

## Reactions of Wood Components with Hydrogen Sulfide. VIII. Influence of Cation and Base Catalysts on the Reductive Thiolation Reaction at Cellulose-Reducing Endgroups\*

A. R. PROCTER, *MacMillan Bloedel Research Limited,  
Vancouver, B.C., Canada*

### Synopsis

In the presence of calcium, magnesium, and ammonium ions, the reductive thiolation reaction at cellulose-reducing endgroups by a hydrogen sulfide-hydrosulfide ion buffer system is more efficient when compared to the sodium base system. The calcium and magnesium base systems show a maximum reaction rate when the buffer pH is 5.9, thus behaving similarly to the previously described sodium base system. In the ammonium base system, however, there is a specific ammonia-catalyzed reaction with no maximum in the reaction rate over the available pH range. The increased efficiency of the bivalent ion systems is thought to be due to the formation of a salt-like complex between the cation and an intermediate gem-dithiol structure in the reductive thiolation reaction scheme. Ammonia enters into the kinetics of the reaction, but the exact mechanism of its action is unclear. Some other nitrogenous bases also catalyze the reductive thiolation. The use of ammonium hydrosulfide to carry out the reductive thiolation reaction is also briefly described.

### INTRODUCTION

In previous work<sup>1</sup> we have shown that when cellulose is treated with a hydrogen sulfide-sodium hydrosulfide buffer system at elevated temperatures, a portion of the reducing endunits undergoes reductive thiolation to form 1-thio-D-glucitol functions. This reaction is thought to take place by a two-step process involving an initial thiolation followed by a two electron reduction of the thiol intermediate.<sup>2,3</sup> Possible structures for this intermediate<sup>2</sup> are a hydroxythiol, gem-dithiol, vinyl thiol, or thioaldehyde. As this endgroup reaction stabilizes the cellulose molecule to alkaline degradation,<sup>1</sup> the extent of reaction is readily measured by determining the alkaline stability of the treated cellulose. We have shown<sup>3</sup> that the reductive thiolation reaction rate has a maximum when the hydrosulfide ion concentration is 0.05*M*. Under these conditions the hydrogen sulfide-hydrosulfide ion buffer system has a pH of about 6. In later studies, this

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reaction rate was found to be influenced by the nature of the cation present in the hydrogen sulfide-hydrosulfide ion buffer. The results of this work are reported here, together with conclusions on the fine mechanism of the reductive thiolation reaction.

## EXPERIMENTAL

The experimental techniques have been detailed elsewhere.<sup>1,3</sup> Hydrocellulose samples,  $\overline{DP}_n = 46$ , were slurried in an aqueous solution of the hydrosulfide salt before charging to a pressure reaction vessel. Hydrogen sulfide gas was added, and the vessel was heated to the required temperature and pressure conditions. The reaction time was taken as the time at temperature plus one third of the warm-up time of 21 min. Treated hydrocelluloses were isolated in yields of 100%, and the extent of reductive thiolation, expressed as the per cent of endunits substituted, *PES*, was determined from the alkaline stability under standard conditions.<sup>1,3</sup> To confirm that the *PES* values calculated from the alkaline stability referred to endgroups that had undergone the reductive thiolation, *PES* values were also calculated from the per cent sulfur of some of the reacted hydrocelluloses.<sup>1</sup> *PES* values are a measure of the reductive thiolation reaction rate under standard time conditions.

Western hemlock wood meal was also treated in the same manner as the cellulose. Treated wood meal samples were then subjected to simulated Kraft pulping, using a Kraft liquor containing 1*M* sodium hydroxide and 0.13*M* sodium sulfide. The liquor-to-wood ratio was 40 to 1, and the digestion conditions were 170°C for 61 min. The resultant cooked wood was measured for yield and per cent lignin using standard procedures.

