Dyes and Pigments, Vol. 29, No. 4, pp. 275–294, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0143-7208/95 \$9.50 + 0.00
0143-7208(95)00051-8

Substituted Thiol Derivatives of Vinyl Sulphone Dyes

D. M. Lewis[a]* & S. M. Smith[b]

[a] Department of Colour Chemistry and Dyeing, The University of Leeds,
Leeds LS2 9JT, UK
[b] International Wool Secretariat, Valley Drive, Ilkley,
West Yorkshire LS29 8PB, UK

(Received 11 May 1995; accepted 6 June 1995)

ABSTRACT

This paper reports on the synthesis and application to wool of eight substituted thiol derivatives of a model vinylsulphone dye. The prepared compounds were classified by their dyeing characteristics into those dyes able to β-eliminate (i.e. reactive) and those unable to β-eliminate (i.e. unreactive). HPLC was employed to help the identification of these thiol adducts.

1 INTRODUCTION

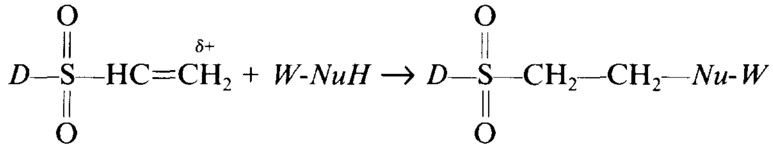
Dyes which contain substituted ethyl sulphonyl groups which β-eliminate to form the reactive vinylsulphone species enable wool to be dyed with excellent levelness and high wetfastness; their degree of reactivity will largely depend on the nature of the vinylsulphone precursor. Various vinylsulphone precursors have been synthesised and evaluated including the widely used β-sulphatoethylsulphone. The *S*-thiosulphatoethylsulphone (Bunte salt) derivative has been previously evaluated as a reactive dyeing system for wool[1] and cotton;[2] the symmetrical disulphide and thioether have also been studied by the present authors.[3] However, the synthesis and dyeing evaluation of an iso-thiouronium analogue is previously unreported. These precursors have been compared with unreactive analogues which have also been prepared from the model vinylsulphone compound.

---

* To whom correspondence should be addressed.

The first reactive dye range for wool was the Remalan, marketed by Hoechst in 1952. These dyestuffs contained a free vinylsulphone group or a vinylsulphone precursor (β-sulphatoethylsulphone group), developed and patented by Heyna and Schumacher in 1949.[4]

Vinylsulphone dyes react with wool by a nucleophilic addition mechanism since they possess a polarised olefinic double bond due to the adjacent strongly electron-withdrawing sulphone group. Reaction occurs by Michael addition; nucleophilic attack occurs on the positive side of the double bond as shown below, where *W-NuH* represents a nucleophilic group in the wool and *D* the sulphonated chromophoric residue:



$$D\text{—}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}\text{—}\overset{\delta+}{HC}{=}CH_2 + W\text{-}NuH \rightarrow D\text{—}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}\text{—}CH_2\text{—}CH_2\text{—}Nu\text{-}W$$

In 1958 Hoechst marketed the Remalan Fast E dyestuffs for wool. These were β-sulphatoethylsulphone dyestuffs able to β-eliminate during dyeing at pH 5–7 to give the reactive vinylsulphone as indicated below:

$$D\text{—}SO_2\text{—}CH_2CH_2\text{—}OSO_3^- \xrightarrow[\beta\text{-elimination}]{} D\text{—}SO_2CH{=}CH_2 + HSO_4^-$$

During dyeing the β-sulphatoethylsulphone dye gradually converts to the reactive vinylsulphone form at a rate which increases with increasing pH; thus at pH 5 conversion is very slow but at pH 6·5, depending to some extent on the dye, almost complete conversion will have occurred after 1 h at the boil. Since the β-sulphatoethylsulphone dye will behave like an acid dye it has the advantage of undergoing a certain degree of migration prior to formation of the reactive form. In order to achieve a high degree of conversion to the reactive vinyl sulphone at pH 5, where maximum dye substantivity is achieved, Hoechst developed *N*-methyltaurine adducts (Hostalan E dyes)[5] which β-eliminate readily at the boil under these conditions. Von der Eltz[2] has reviewed the Hoechst contributions in this area.

