THE INFRA-RED SPECTRUM OF PERACETIC ACID-TREATED WOOL

by

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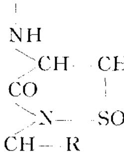
INTRODUCTION

The treatment of wool with peracetic acid has been studied chemically by ALEXANDER, CARTER AND EARLAND[1], who found that all the disulphide bonds were readily accessible and could be oxidised completely. On the basis of the formation of cysteic acid after acid hydrolysis, the following mechanism was proposed for the reaction:

$$>CH-CH_2-S-S-CH_2-CH< \;\rightarrow\; >CH-CH_2-SO_3H + HSO_3-CH_2-CH<$$

However, attempts to detect sulphonic acid groups in the wool were unsuccessful[3]. Thus no ion exchange of the expected sulphonic acid groups could be detected, and after the fibres had been treated with mild alkali, cysteic acid could no longer be found in the hydrolysates in spite of the fact that no sulphur had been removed by the alkali. It was therefore suggested that oxidation by peracetic acid leads to an intermediate of the sulphonamide type (I), which yields cysteic acid on acid hydrolysis but on mild alkali treatment gives a product highly resistant to acid hydrolysis.


(I)

Owing to the difficulty in distinguishing between these mechanisms by chemical means, the infra-red spectroscopic method has been used to study the reaction and the results obtained are described in this paper.

EXPERIMENTAL

Infra-red spectra of the following materials were obtained using a Grubb Parson's S.3.A. single-beam spectrometer.

1. Virgin wool of 64's quality: Before use, this wool was scoured twice in a warm solution of soap and ammonia followed by thorough washing in water and then extraction with ether and alcohol.
2. Peracetic acid-treated wool: A sample of the virgin wool, as treated above, was oxidised with 100% excess of a 2% aqueous solution of peracetic acid for 30 h at room temperature.
3. L-Cysteic acid: This was obtained from L-LIGHT & Co., Ltd, Colnbrook, Bucks, and on analysis gave 8.45% nitrogen as against 8.3% theoretical.

The spectra were all obtained using the materials in the solid state, and in order to obtain good results the following procedure was used:

All the materials were finely ground and made into discs with potassium bromide powder[8]. It was found that this method gave much clearer spectra, especially for wool, than the more usual technique of moistening the fibres with liquid paraffin between rock-salt plates.

RESULTS

The infra-red spectra of wool, peracetic acid-treated wool and L-cysteic acid are shown in Fig. 1 (a. b. c). The frequency range covered by these spectra is from 1400 cm^{-1} to 900 cm^{-1}. Absorption peaks were found in this range at the following frequencies (the

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letters s, m and w indicate relative intensities of absorption, strong, medium and weak respectively).

1. Virgin Wool

1390 cm^{-1} (s) : 1315 cm^{-1} (w) : 1240 cm^{-1} (s) : 1170 cm^{-1} (w) : 1150 cm^{-1} (w)
1110 cm^{-1} (w) : 1060 cm^{-1} (w) : 1045 cm^{-1} (w) : 980 cm^{-1} (w) : 930 cm^{-1} (w)

2. Peracetic Acid-Treated Wool

1390 cm^{-1} (s) : 1315 cm^{-1} (w) : 1240 cm^{-1} (s) : 1175 cm^{-1} (s) : 1120 cm^{-1} (m)
1070 cm^{-1} (w) : 1040 cm^{-1} (s) : 980 cm^{-1} (w) : 950 cm^{-1} (w)

3. L-Cysteic Acid

1370 cm^{-1} (w) : 1180 cm^{-1} (s) : 1145 cm^{-1} (w) : 1120 cm^{-1} (w) : 1070 cm^{-1} (w)
1040 cm^{-1} (s) : 950 cm^{-1} (w)

DISCUSSION

From Figs. 1a and 1b it can be seen that a marked change takes place in the spectrum of wool after peracetic acid treatment. Thus two strong absorption bands appear at approx. 1175 cm^{-1} and 1040 cm^{-1} which are not present in virgin wool. If 1b is now compared with 1c, it can be seen that these two strong bands are matched in relative intensity and position by the two strong bands of L-cysteic acid. From data on other sulphonic acids, BELLAMY[4] suggests that bands appearing in the frequency ranges:

(a) 1210–1150 cm^{-1} and
(b) 1060–1030 cm^{-1}

are characteristic of sulphonic acid groups.

From this evidence the two peaks at 1180 cm^{-1} and 1040 cm^{-1} in L-cysteic acid can be assigned to sulphonic acid groups, and therefore by comparison it is probable that the two new peaks arising in peracetic acid-treated wool are due to the presence of sulphonic acid groups.