## RESULTS AND DISCUSSION

### The Effect of Monovalent Cations

The extent of reductive thiolation under a specific set of reaction conditions for various monovalent ion base systems is shown in Table I. All the systems examined showed essentially the same reaction rate, within experimental error, except the hydrogen sulfide-ammonium hydrosulfide system, which was examined in more detail over a range of hydrosulfide ion concentrations. The results, Figure 1, show that not only is the reaction rate faster in the ammonium system, but the characteristic maximum at a 0.05*M* hydrosulfide ion concentration found in the sodium base system<sup>3</sup> is absent. To assess the effect of the ammonium ions on the reaction system, ammonium chloride was added to some of the ammonium base buffer systems. The results, Table II, suggest that the ammonium ions enter into the kinetics of the reductive thiolation, since *PES* values obtained with the systems containing extra ammonium ions, as ammonium chloride, were found essentially the same as systems with an equivalent amount of ammonium present entirely as ammonium hydrosulfide. *PES* values calculated

TABLE I  
Reaction Rate of Reductive Thiolation of Cellulose Reducing Endgroups<sup>a</sup>

Monovalent cation system	<i>PES</i> ( $\pm 2$ )	Bivalent cation system	<i>PES</i> , ( $\pm 2$ )
Li <sup>+</sup>	51		
Na <sup>+</sup>	48	Mg <sup>2+</sup>	54
K <sup>+</sup>	51	Ca <sup>2+</sup>	66
Cs <sup>+</sup>	51	Sr <sup>2+</sup>	55
NH <sub>4</sub> <sup>+</sup>	57	Ba <sup>2+</sup>	56
NMe <sub>4</sub> <sup>+</sup>	49		
NEt <sub>4</sub> <sup>+</sup>	52		

<sup>a</sup> On treatment with a hydrogen sulfide-hydrosulfide ion buffer system containing various cations as a base to the system. Results are expressed as per cent of endunits substituted, *PES*, under the standard conditions of 0.05*N* M<sup>+</sup>, 0.05*N* SH<sup>-</sup>, 0.241*M* H<sub>2</sub>S, 125°C, 47 min (M<sup>+</sup> is the cation under study). These conditions entail a total hydrogen sulfide and steam pressure of 150 psi.

TABLE II  
Reaction Rate of Reductive Thiolation of Cellulose-Reducing Endgroups<sup>a</sup>

Reaction systems with 0.241 <i>M</i> H <sub>2</sub> S at 125°C	Reaction time, min	<i>PES</i> , ( $\pm 2$ )
0.5 <i>N</i> NH <sub>4</sub> SH	20	56
0.05 <i>N</i> NH <sub>4</sub> SH	20	44
0.05 <i>N</i> NH <sub>4</sub> SH + 0.45 <i>N</i> NH <sub>4</sub> Cl	20	58
0.05 <i>N</i> NH <sub>4</sub> SH	47	56
0.005 <i>N</i> NH <sub>4</sub> SH	47	41
0.005 <i>N</i> NH <sub>4</sub> SH + 0.045 <i>N</i> NH <sub>4</sub> Cl	47	54
0.5 <i>N</i> Ca(SH) <sub>2</sub>	20	35 <sup>b</sup>
0.05 <i>N</i> Ca(SH) <sub>2</sub>	20	41
0.05 <i>N</i> Ca(SH) <sub>2</sub> + 0.45 <i>N</i> CaCl <sub>2</sub>	20	41
0.05 <i>N</i> Ca(SH) <sub>2</sub>	47	66
0.005 <i>N</i> Ca(SH) <sub>2</sub>	47	44
0.005 <i>N</i> Ca(SH) <sub>2</sub> + 0.045 <i>N</i> CaCl <sub>2</sub>	47	44

<sup>a</sup> On treatment with hydrogen sulfide-hydrosulfide ion buffer systems containing various amounts of cation. Results are expressed as per cent of endunits substituted.

<sup>b</sup> Extrapolated from Figure 3.

from the alkaline stability were the same as those calculated from the %S, confirming that the observed effects were a result of the reductive thiolation action.<sup>1</sup> Addition of small amounts of ammonium chloride to a hydrogen sulfide-0.05*M* sodium hydrosulfide system also increased the reaction rate, Figure 2.

