethylformamide at 80°C followed by reduction with tri-*n*-butylphosphine in methanol containing 10% water, as described in a previous paper.<sup>1</sup>

Direct Sky Blue A was purified according to the literature.<sup>4</sup> Orange II was purified by recrystallization from water. Cadoxen containing 0.5% sodium hydroxide was prepared according to the procedure of Achwal and Gupta.<sup>5</sup>

### Treatment of RDTC with Methyl Iodide

**Procedure A.** RDTC was treated with 2% methyl iodide in a methanol-water (4:1) mixture containing 0.5% sodium bicarbonate at boiling temperature for 5 hr, with a liquor ratio of 1:50. The treated sample (MRDTC<sub>i</sub>) was washed with water, extracted with acetone in a Soxhlet apparatus, and dried in vacuo.

**Procedure B.** RDTC was treated with 2.5% methyl iodide in a 1:1 mixture of a buffer of pH 8.0 and methanol at room temperature for 40 hr, with a liquor ratio of 1:100. The treated sample (MRDTC<sub>i</sub>) was washed and dried as in procedure A.

### Dyeing

The sample was dyed with 0.5 mmole/l. Direct Sky Blue A containing 5 g/l. sodium chloride at 40°C for five days, with a liquor ratio of 1:20 or 1:40. The dyebath was shaken for the first several hours mechanically in a thermostat and then kept there without shaking. The dyed sample was rinsed thoroughly with cold water and dried in vacuo. The adsorbed dye was extracted with Cadoxen containing 0.5% sodium hydroxide at room

temperature for up to one day, and its amount was determined spectrophotometrically.

### Analysis

Mercaptan and disulfide in modified cotton were determined by the polarographic method.<sup>6</sup>

Sulfur was determined by the Safford-Mitsui method<sup>7</sup> with a Mitamura Micro Elemental Analyzer where sulfur was weighed as silver sulfate. Halogens if present in the sample also cause weight increase of silver because of the formation of silver halides.

Potentiometric titration of the sulfonium hydroxide derivative (MRDTC<sub>b</sub>) was carried out similarly to the procedure used for cellulose quaternary ammonium derivatives,<sup>8</sup> as follows: MRDTC<sub>i</sub> was treated with 0.05*N* sodium hydroxide for several times, washed thoroughly with distilled water, and placed in distilled water with nitrogen bubbled through, and dried in vacuo. The sample was placed in 1 *M* sodium chloride under nitrogen and titrated potentiometrically with 0.1*N* hydrochloric acid in ca. 8 hr.

The infrared analysis of the urethane concentration in modified cotton was made with the KBr disk technique as described previously.<sup>2</sup>

## RESULTS AND DISCUSSION

### Formation of Sulfonium Salt

RDTC samples of three different levels of sulfur content were prepared<sup>1</sup> and treated with excess methyl iodide in a boiling methanol-water (4:1) mixture containing 0.5% sodium bicarbonate for 5 hr (reaction procedure A). The mercaptan and disulfide contents of the products (MRDTC<sub>i</sub>) were determined by the polarographic method<sup>6</sup> to reveal that all mercapto groups in RDTC were substituted without formation of disulfide groups (Table I). The sulfur content of MRDTC<sub>i</sub> was determined by the Safford-

TABLE I  
Sulfonium Derivatives from RDTC

Reaction procedure <sup>a</sup>	RDTC S, %	MRDTC <sub>i</sub>			MRDTC <sub>b</sub>	MRDTC <sub>c</sub>	
		SH, $\mu$ mole/g	SS, $\mu$ mole/g	I, $\mu$ mole/g	Sulfonium, $\mu$ mole/g	Cl, $\mu$ mole/g	
A	0.31	4	0	31	0.16	20	
A	1.48	1	2	161	1.06	150	
A	2.84	5	0	247	2.15	235	228
B	1.48			125	1.35	245	220
B	2.84			130	2.25	335	328

<sup>a</sup> A: Treated with 2% methyl iodide in methanol-water (4:1) containing 0.05% sodium bicarbonate at boiling temperature for 5 hr; B: treated with 2.5% methyl iodide in a 1:1 mixture of a buffer of pH 8.0 and methanol at room temperature for 40 hr.

