

Cleavage of Disulfide Polymers. I. By Inorganic Sulfides*

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INTRODUCTION

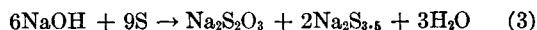
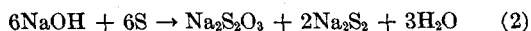
The main method of producing polysulfide polymers has been by the reaction of organic dihalides with sodium polysulfide;¹⁻³ however, it has been shown that polysulfide polymers, in the presence of sodium disulfide, are capable of exchange or redistribution reactions.⁴ Indeed, copolymers can be prepared by heating together two separate disulfide polymers in the presence of sodium polysulfide. Also, if a polysulfide polymer is separated without washing from the polysulfide solution in which it was prepared, the polymer is of low molecular weight but can then be converted to a high polymer by washing it free of excess polysulfide. These experiments certainly indicate the probability of cleavage of the disulfide bonds by the aqueous inorganic polysulfide, even though the latter is one of the reactants in the polymerization process.

It was shown in 1886 that both aliphatic and aromatic disulfides could be converted to the corresponding salts of the thiols by treatment with potassium monosulfide.⁵ The potassium monosulfide itself was changed to potassium disulfide. However, it was found that potassium disulfide could not convert the organic disulfide to the mercaptide. In fact, it was later shown that an alkaline solution of a thiol could be converted to the disulfide by treatment with either sodium disulfide or sodium tetrasulfide.⁶ The experimental results can be reconciled with the following reversible reaction.



Other authors⁸⁻¹⁰ have used various inorganic

sulfides to prepare thiols from the corresponding disulfides. In some cases sulfur has been used alone in an alkaline environment to convert thiols to disulfides.¹¹ This is, of course, equivalent to using an inorganic polysulfide, as sulfur reacts very readily with sodium hydroxide to form a sodium polysulfide of a rank dependent on the ratio of sulfur to caustic. Sodium thiosulfate is always formed also.^{12,13} Equations (2) and (3) show the ranks of sodium polysulfides formed from two different ratios of sulfur to sodium hydroxide.



At this point it should be noted that the effect of alkalis, in particular inorganic polysulfides, on typical aliphatic and aromatic disulfides is quite different from the effect of alkalis on the disulfide in the amino acid cystine. An exhaustive and specialized literature exists pertaining to the effect of alkali materials on the combined cystine present in proteins such as hair and wool. Much of this work is confusing and contradictory, owing in part to the complexity of the protein systems studied and in part to the extreme lability of the sulfur in combined cystine. The effect of alkali, which has been reviewed recently,¹⁴ is to extract one sulfur atom from part of the combined cystine, converting it from a disulfide to the amino acid lanthionine¹⁵ which is the corresponding monosulfide. As sodium polysulfides, especially the monosulfide, are extremely alkaline in aqueous solution, their action on proteins containing cystine might be expected to be similar to the action of sodium hydroxide. The use of sodium monosulfide for dissolving keratinaceous proteins has been known for a long time. Although at first the action was regarded wholly as a hydrolysis,^{16,17} later it was realized that the attack was on the disulfide groups^{18,19} and then specifically that the combined cystine was cleaved to combined cysteine.²⁰⁻²³ Sodium sulfide reacts with the disulfide group in combined cystine to produce

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combined cysteine, thus breaking the crosslink. In contrast, alkalis such as sodium hydroxide extract a sulfur from the disulfide, converting it to monosulfide without permanent cleavage of the crosslink between protein chains. The cleavage by sodium sulfide of disulfide to thiol in combined cysteine parallels the results with simple disulfides already summarized.

These two separate actions, of alkali on one hand and sodium sulfide on the other, usually proceed concurrently in experiments. When alkali extracts sulfur from combined cysteine, sodium polysulfide is formed; when aqueous solutions of sodium sulfide are used, hydrolysis occurs to form sodium hydroxide.²⁴ It is difficult, therefore, to separate the two actions, although the attempts to do so^{25,26} have confirmed the two mechanisms. This discussion of the atypical disulfide, combined cysteine, is pertinent because almost all the experimental results on the action of inorganic sulfides upon organic disulfides pertain to this disulfide. As a result, there has been an irresistible impulse to ascribe the results to the disulfide linkage itself rather than to this linkage in combined cysteine. Other disulfides such as 3-thiaglutaric acid²⁷ do show some of the peculiarities of combined cysteine, but ordinary aliphatic disulfides do not.