The reason for the observed behavior in the presence of ammonia is not entirely clear, but the formation of a more readily thiolated gem-hydroxy-amino compound<sup>4</sup> would seem to be one possibility. It has also been suggested<sup>4</sup> that nitrogenous bases increase the nucleophilic properties of hydrogen sulfide so that addition to the polarized carbonyl is facilitated. Some support for these speculations has been found from the behavior of

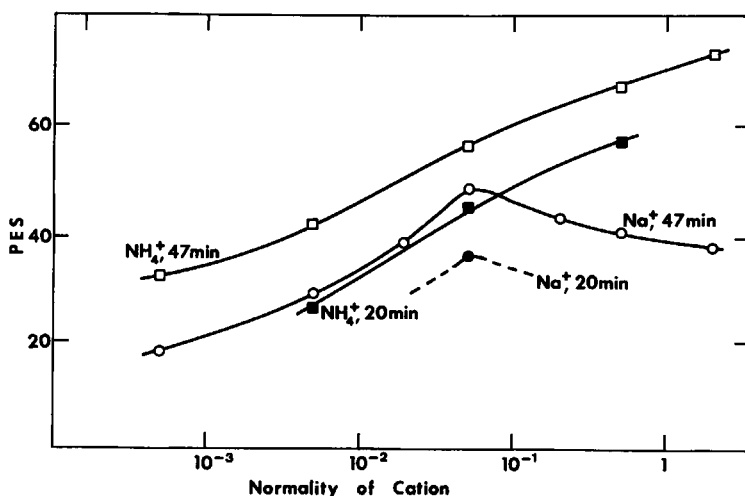


Fig. 1. Per cent of endgroups substituted, *PES*, on reductive thiolation of cellulose-reducing endgroups by sodium and ammonium-based hydrogen sulfide-hydrosulfide ion buffer systems. Reaction times are 20 and 47 min, at 125°C and 150 psi total pressure.

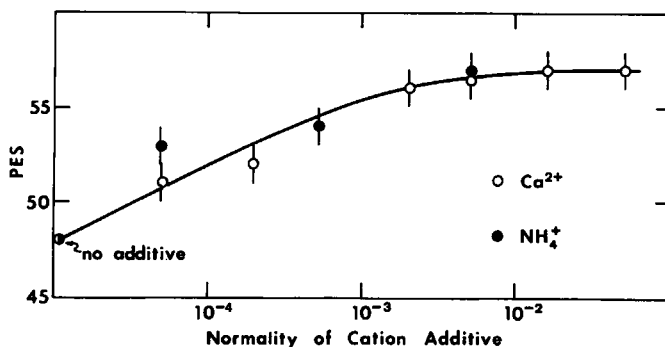


Fig. 2. Per cent of endgroups substituted, *PES*, on reductive thiolation of cellulose-reducing endgroups by a hydrogen sulfide-0.05*N* sodium hydrosulfide buffer system in the presence of cation additives (as chloride). Reaction conditions are 125°C, 150 psi total pressure, 47 min.

other basic nitrogen-containing compounds, which also accelerate the reductive thiolation reaction to different degrees when added to the hydrogen sulfide-sodium hydrosulfide reaction system, Table III.

### The Effect of Bivalent Ions

All the bivalent ion reaction systems studied were more efficient for reductive thiolation than the sodium base system (Table I). The rate effect is particularly striking with the calcium system. A closer study of the magnesium and calcium base systems showed, unlike the ammonium base system, the presence of a maximum in the reaction efficiency at a

TABLE III  
Effect of Various Nitrogenous Base Additives on Reductive Thiolation Reaction Rate at Cellulose-Reducing Endgroups<sup>a</sup>

Additive base	Concentration, <i>M</i>	<i>PES</i> ( $\pm 2$ )
None	—	48
Formamide	0.02	48
Thiourea	0.02	49
Trimethylamine	0.02	49
Dimethylformamide	0.02	51
Dimethylamine	0.02	51
2-Pyridone	0.02	51
Urea	0.02	52
Ethanolamine	0.02	52
Cyanamide	0.02	53
Methylamine	0.02	54
Pyridine	0.02	56
Morpholine	0.02	59
Hydroxylamine	0.02	60
Hydrazine <sup>b</sup>	0.01	67
	0.02	71
	0.05	71
	0.2	89

<sup>a</sup> Results are expressed as per cent of endunits substituted, *PES*, under reaction conditions of 0.05*N* NaSH, 0.241*M* H<sub>2</sub>S, 125°C, 47 min.