TABLE II  
Infrared Analyses of Sulfonium Derivatives

RDTC S found, %	MRDTC <sub>i</sub> S calcd., <sup>a</sup> %		MRDTC <sub>h</sub> S found, %	MRDTC <sub>h</sub> S calcd., <sup>a</sup> %		MRDTC <sub>c</sub> S calcd., <sup>a</sup> %	
	I	II		I	II	I	II
	1.48	1.25		1.20	1.03	1.20	1.20
2.84	2.40	2.20	2.15	2.30	1.95	2.30	2.15

<sup>a</sup> Sulfur contents were calculated from urethane contents obtained from intensities of infrared absorptions of amide I band (I) and amide II band (II).

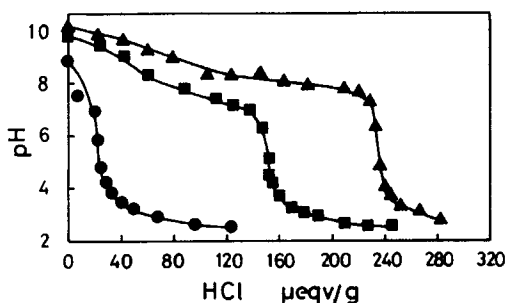


Fig. 1. Potentiometric titration curves of MRDTC<sub>h</sub> with 0.1N HCl in the presence of 1M NaCl. Sulfur contents of MRDTC<sub>h</sub>: (●) 0.16%; (■) 1.06%; (▲) 2.15%.

Mitsui method.<sup>7</sup> The apparent sulfur content was increased by the treatment. Halogens as well as sulfur can increase the weight of silver in the elemental analysis system used. Therefore, the apparent increase in the sulfur content was attributable to the presence of iodine as sulfonium iodide which was produced by the successive reaction of excess methyl iodide with S-methyl groups first formed.

MRDTC<sub>i</sub> assumed to be an iodide was treated with dilute alkali, washed thoroughly with water, and titrated potentiometrically with 0.1N hydrochloric acid. The titration curves are given in Figure 1. The amount of sulfonium groups in the hydroxide derivative (MRDTC<sub>h</sub>) was calculated to show that 21–33% of mercapto groups in RDTC were converted to sulfonium groups under procedure A.

The sulfur content of MRDTC<sub>h</sub>, which was supposed to contain no iodide ion, was found to be smaller than that of the original RDTC. This seemed to suggest that some of urethane linkages were hydrolyzed during the treatment. The urethane contents of RDTC and its derivatives were determined by the infrared technique<sup>2</sup> by use of amide I or II absorption intensity. The urethane content in Table II is expressed as the equivalent sulfur content. The sulfur content of MRDTC<sub>h</sub> calculated from the infrared analysis was nearly equal to that obtained by the elemental analysis. The urethane content calculated for MRDTC<sub>i</sub> was equal to that of the corresponding MRDTC<sub>h</sub>, indicating that the hydrolysis of urethane groups occurred during the methyl iodide treatment and not during the subsequent



duced wool was treated with methyl iodide through the elimination of dimethyl sulfide to form  $\beta$ -aminoacrylic acid residues as intermediates.<sup>11</sup> The loss in sulfur during the treatment of RDTC with methyl iodide is due to the hydrolysis of urethane linkages, and the sulfonium group probably acts as built-in catalyst.

### The Dyeing Behavior of RDTC and the Sulfonium Derivatives

RDTC and the sulfonium derivatives were dyed with Direct Sky Blue A (CI-24400) at 40°C, and the equilibrium uptakes of the dye were determined (Table III). The uptake of the dye by RDTC decreased remarkably with increasing sulfur content of RDTC. The dye adsorbed by the RDTC of 2.84% sulfur was only 15% of that by control cotton. The substitution of hydroxy groups of cellulose with bulky groups in the accessible region of cotton seems to lessen the affinity toward direct dyes.

The sulfonium derivatives, on the other hand, were found to adsorb the dye much more than the control cotton. The uptake was not affected to any appreciable extent by the counterions of the sulfonium groups. The dye in the control cotton and RDTC could be extracted easily with aqueous pyridine. Dye in the sulfonium derivatives could not be extracted with pyridine, but could be extracted with Cadoxen containing 0.5% sodium hydroxide. The dyeing mechanism of Direct Sky Blue A with the sulfonium derivatives seems to be different from that with unmodified cotton, probably being the ionic interaction.