BELLAMY[5] also quotes the following ranges for strong absorption bands due to the sulphonamide type of grouping $-SO_2 \cdot N-$

(1) 1180–1140 cm^{-1}
(2) 1350–1300 cm^{-1}

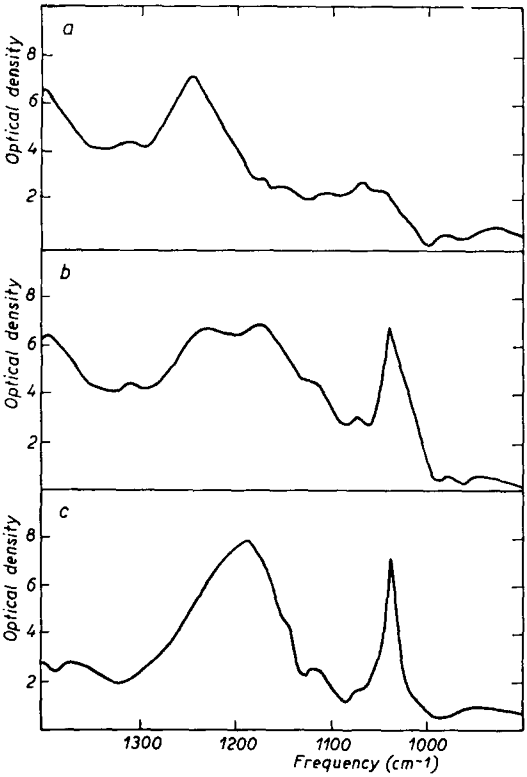

Fig. 1. (a) Infra-red spectrum of virgin wool;
(b) Infra-red spectrum of peracetic acid-treated wool;
(c) Infra-red spectrum of L-cysteic acid.

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The first of these ranges overlaps the range given for one of the sulphonic acid absorption bands, but the second is distinct and an absorption peak should be observable in peracetic acid-treated wool if sulphonamide groups are present. No new peak in this region is observed with the treated wool and it is therefore concluded that the sulphonamide grouping is absent.

It is possible to obtain fractions from the peracetic acid-treated wool by solution in ammonia[2], and the spectra of these fractions have also been examined in this frequency range. All the fractions show the two characteristic sulphonic acid peaks. The question as to whether the sulphonic acid groups are present as SO_3^- or SO_3H cannot at present be answered unambiguously from the available infra-red data. It is believed, however, that SO_3^- groups are present in L-cysteic acid as zwitterions with NH_3^+ groups. In support of this, infra-red data show L-cysteic acid to have an absorption peak at 1730 cm^{-1} characteristic of unionized carboxyl groups and also a band at approx. 2050 cm^{-1} which has been tentatively assigned to the NH_3^+ group[6]. Since treated wool has its new absorption peaks close in position to those of L-cysteic acid, this constitutes evidence for SO_3^- groups rather than $-SO_3H$, and it seems probable that strong salt links of the type $-NH_3^- \cdots SO_3-$ are present in treated wool. This matter is discussed more fully elsewhere[7].

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SUMMARY

Infra-red spectra in the range 1400 cm^{-1}–900 cm^{-1} are presented for virgin wool, peracetic acid-treated wool and L-cysteic acid. Spectral evidence, using established correlations between absorption frequencies and atomic groupings, has been obtained in favour of the direct formation of sulphonic acid groups and not an intermediate sulphonamide as a result of treating wool with peracetic acid.

RÉSUMÉ

Les spectres infrarouges, dans la région 1400 cm^{-1}–900 cm^{-1}, de la laine intacte, de la laine oxydée par l'acide peracétique et de l'acide L-cystéique sont présentés. Les indications spectrales, interprétées à l'aide des corrélations connues entre les fréquences d'absorption et les groupements d'atomes, montrent que le traitement de la laine par l'acide peracétique donne lieu à la formation directe de groupes sulfoniques et non à la formation intermédiaire de sulfonamides.

ZUSAMMENFASSUNG

Infrarote Spektra im Bereiche von 1400 cm^{-1}–1900 cm^{-1} wurden für Naturwolle, mit Peressigsäure behandelte Wolle und L-Cysteinsäure gemessen. Auf Grund von zwischen Absorptionsfrequenzen und Atomgruppen festgestellten Wechselbeziehungen wurden spektrale Beweise zu Gunsten einer direkten Bildung von Sulfonsäuregruppen erbracht, ohne durch Peressigsäurebehandlung der Wolle verursachte Zwischenbildung von Sulfonamiden.

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