The conversion of the cyclic disulfide 1-oxa-4,5-dithiacycloheptane to a disulfide polymer by sodium disulfide²⁸ must necessarily involve cleavage of the disulfide by inorganic sulfide.

EXPERIMENTAL

Polymer Preparation

All the polysulfide polymers were made according to the standardized polymerization procedure previously described.⁴ In some cases, as stated in the following sections, the excess of sodium polysulfide was varied instead of maintained constant at 1.20 moles of sodium polysulfide per mole of organic dihalide.

Polymer Treatment

The treatment of aqueous dispersions of polysulfide polymers with various chemical reagents was carried out by use of a previously described procedure.⁴

DISCUSSION

Sodium Polysulfide

The treatment of aqueous dispersions of sulfide polymers with sodium monosulfide or sodium di-

sulfide has been used extensively to increase rather than decrease the molecular weight of the polymer.²⁹ The reaction of one mole of a reactive dihalide such as dichloroethyl formal with one mole of sodium disulfide yields a polymer of low molecular weight. As the number of moles of sodium disulfide per mole of dihalide is increased, the molecular weight of the polysulfide increases. A quantity of 1.20 moles of sodium disulfide per mole of this dihalide is required in order to obtain a polyethyl formal disulfide of sufficient molecular size that it is firm and rubbery rather than soft and sticky. Furthermore, secondary treatment of the aqueous dispersion of polysulfide polymer with additional quantities of aqueous sodium polysulfide produces an additional increase in molecular weight, evidenced by a reduction in the plasticity of the elastomer. An equivalent result is produced by using sodium hydroxide to treat a polymeric tetrasulfide, as the sulfur in excess of that for a disulfide is removed by alkali and reacts with it to form sodium polysulfide.^{1,2}

A superficial consideration of these facts would not lead to the conclusion that sodium monosulfide and disulfide cause any cleavage of the disulfide links in polysulfide polymers; there are additional facts that are important for a more complete understanding. The aqueous dispersions of polysulfide polymers are customarily washed free of aqueous sulfides by successive decantations before examination of the polymer. Bertozzi, Davis, and Fettes⁴ have shown that identical samples of a polysulfide polymer are of high molecular weight when washed free of sulfide ions but of appreciably lower molecular weight when separated without washing from the aqueous solution containing sulfide ions. Subsequent washing of the soft gum by kneading under water, to remove sulfide ions, converts it to a tough, rubbery polymer. Speakman²² showed that sodium sulfide, in cleaving the cystine in wool, has a similar effect, since the reaction was reversed when the sodium sulfide was washed out with water.

It has been found that the yield of polymer diminishes significantly the greater the excess of sodium disulfide over the stoichiometric equivalent for reaction with the dihalide. This loss of yield cannot be due to mechanical losses of polymer particles in the washing operation, as this loss occurs even when the utmost care is used in the decantation process. The conclusion is inescapable that the product is dissolved in the aqueous phase and thus is lost in the washing

operation. The high polymer is completely insoluble in water so that lost material must consist of low molecular weight fragments soluble in the aqueous phase as monomeric or possibly dimeric fragments of the dimercaptides NaSRNa .

A series of experiments was carried out in order to supplement our qualitative data with quantitative data on the effect of inorganic sulfides on polysulfide polymers. A polymeric dispersion was prepared from dichloroethyl formal with the use of a 20% molar excess of sodium disulfide. Portions of the dispersion containing 30% solids were treated with 0.25 mole of sodium disulfide per mole of segment weight of polymer for 30, 60, and 90 min. at each of three temperatures, 71.1, 82.2, and 94.4°C. After careful washing, the loss of polymer in each case was found to be about 10%. When the solids of the dispersion were varied from 10 to 40%, the same 10% loss of polymer occurred.