<sup>b</sup> A side reaction between hydrazine and hydrogen sulfide to produce elemental sulfur takes place during the reaction, which may have some effect on the reductive thiolation reaction through the formation of ammonia.

0.05*M* hydrosulfide ion concentration, Figure 3. This behavior was confirmed from the *PES* values calculated from the sulfur contents on some of the samples. In a similar manner to the ammonium base system, some reactions were carried out with excess calcium ions as calcium chloride, in order to assess any kinetic effect of the bivalent ion on the reductive thiolation reaction. The results, Table II, show that unlike ammonium ions, the calcium ions had no effect on the kinetics. Compared to sodium ions, the calcium ions must therefore act in some catalytic manner, while preserving the basic reductive thiolation mechanism by the hydrogen sulfide-hydrosulfide ion buffer system. Since thiols readily form strong salts with metal ions,<sup>5</sup> a possible mechanism for the catalytic effect of bivalent metal ions might be in the stabilization, by salt formation, of some bifunctional thiol intermediate in the reductive thiolation reaction. The most likely intermediate would be a gem-dithiol (structure III in Fig. 4). Gem-dithiol structures are known products in the reaction of certain carbonyl compounds with hydrogen sulfide,<sup>6</sup> and in stabilizing such a structure, the equilibrium reaction II  $\rightleftharpoons$  III shown in Figure 4 would be displaced to the right. The catalytic effect of the bivalent ions could then be explained if the concentration of this dithiol intermediate were partly rate controlling for the overall reductive thiolation reaction.

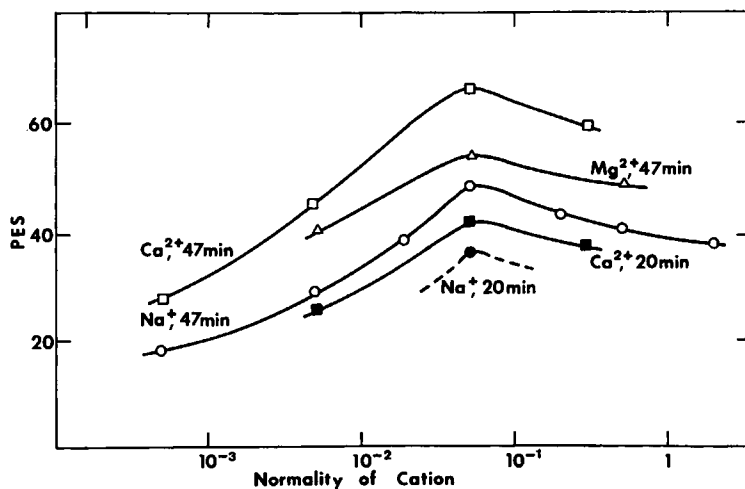


Fig. 3. Per cent of endgroups substituted, *PES*, on reductive thiolation of cellulose-reducing endgroups by sodium, calcium, and magnesium-based hydrogen sulfide-hydrosulfide ion buffer systems. Reaction times are 20 and 47 min, at 125°C and 150 psi total pressure.

