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REACTION OF WOOL WITH HYDROGEN PEROXIDE

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ABSTRACT

The reaction of wool with hydrogen peroxide was investigated. The basic groups in wool are unaffected during treatment with hydrogen peroxide, as indicated by the determination of the amino nitrogen, arginine, and lysine contents. The percentage of each of the elements in wool with the exception of oxygen decreases with increased oxidation but the ratios of these elements remain constant. The results constitute further evidence that the main reaction of wool with hydrogen peroxide is the addition of oxygen to the disulfide groups.

CONTENTS

I. INTRODUCTION

The effect of hydrogen peroxide on wool, chiefly from the standpoint of the effect on the disulfide group, has been studied extensively by Smith and Harris [1].[2] The results of the investigations indicate that intermediate oxidation products of the disulfide group of the cystine in wool, similar to those obtained from cystine itself by Toennies and Lavine [2, 3] were formed. The latter workers isolated and studied two of these partially oxidized derivatives of cystine. Because of the lability of these compounds in acid and alkaline solutions, it was impossible to isolate any of them from the hydrolysates of oxidized wool, and as a result, the experimental evidence on which was based the postulation that partially oxidized sulfur compounds are present in oxidized wool, was of an indirect nature.

The present investigation, which is an extension of the earlier work, was undertaken to obtain more direct evidence on the nature of the effect of hydrogen peroxide on wool. The results of studies on the possibilities of oxidation of basic groups in wool are also included.

II. RESULTS AND DISCUSSION

Data which were presented in connection with a paper [4] on the nature of the acid-dyeing process showed that the acid-combining

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[2] Numbers in brackets indicate literature references at the end of the paper.

capacity of wool decreased with increasing degrees of oxidation by hydrogen peroxide. Preliminary analyses of these oxidized samples also indicated that the total nitrogen content decreased with increased oxidation. These results at first suggested that an oxidative deamination was probably the cause of the decreased basicity of the samples. However, analyses of the basic groups and basic amino acids in oxidized wool did not substantiate such a mechanism. Determinations of the amino nitrogen in the different samples by the method of Rutherford, Harris, and Smith [5] showed no decrease with increasing amount of oxidation. Furthermore, the contents of arginine and lysine in the most highly oxidized sample, as determined by isolation as the flavianate [6] and picrate [7], respectively, were the same as those of a sample of the untreated wool. The complete data are given in table 1.

It is obvious that the basic groups of wool were not appreciably affected by the treatment with hydrogen peroxide, and it was therefore necessary to account in some other way for the decreases in nitrogen content and acid-combining capacity. If it is assumed that oxidation by hydrogen peroxide results in the addition of oxygen to the disulfide groups to form such compounds as R—SO—S—R, R—SO—SO—R, R—SO_2—SO—R, etc., then an answer to the apparently conflicting data in table 1 is readily found. The oxidation derivatives of the types shown are relatively strong acids and therefore decrease the amount of acid combined with the wool. Also, if oxygen has been added, there will be an increase in weight accompanied by an apparent decrease in nitrogen content.

TABLE 1.—*Effect on wool of treatment with a 3-percent solution of hydrogen peroxide at 50° C for different lengths of time*

Duration ot treatment	Total nitrogen	Acid-combining capacity	Amino nitrogen	Arginine	Lysine
hr	%	M-eq/g of wool	mg/g	%	%
0[1]	16.37	0.80	3.2	7.1	1.7
3	16.24	.60	3.0	---	---
6	16.16	.53	3.2	---	---
10	15.98	.42	3.2	---	---
15	15.99	.34	3.3	---	---
20	16.04	.32	3.2	7.2	1.9

[1] Untreated.

In order to determine whether an increase in weight of the sample actually occurred during oxidation, the following experiments were made. Skeins, weighing approximately 5 g each, were placed in U-tubes and dried to constant weight in a stream of dry nitrogen at 105° C. The skeins were then treated with 200 ml of a 3-percent solution of purified hydrogen peroxide at 50° C for different lengths of time. The hydrogen peroxide used in these experiments was prepared by distillation, under reduced pressure, of a 30-percent solution of cp hydrogen peroxide, the distillate finally being diluted to 3 percent. The skeins of oxidized wool were finally washed with distilled water until the wash water was free from hydrogen peroxide. The mother liquor and wash waters of each sample were combined and evaporated nearly to dryness on a steam bath. The solutions were then transferred to weighing bottles, evaporated to dryness at about 60° C, and finally dried to constant weight at 105° C. Microscopic examination of the residue indicated that the bulk of the material was in the form of fine fibers which had been lost during the treatment. The weights of the residues accounted for only a part of the net increases in the weights of the samples. The weights of the dry residues were added to the weights of the corresponding oxidized samples, which had been dried at 105° C in a stream of dry nitrogen. The following increases in the weight of wool samples after oxidation with a 3-percent solution of hydrogen peroxide at 50° C for different lengths of time are very appreciable and account for a large portion of the apparent decrease in nitrogen contents shown in table 1:

Duration of treatment	Increase in weight
hr	Percent
3	0. 28
6	. 90
10	1. 02
15	1. 36
20	1. 17

If the principal effect of this type of oxidation of wool is the addition of oxygen to the disulfide groups, then the percentage of each of the elements, except oxygen in wool, should decrease with increased oxidation, but the ratios of these elements in any sample should be constant. Analyses given in table 2 for the carbon, hydrogen, nitrogen, and sulfur in untreated samples and in samples oxidized for 10 and for 20 hours by the procedure previously described, show that this is so. The results constitute further evidence that the main reaction of wool with hydrogen peroxide is the addition of oxygen to the disulfide groups.

TABLE 2.—*Elementary analyses of untreated samples of wool and of samples which had been treated with a 3-percent solution of hydrogen peroxide at 50° C for 10 and for 20 hours*

Duration of treatment	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen (by difference)	Ratio C:H:N:S
hr	%	%	%	%	%	
0[1]	50. 04	6. 92	16. 37	3. 58	23. 09	1 : 0. 138 : 0. 328 : 0. 0715
10	49. 72	6. 83	15. 98	3. 45	24. 02	1 : 0. 137 : 0. 322 : 0. 0694
20	49. 15	6. 80	16. 04	3. 39	24. 61	1 : 0. 138 : 0. 326 : 0. 0690

[1] Untreated.

III. REFERENCES

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