Variation of the mole ratio of sodium disulfide and also sodium monosulfide to polymer resulted in markedly differing losses of polymer. The results are shown in Table I. It is seen that the loss of polymer becomes pronounced as the ratio of inorganic sulfide to polymer is increased. Considerably more polymer is lost when the more alkaline sulfide, sodium monosulfide, is used. In both cases the molecular weight of the polymer, as judged by the hardness, is increased slightly.

Similar runs were made with sodium tetrasulfide, polysulfide of rank 4.57, and calcium polysulfide of rank 4.77. In all cases the loss of polymer was

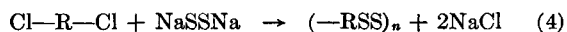
negligible; in fact, a slight gain in weight was found in a number of cases. A few of the polymers were analyzed for sulfur content and it was found that the sulfur content had increased during treatment with polysulfides of high rank. Any actual loss of polymer by solubilization was obscured by the increase in the rank of the polymer, so that the yield measurements have no significance.

It is clear that sodium monosulfide and disulfide are fully capable of cleaving the disulfide linkages in aliphatic disulfide polymers. The cleavage is reversible and the process of washing free of sulfides the aqueous dispersion of polymer forces the recombination of mercaptides and hence the regeneration of the disulfide bonds. Low molecular weight fragments of the chain are solubilized as sodium salts of dithiols and are lost when the polymer is washed free of inorganic salts.

Mechanism of Polysulfide Polymerization

It has been shown that both sodium disulfide and sodium monosulfide readily cleave the disulfide linkage in aliphatic polysulfide polymers. It is clear that the reaction is reversible, because the molecular weight of the polymer after being washed free of sodium polysulfides is not lowered—in fact, the tendency is definitely toward an increase in hardness and hence in molecular weight. This fact, together with the increasing loss of yield as the molar ratio of sodium polysulfide to the organic dihalide is increased, is of interest in a consideration of the mechanism of polymerization. It has already been pointed out that a substantial excess of sodium polysulfide over the amount needed for a stoichiometric reaction with the organic dihalide is required if polymers of high molecular weight are to be obtained. This condition is quite different from that known for other condensation polymerizations, wherein invariably polymers of the highest molecular weight are formed when exact equivalents of the two bifunctional reactants are used.

On examination of the polymerization reaction



it can be seen that we do not have a chemical combination of reactants that are equivalent, such as we have in the formation of a polyester from a dibasic acid and a glycol. An excess of organic dihalide would produce a polymer of low molecular weight with chlorine terminals: $\text{Cl}-(\text{-RSS})_n\text{-R-Cl}$ whereas an excess of sodium

TABLE I
Effect of Inorganic Sulfides on Loss of Polymer^a

Inorganic sulfide ^b	Amt. sulfide, moles/mole polymer ^c	Shore hardness ^d	Yield, %
Sodium disulfide	0.05	46	98.8
	0.10	46	97.2
	0.15	46	91.4
	0.25	48	87.9
	0.50	50	86.3
Sodium monosulfide	0.05	46	96.0
	0.10	46	95.3
	0.15	48	90.4
	0.25	49	84.7
	0.50	50	65.0

^a Polymeric disulfide from 98% dichloroethyl formal and 2% 1,2,3-trichloropropane with 20 mole-% excess sodium disulfide in polymerization.

^b 30 min. heating at 82.2°C.

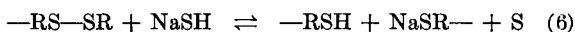
^c Segment weight.

^d Shore Durometer A (ASTM D676-55T).

The measured loss of polymer by its partial solubilization in inorganic polysulfides, and the observed elimination of added hydroxyl terminals, support the postulated mechanism of polymerization.

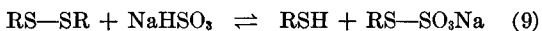
Sodium Hydrosulfide and Sodium Sulfite

Patrick and Ferguson³² discovered that a mixture of sodium hydrosulfide and sodium sulfite could be used to convert disulfide links of polysulfide polymers into terminal thiol groups. They postulated the following reactions:



The sodium sulfite removes the sulfur by formation of sodium thiosulfate, and displaces the equilibrium. It is quite plausible that the first reaction would be reversible, as sulfur in an alkaline environment is known to effect oxidation of thiol groups to disulfides.¹¹

A review of the literature reveals a quite different mechanism^{33,34} for the reaction of sodium sulfite or bisulfite with the disulfide group in cystine.