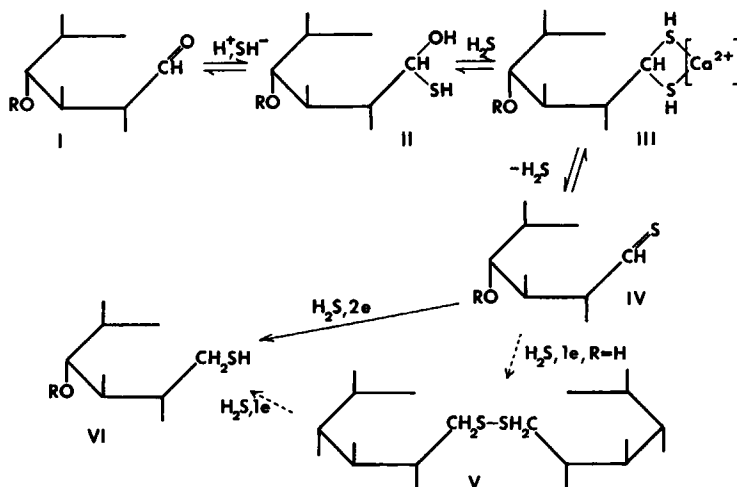


Fig. 4. Reaction scheme for the reductive thiolation of cellulose-reducing endgroups by a hydrogen sulfide-hydrosulfide ion buffer system. Suggested scheme in the presence of calcium ions is also shown.

From Figure 3 it is apparent that as little as a 10<sup>-3</sup>*M* concentration of calcium ions is able to catalyze the reductive thiolation. If the above mechanism is correct, additions of small amounts of calcium ions should increase the reaction rate of the sodium base system at its optimum pH. Several reactions were carried out using the hydrogen sulfide-0.05*M* sodium hydrosulfide system together with small amounts of calcium chlo-

ride. The results, Figure 2, confirm the catalytic effect of small amounts of calcium ions.

The possibility that the cellulose endgroup is solvated by calcium ions is an unlikely explanation for the observed effects, since similar reaction rates have been obtained with both cellulose and amylose-reducing endgroups in sodium base systems.<sup>2</sup> In these experiments, the latter polysaccharide was highly solvated in the reaction system. Complexing of the bivalent ion between a C1 thiol group and a C2 hydroxyl group, although a possibility,<sup>7</sup> is less likely since at the pH of the reaction system the hydroxyl group would not be ionized.

### The Reductive Thiolation Mechanism

Cairns and co-workers<sup>6</sup> have shown that gem-dithiols are readily formed from carbonyls on mild reaction with hydrogen sulfide. Under more vigorous conditions, the authors show that the gem-dithiols are converted to disulfides. In essence, this is a one-electron reduction step and is analogous to the reductive thiolation of glucose with hydrogen sulfide<sup>8</sup> to produce 1,1'-dithiobis(1-deoxy-D-glucitol). Other work<sup>9</sup> indicates that gem-dithiols are readily reduced to thiols, a two-electron reducing step.

Some recent work by Elofson and co-workers<sup>10</sup> on the reduction of thioketones suggests that a thioaldehyde may actually be the active species undergoing the reduction in the presence of hydrogen sulfide. The presence of an  $\alpha$ -hydroxyl group also makes such a thioaldehyde a powerful oxidizing agent.<sup>11</sup> Finally, Cairns<sup>6</sup> has shown that gem-dithiols are readily decomposed to thioaldehydes in the presence of trace amounts of base. From these observations, an overall scheme for the reductive thiolation reaction mechanism is presented in Figure 4.

In this scheme, a hydroxythiol, II, a gem-dithiol, III, and a thioaldehyde, IV, are in equilibrium with the glucose aldehyde endgroup I.<sup>12,13</sup> A vinyl thiol is an unlikely intermediate,<sup>12</sup> since thiomannitol products were not found on treatment of glucose with hydrogen sulfide.<sup>8</sup> This equilibrium system appears to be established only under a hydrogen sulfide pressure with the thiol products in relatively small concentration, since these compounds are not isolated when glucose is treated with hydrogen sulfide under the reductive thiolation conditions.<sup>8</sup> Moreover, when an aqueous thio-glucose solution (compare endgroup configuration IV) is treated with hydrogen sulfide under pressure, large amounts of glucose as well as some 1-thio-D-glucitol (compare VI) are formed.<sup>14</sup>

As suggested above, the concentration of the gem-dithiol (III) is seen as an important factor in the overall reductive thiolation, and the function of calcium ions is visualized as stabilizing this intermediate to displace the equilibrium toward higher gem-dithiol concentrations. The pH dependence of the reaction must be related to the hydroxy thiol formation.<sup>15,16</sup>