Direct Sky Blue A contains four sulfonic acid groups per molecule. The ratio of the molar adsorbed dye concentration to the molar sulfonium content was much higher than the theoretical value of 0.25 calculated on basis of the 1:1 ionic bonding between sulfonium and sulfonic groups. The ratio increases with decreasing sulfonium concentration. MRDTC<sub>h</sub> containing 20  $\mu$ mole/g sulfonium groups adsorbed about an equimolar amount of the dye. Some of the dye adsorbed on this particular sample may be adsorbed owing to the substantivity of the dye, since the corresponding RDTC

TABLE III  
Equilibrium Uptakes of Direct Sky Blue A by RDTC and the Corresponding Sulfonium Derivatives<sup>a</sup>

S, %	RDTC	MRDTC <sub>i</sub>	MRDTC <sub>h</sub>	MRDTC <sub>c</sub>
	Uptake of dye, $\mu$ mole/g	Uptake of dye, $\mu$ mole/g	Sulfonium content, $\mu$ mole/g	Uptake of dye, $\mu$ mole/g
0.31	13	26.0	20	25.3
1.48	7.8	73.2	150	62.7
2.84	1.9	99.2	235	82.5

<sup>a</sup> Dyed with 0.5 mmole/l. Direct Sky Blue A solution containing 5 g/l. sodium chloride at 40°C for five days with a liquor ratio of 1:20 for RDTC and 1:40 for the others. The equilibrium uptake of the dye by dimethylformamide-treated control cotton was 13.6  $\mu$ mole/g.

TABLE IV  
The Relationship Between Equilibrium Uptake of Direct Sky Blue A and Sulfonium Content of MRDTC<sub>h</sub>

Equilibrium Uptake of Direct Sky Blue A, $\mu\text{mole/g}$			Sulfonium content (III), $\mu\text{mole/g}$	I/III	II/III
Total (I)	By substantivity	By ionic bonding (II)			
25.3	13	12.3	20	1.27	0.62
62.7	7.8	54.9	150	0.42	0.37
82.5	1.9	80.6	235	0.35	0.34

adsorbed as much dye as control cotton. The dyeing was carried out in the presence of sodium chloride. If one assumes that the dye adsorbed via the substantivity onto MRDTC<sub>h</sub> is equal to the dye uptake of the precursor (RDTC), the rest of the adsorbed dye onto the MRDTC<sub>h</sub> is combined with cotton via the sulfonium dye anion interaction. The ratio (0.62) of the estimated dye uptake via the ionic interaction to the sulfonium content for MRDTC<sub>h</sub> of the lowest sulfonium substitution was still much higher than the theoretical value. The ratio decreases as the sulfonium content increases, as shown in Table IV.

It seems unlikely that each of the sulfonium groups would be so favorably distributed, especially when the concentration is low, in the polymer matrix, that they completely block the four acidic groups of the dye molecule. Delmenico et al.<sup>14</sup> reported that the monosulfonated dye combined with the amino groups in wool stoichiometrically while some of the sulfonic groups in polysulfonated dyes did not combine with the amino groups and explained these findings in terms of the similar spatial effect. It was expected that the equilibrium uptake of a monoacidic dye would be equal to the sulfonium content because the spatial limitation did not exist in this case. The sulfonium derivative was dyed with aqueous Orange II (CI-15510) and Direct Sky Blue A at 45°C in the absence of sodium chloride. The equilibrium uptakes of monosulfonated and tetrasulfonated dyes were 230  $\mu\text{mole/g}$  and 97.6  $\mu\text{mole/g}$  (390  $\mu\text{equiv/g}$ ), respectively, whereas the sulfonium content of the substrate was 245  $\mu\text{mole/g}$ . The precursor RDTC adsorbed only 0.51  $\mu\text{mole/g}$  of Orange II and 0.32  $\mu\text{mole/g}$  of Direct Sky Blue A, respectively. These results seem to support the spatial consideration discussed above. The spatial effect was also considered for the oxidation of mercapto groups in modified cottons.<sup>6,15,16</sup>

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Received July 10, 1972