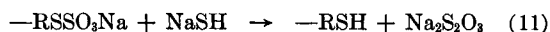
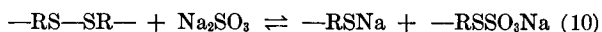


In the work referred to, no difference is shown between the use of sodium sulfite or the bisulfite as the reactant, because in most cases the pH of the reaction was separately controlled. The reactions in eqs. (6) and (7) are written as reversible because the formation of disulfide and sulfite from S-alkyl or S-aryl thiosulfates (commonly called Bunte³⁵ salts) and thiols is known.³⁶ Although the action of sodium bisulfite upon aromatic disulfides has been used³⁷ as a method for preparing S-aryl thiosulfates, most studies on the action of sulfite on disulfide links have dealt with cystine, usually as combined in a polypeptide.³⁸⁻⁴⁴

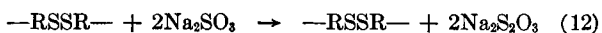
In wool as well as in other proteins part of the cystine reacts as in eq. (8) or (9). This partial reactivity is believed to be due to the influence of other functional groups in the vicinity of the disulfide linkage. About half of the disulfide in cystine that does react will undergo the reverse reaction upon washing with water, and the disulfide link will reform. It is believed that this nonreversibility of the cleavage of part of the cystine is a steric effect, in that the thiol and the thiosulfate group, which are on different chains, cannot come close enough together to recombine. The rates of cleavage of disulfides with structures similar to

cystine have been studied,^{27,45} and it has been found the reaction with combined cystine is faster than that with free cystine, which in turn is faster than that with 3-thiaglutaric acid. The dependence of the reaction on pH was studied⁴⁶ and the maximum rate of cleavage of disulfide was found at pH 5-7. The cleavage of 3-thiaglutaric acid is similar to that of cystine in reaction both with sulfite and with alkali.^{27,47} Recently, studies have been made on the kinetics of the reactions of sulfite with cystine and its analogs,⁴⁴ and on the equilibrium constants of reactions of sulfite with cystine, 3-thiaglutaric acid,⁴⁸ and oxidized glutathione.⁴⁹ Again, the extreme reactivity of cystine and cystinelike disulfides is involved, and little light is cast upon the reactivity of less complex disulfides.

The work cited makes it evident that cystine and analogous active disulfides react readily with sodium sulfite, especially in the range of pH 5 to 7, to yield thiol and Bunte salt. The reaction is reversible, so that the precise structure of any disulfide determines whether a significant amount of cleavage occurs. No work at all has been reported on aliphatic disulfides. A general knowledge of the effect of disulfide structure upon reactivity would lead one to suspect that little if any cleavage would occur with an aliphatic disulfide. If the studies on cystine are applicable to aliphatic disulfides, the cleavage by a mixture of sodium sulfite and sodium hydrosulfide should occur as follows:

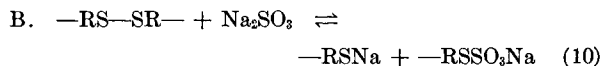
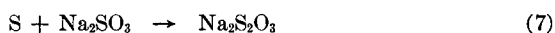
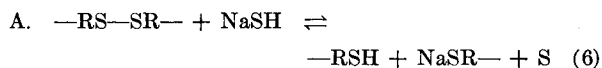


The fact that sodium sulfite has been used to convert tetrasulfide polymers to disulfides,

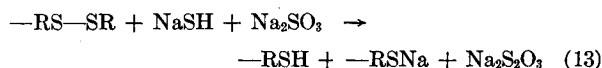


without any lowering of the molecular weight of the polymer, could well be advanced as evidence against any cleavage of the disulfide linkage by sodium sulfite. However, the aqueous dispersions are customarily washed free of inorganic salts before coagulation and subsequent examination. A reversible reaction, as is found with the combined cystine in wool, would permit reformation of the disulfide linkage on washing.

A number of experiments were planned in order to examine the mechanism of cleavage by a mixture of sodium sulfite and hydrosulfide. The two courses of this cleavage considered previously are the following.