A two-electron reduction of the thioaldehyde to the thioalditol takes place when the carbohydrate forms the endgroup of a cellulose molecule;

however, with the free sugar in solution ( $R = H$  in Fig. 4), one-electron reduction steps through the disulfide (V) may take place.<sup>2,8</sup>

The pH-dependent thiolation reaction does not appear to operate by the same mechanism in the presence of ammonia. Some tentative mechanisms for the action of nitrogenous bases have been put forward by Mayer<sup>4</sup> (see earlier). These could involve primary nucleophilic attack of the carbonyl by ammonia, followed perhaps by a Schiff-base-type intermediate. However, the precise mechanism of this system must await further clarification. In the ammonium base system, the concentration of structure II is no longer rate limiting on the reductive thiolation through the pH of the system, but is now, at least partly, controlled by the ammonium ion concentration.

These observations suggest that the reduction step is fast compared with the thiolation equilibrium, where the rates of formation of the hydroxythiol and to a lesser extent the gem-dithiol are rate determining on the overall reductive thiolation.

#### **Reductive Thiolation with Ammonium Hydrosulfide**

Cellulose-reducing endgroups were also found to undergo the reductive thiolation reaction on treatment with aqueous ammonium hydrosulfide at elevated temperatures, in the absence of added hydrogen sulfide. A treatment with 0.5*M* ammonium hydrosulfide at 125°C for 47 min gave a *PES* value of 38. Under the reaction conditions, a portion of the ammonium hydrosulfide was decomposed to hydrogen sulfide and ammonia, the reductive thiolation presumably proceeding by the same mechanism as described earlier. However, the catalytic effect of the ammonium ions was evidenced by fairly extensive reaction under the relatively low hydrogen sulfide partial pressure of about 30 psi.<sup>8</sup> Celluloses similarly treated with ammonium polysulfide did not undergo any extensive reductive thiolation.

A similar reaction with ammonium hydrosulfide has been described by Kipnis and co-workers<sup>17</sup> for preparing disulfides from heterocyclic or aromatic aldehydes. In this case a one-electron reduction step is operating and is analogous to systems described elsewhere.<sup>6,8</sup>

#### **Application of the Reductive Thiolation Systems in Wood Pulping**

Reductive thiolation of wood hemicellulose-reducing endgroups with the hydrogen sulfide-sodium hydrosulfide system has been used as a pretreatment to alkaline wood pulping processes for improving pulp yield.<sup>2,18</sup> Some comparative results using the sodium, ammonium, and calcium base systems as pretreatments to simulated Kraft pulping are shown in Table IV. The greater efficiency for reductive thiolation of the ammonium and calcium base systems over the sodium system under the same reaction conditions is reflected in the pulp yield, which is a direct result of hemicellulose stabilization in the pretreatment stage through the reductive thiolation reaction. Similarly, wood pretreatments with ammonium hydrosulfide prior to Kraft pulping gave small yield increases of 2%-3%



TABLE IV  
Results of Simulated Pulping of Western Hemlock Wood Meal After Pretreatment with Hydrogen Sulfide-Hydrosulfide Ion Systems, with Sodium, Ammonium, and Calcium Bases<sup>a</sup>

Pretreatment time and liquor base	Yield, <sup>b</sup> $\pm 0.2\%$	Yield increase over untreated wood, %
No pretreatment	46.0	—
Na <sup>+</sup> , 20 min	50.2	4.2
Na <sup>+</sup> , 47 min	51.0	5.0
NH <sub>4</sub> <sup>+</sup> , 20 min	50.6	4.6
NH <sub>4</sub> <sup>+</sup> , 47 min	52.7	6.7
Ca <sup>2+</sup> , 20 min	51.4	5.4
Ca <sup>2+</sup> , 47 min	53.2	7.2

<sup>a</sup> Conditions of wood pretreatments were 0.05*N* sodium, ammonium, or calcium hydrosulfide; 0.241*M* hydrogen sulfide at 125°C (total pressure 150 psi).

<sup>b</sup> Yields of cooked wood are compared at a constant 6% lignin content.

over controls without pretreatment. In commercial practice, however, it is more convenient to use the sodium base system since Kraft pulping is also sodium based.

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