The overall reaction is the same in A and B.



The effect on the polymer is that some of the disulfide links are converted to thiol terminals, which thus lowers the molecular weight. This

TABLE III

Effectiveness of Sodium Sulfite^a and Various Inorganic Sulfides^b in Cleaving a Polysulfide Polymer^c

Inorganic sulfide	Resulting state of polymer ^d
NaSH	Liquid
NaSNa	Soft rubber
NaSSNa	Tough rubber
NaOH	No cleavage

^a 1.10 moles of sodium sulfite per mole of polymer (segment weight).

^b 0.10 mole of sulfide per mole of polymer (segment weight).

^c Disulfide from 98% dichloroethyl formal and 2% 1,2,3-trichloropropane.

^d After reaction for 30 min. at 82.2°C.

result is, of course, known^{32,50} but the over-all equation does not show how it is obtained.

A comparison was made of various inorganic sulfides with regard to their effectiveness in promoting cleavage when used in conjunction with sodium sulfite. The experimental results shown in Table III demonstrate that sodium hydrosulfide is very efficient as a cleaving agent, sodium monosulfide is fair, and sodium disulfide and hydroxide have little effect.

The lack of cleavage of the polymer by sodium hydroxide and sodium sulfite is in accord with mechanism (A), wherein sodium hydroxide would have to cleave disulfide groups as in eq. (6). Sodium hydroxide, in spite of its action on cystine and active disulfides, has not been found to cleave aliphatic disulfides. The lack of cleavage is also in accord with mechanism (B), wherein the sodium hydroxide would have to convert a Bunte salt into the sodium salt of the thiol. This would not occur, as it is known that sodium hydroxide converts Bunte salts into disulfides. To account for the total lack of cleavage found with sodium hydroxide, this reconversion of the Bunte salt to disulfide would have to be completely quantitative. In the conversion of S-ethyl and S-benzyl thiosulfate to the disulfide,³⁶ the yields were never over 60% and definite by-products were found. Even 1% of such a side reaction would result in a notice-

TABLE IV

Effectiveness of Sodium Sulfite and Hydrosulfide in Cleaving Polysulfide Polymers^a

Sodium hydrosulfide ^b	Sodium sulfite ^b	Viscosity, poises	Total sodium sulfite consumed ^{b,c}	Sodium sulfite consumed in cleavage ^{b,d}
Run A				
—	1.10	No change	0.19	—
0.10	1.10	310	0.33	0.14
0.20	1.10	75	0.45	0.26
0.30	1.10	40	0.56	0.37
0.50	1.10	20	0.66	0.47
0.10	—	Rubber	—	—
0.10	0.10	Rubber	0.10	—
0.10	0.20	Very viscous	0.20	0.01
0.10	0.30	450	0.29	0.10
0.10	0.55	290	0.32	0.12
Run B				
0.20	0.30	150	0.30	0.11
0.20	0.40	93	0.38	0.19
0.20	0.50	88	0.36	0.17
0.20	1.10	39	0.42	0.23

^a Disulfide polymers from 98% dichloroethyl formal and 2% 1,2,3-trichloropropane.

^b Moles per mole of polymer (segment weight).

^c Total determined by measurement of sulfite/thiosulfate ratio in supernatant liquor.

^d Amount consumed in desulfurizing polymer, 0.19 subtracted from total sodium sulfite consumed.

able lowering of the molecular weight of the high polymer. This result therefore favors mechanism (A).

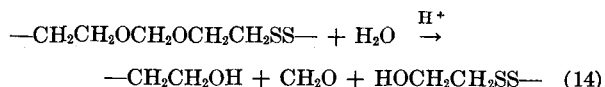
In a series of experiments with a disulfide polymer the amounts of sodium hydrosulfide and sodium sulfite were varied. The results are shown in Table IV. The polymer contained enough polysulfide sulfur to consume 0.19 mole of sodium sulfite when no sodium hydrosulfide was used. This value was therefore deducted from the total sulfite consumed, to obtain the amount used in the actual cleaving.

The results again point to mechanism (A), with sodium hydrosulfide, not sodium sulfite, as the cleaving agent. Some lowering of molecular weight occurred when sodium hydrosulfide was used alone, but none when only sodium sulfite was used. The amount of cleavage, as measured by the viscosity of the polymers produced, seems to depend on the amount of sodium hydrosulfide used, provided that a minimum quantity of sodium sulfite is present. In most cases the number of moles of sodium hydrosulfide consumed in cleavage was approximately equal to the number of moles of sodium hydrosulfide used. In some other runs higher ratios of sulfite to hydrosulfide were noted, but these were believed due to some oxidation of the sulfite by air during the washing of the split polymer.

It has been pointed out that the cleavage of disulfide polymers by sodium disulfide is not observable if the polymer is washed free of the sulfide before examination.⁴ The reverse reaction of eq. (1) is favored and the mercaptide groups recombine. This same reversibility upon washing has been noted in the cleavage of combined cystine by sodium bisulfite.^{41,42} The observed absence of cleavage of polysulfide polymers by sodium sulfite might be due to an actual reversal of cleavage by the subsequent washing.

An experiment was run to determine the effect of sodium sulfite and also sodium bisulfite on polymeric disulfides. Sodium bisulfite was used, as it had been shown⁴⁶ that the maximum rate of cleavage of cystine with sulfite ion is in the pH range of 5 to 7. The polymers, both washed and unwashed after treatment with sodium sulfite, were the same and indistinguishable from the untreated polymer. The polymers, both washed and unwashed, after treatment with sodium bisulfite were soft and tacky and had a slight odor of formaldehyde. It is believed that the observed softening effect may well have been an acidic

cleavage of the formal link in the polymer rather than of the disulfide link:⁵¹



The experiment was repeated with both sodium sulfite and sodium bisulfite and a disulfide polymer prepared from bis-4-chlorobutyl ether. This polymer would not be susceptible to acidic cleavage. All treatments resulted in polymers identical in hardness and appearance with the untreated polymer. This demonstrated that the softening encountered with sodium bisulfite on polymers from dichloroethyl formal was in reality a cleavage of the formal linkage.

The conclusion drawn from all these experiments is that sodium sulfite has no cleaving effect on aliphatic disulfide polymers. The cleavage of these polymers by a mixture of sodium sulfite and sodium hydrosulfide is due to the stabilization by the sulfite of the cleavage effected by the sodium hydrosulfide.

References

1. Patrick, J. C., *Trans. Faraday Soc.*, **32**, 347 (1936).
2. Martin, S. M., Jr., and J. C. Patrick, *Ind. Eng. Chem.*, **28**, 1145 (1936).
3. Fettes, E. M., and J. S. Jorczak, *Ind. Eng. Chem.*, **42**, 2217 (1950).
4. Bertozzi, E. R., F. O. Davis, and E. M. Fettes, *J. Polymer Sci.*, **19**, 17 (1956).
5. Otto, R., and A. Rossing, *Ber.*, **19**, 3129 (1886).
6. Brand, K., *Ber.*, **42**, 3463 (1909).
7. Brand, K., and A. Wirsing, *Ber.*, **46**, 820 (1913).
8. Waldron, W. R., and E. E. Reid, *J. Am. Chem. Soc.*, **45**, 2399 (1923).
9. Price, C. C., and G. W. Stacy, *J. Am. Chem. Soc.*, **68**, 498 (1946).
10. Lukashevich, V. O., and M. M. Sergeeva, *Doklady Akad. Nauk. S.S.S.R.*, **67**, 1041 (1949).
11. Holmberg, B., *Ann.*, **369**, 81 (1908).
12. Haywood, J. K., *J. Am. Chem. Soc.*, **27**, 244 (1905).
13. Tartar, H. V., *J. Am. Chem. Soc.*, **35**, 1741 (1913).
14. Alexander, P., and R. F. Hudson, *Wool, Its Chemistry and Physics*, Reinhold, New York, 1954.
15. Horn, M. J., D. B. Jones, and S. J. Ringel, *J. Biol. Chem.*, **138**, 141 (1941).
16. Merrill, H. B., *Ind. Eng. Chem.*, **17**, 36 (1925).
17. Bergmann, M., and F. Stather, *Collegium*, **109** (1925).
18. Pulevka, P., *Z. physiol. Chem.*, **146**, 130 (1925).
19. Kuster, W., and W. Koppel, *Z. physiol. Chem.*, **171**, 114 (1927).
20. Marriott, R. H., *J. Intern. Soc. Leather Trades Chem.*, **184**, 216 (1928).
21. Kuster, W., and W. Irion, *Z. physiol. Chem.*, **184**, 225 (1929).
22. Speakman, J. B., *J. Chem. Soc. Ind.*, **50**, 1 (1931).

23. Goddard, D. R., and L. Michaelis, *J. Biol. Chem.*, **106**, 605 (1934).
24. Kuster, F. W., and E. Heberlain, *Z. anorg. Chem.*, **43**, 53 (1905).
25. Crowder, J. A., and M. Harris, *J. Research Natl. Bur. Standards*, **16**, 475 (1936).
26. Mizell, L. R., and M. Harris, *J. Research Natl. Bur. Standards*, **30**, 47 (1943).
27. Schoberl, A., and E. Ludwig, *Ber.*, **70B**, 1422 (1937).
28. Davis, F. O., and E. M. Fettes, *J. Am. Chem. Soc.*, **70**, 2611 (1948).
29. Fettes, E. M., and J. S. Jorzczak, *Polymer Processes*, ed. by C. S. Schildknecht, Interscience, New York, 1956, Chap. 11.
30. Davis, F. O., private communication.
31. Fettes, E. M., J. S. Jorzczak, and J. R. Panek, *Ind. Eng. Chem.*, **46**, 1539 (1954).
32. Patrick, J. C., and H. R. Ferguson, U.S. Pat. 2,466,963 (April 12, 1949).
33. Clarke, H. T., *J. Biol. Chem.*, **97**, 235 (1932).
34. Lugg, J. W. H., *Biochem. J.*, **26**, 2144 (1932).
35. Bunte, H., *Ber.*, **7**, 646 (1874).
36. Footner, H. B., and S. Smiles, *J. Chem. Soc.*, **1925**, 2887.
37. Lecher, H. Z., and E. Hardy, *J. Org. Chem.*, **20**, 475 (1955).
38. Speakman, J. B., *J. Soc. Dyers Colourists*, **52**, 335 (1936).
39. Elsworth, F. F., and H. Phillips, *Biochem. J.*, **32**, 837 (1938).
40. Elsworth, F. F., and H. Phillips, *Biochem. J.*, **35**, 135 (1941).
41. Middlebrook, W. R., and H. Phillips, *Biochem. J.*, **36**, 428 (1942).
42. Shuringa, G. J., C. Schooneveldt, and T. Konings, *Textile Research J.*, **21**, 281 (1951).
43. Fraenkel-Conrat, H. L., *J. Biol. Chem.*, **142**, 119 (1942).
44. Cecil, R., and J. R. McPhee, *Biochem. J.*, **60**, 496 (1955).
45. Kassell, B., and E. Brand, *J. Biol. Chem.*, **125**, 131 (1938).
46. Schoberl, A., and F. Krumej, *Ber.*, **71B**, 2631 (1938).
47. Schoberl, A., and H. Eck, *Ann.*, **522**, 97 (1936).
48. Stricks, W., and I. M. Kolthoff, *J. Am. Chem. Soc.*, **73**, 4569 (1951).
49. Stricks, W., I. M. Kolthoff, and R. C. Kapoor, *J. Am. Chem. Soc.*, **77**, 2057 (1955).
50. Jorzczak, J. S., and E. M. Fettes, *Ind. Eng. Chem.*, **43**, 324 (1951).
51. Rosenthal, N. A., and M. B. Berenbaum, paper presented at 131st Meeting of American Chemical Society, Miami, Fla., April 7-12, 1957.

Synopsis

Although sodium disulfide is one of the chief reactants in the preparation of polymeric disulfides, it has the ability to cleave the disulfide links in the polymer, as is shown in this paper. This cleavage is responsible for losses in yield of polymer through solubilization of fragments of low molecular weight, but is it also necessary in producing high polymers. The unreactive terminal hydroxyl groups produced by the side reaction of alkaline hydrolysis of reactive chloride ter-

minals would ordinarily limit the chain length of the polymer; however, the preferential solubilization of the terminal fragments, because of the hydrophilic hydroxy group, permits the molecular weight of the polymer to be increased greatly. An excess of sodium disulfide is thus needed in order to obtain disulfide polymers of high molecular weight, in contrast to the usual condensation polymerization wherein an exact equivalence of reactants is needed. The cleavage of the aliphatic disulfide groups in the polymer by aqueous sodium polysulfide is a reversible reaction with the equilibrium favoring re-formation of the disulfide linkage. The equilibrium is displaced if a reagent capable of binding sulfur is present. A mixture of sodium sulfide, in particular sodium hydrosulfide, with sodium sulfite can be used in an efficient and controllable manner to convert polymer disulfides of high molecular weight to polymers of low molecular weight with terminal thiol groups.

Résumé

Quoique le disulfure de sodium soit une des réactifs principaux lors de la préparation de disulfures polymériques, son aptitude à rompre les liens disulfurés de la chaîne polymérique a été démontrée. Cette rupture est responsable des diminutions de rendement en polymère en raison d'une solubilisation des fragments de bas poids moléculaire mais est également nécessaire à la production de hauts polymères. Les groupements hydroxyles terminaux non réactionnels produits par une réaction connexe d'hydrolyse alcaline des groupements réactifs chlorés terminaux, devraient ordinairement déterminer la longueur de chaîne du polymère. La solubilisation préférentielle des fragments terminaux, en raison du caractère hydrophile des groupements hydroxyles, permet d'accroître considérablement le poids moléculaire du polymère. Un excès de disulfure de sodium est donc nécessaire à la production de polymères disulfurés de haut poids moléculaire; ceci contraste avec les polycondensations usuelles où l'exacte équivalence des réactifs est requise. La rupture des groupes disulfurés aliphatiques dans le polymère par le polysulfure de sodium aqueux est une réaction réversible dans laquelle l'équilibre est favorable à la reformation de liens disulfurés. L'équilibre est déplacé en présence d'un réactif capable de lier le soufre. Un mélange de sulfure de sodium, en particulier de sulfure acide de sodium, et de sulfite de sodium peut être utilisé de façon efficace et contrôlable pour convertir les disulfures polymériques de haut poids moléculaire en polymères de bas poids moléculaire possédant des groupements thiols terminaux.

Zusammenfassung

Obgleich Natriumdisulfid eines der Hauptreagenzien bei der Darstellung von polymeren Disulfiden ist, wird gezeigt, dass es die Fähigkeit zur Spaltung der Disulfidbindungen im Polymeren besitzt. Diese Spaltung ist für die Verluste bei der Ausbeute an Polymeren durch Solubilisierung niedermolekularer Bruchstücke verantwortlich, sie ist aber auch für die Erzeugung von Hochpolymeren notwendig. Die nichtreaktiven, endständigen Hydroxylgruppen, die in einer Nebenreaktion durch alkalische Hydrolyse reaktiver Chloridendgruppen erzeugt werden, würden normalerweise eine Grenze für die Kettenlänge des Polymeren bilden. Die durch die hydrophile Hydroxylgruppe bevorzugte Solubilisierung der Endgruppenfragmente erlaubt eine erhebliche

Steigerung des Molekulargewichts des Polymeren. Es ist daher im Gegensatz zur gewöhnlichen Kondensationspolymerisation, wo eine genaue Äquivalenz der Reaktionsteilnehmer notwendig ist, ein Überschuss an Natriumdisulfid zur Erzeugung von hochmolekularen Disulfidpolymeren erforderlich. Die Spaltung der aliphatischen Disulfidgruppen im Polymeren durch wässriges Natriumpolysulfid ist eine reversible Reaktion, deren Gleichgewicht günstig für die Rückbildung der Disulfidbindung liegt. Das

Gleichgewicht wird durch ein Reagents mit der Fähigkeit zur Schwefelbindung verschoben. Eine Mischung von Natriumsulfid, besonders von Natriumhydrosulfid, mit Natriumsulfit kann in wirksamer und kontrollierbarer Weise zur Umwandlung von hochmolekularen, polymeren Disulfiden in Polymere mit niedrigem Molekulargewicht mit endständigen Thiolgruppen benützt werden.

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