Wool keratin is a heterogeneous protein fibre; many of the protein components are highly crosslinked through cystine disulphide residues. These disulphides are extremely reactive and under mildly acidic dyebath conditions β-eliminate to perthiocysteine and dehydroaniline residues.[3] Perthiocysteine decomposes further liberating hydrogen sulphide and this, being a potent nucleophile, gives rise to thiol derivatives of the vinylsulphone dye.

2 EXPERIMENTAL

2.1 Chemicals and reagents

4-Aminobenzenesulphatoethylsulphone (74% pure) and 2-naphthol-3,6-disulphonic acid (67·6% pure) were supplied by a leading dye manufacturer. Albegal B was supplied by Ciba (UK). All other chemicals and reagents were supplied by Aldrich Chemical Company Limited and BDH Chemicals Limited. The wool fabric used in all dyeings was a botany serge (2/2 twill) supplied by Whalleys Ltd, Bradford.

2.2 Dyestuff preparation

2.2.1 β-Sulphatoethylsulphone dye (I)

The 4-aminobenzenesulphatoethylsulphone (PABSES) (0·03 moles: 74% pure; 11·43 g) was added to a water (100 ml)/sulphuric acid (98% w/w; 2·1 ml) mixture at 0–5°C. To this was added rapidly a solution of sodium nitrite (0·03 moles; 2·07 g) in water (28 ml). After 2 h the diazotised PABSES was added to a solution of disodio-2-naphthol-3,6-disulphonate (0·03 moles: 67·6% pure; 15·49 g) in water (100 ml) over 5 min maintaining pH 5–6. The resulting dye solution was heated to 50°C and sodium chloride (25 g) added; on cooling the precipitated β-sulphatoethylsulphone dye was filtered, washed with 10% aqueous sodium chloride and dried. The yield was 17·0 g (85%).

2.2.2 Vinylsulphone dye (II)

A solution of dye (**I**) was adjusted to pH 8 with sodium carbonate and heated at 50–60°C for 2 h. The resulting activated dye was precipitated by the addition of sodium chloride, filtered and washed with 10% (w/w) aqueous sodium chloride. The yield was 94%.

2.2.3 Sulphoethylsulphone dye (III)

The vinylsulphone dye (**II**) ($3{\cdot}7 \times 10^{-3}$ moles: 2·0 g) and sodium sulphite ($7{\cdot}86 \times 10^{-3}$ moles: 0·99 g) were added to water and the mixture refluxed for 1 h. The dye solution was then neutralised with acetic acid and the dye precipitated by the addition of sodium chloride (8 g). On cooling, the dye was filtered, washed with saturated sodium chloride and dried. The yield was 1·47 g (61%).

$$D\text{—}SO_2\text{—}CH{=}CH_2 + Na_2SO_3 \xrightarrow{H_2O} D\text{—}SO_2\text{—}CH_2CH_2\text{—}SO_3^-Na^+ + NaOH$$

Scheme 1

2.2.4 *S-thioglycoatoethylsulphone dye (IV)*

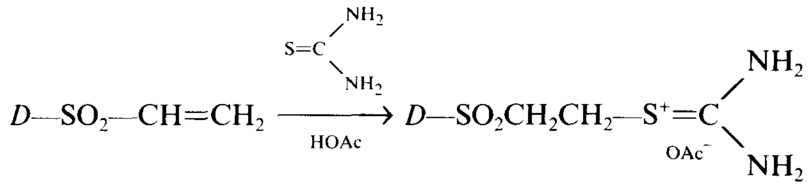
The vinylsulphone dye (**II**) ($1{\cdot}85 \times 10^{-3}$ moles: 1·0 g) was dissolved in water (50 ml) and thioglycolic acid ($1{\cdot}85 \times 10^{-3}$ moles: 0·17 g) added. The reaction mixture was stirred at room temperature for 24 h, neutralised with sodium carbonate and then precipitated by the addition of sodium chloride (10 g). The dye was filtered, washed with saturated sodium chloride and dried. The yield was 0·7 g (60%).

$$D\text{—}SO_2\text{—}CH{=}CH_2 + HS\text{—}CH_2COO^- \rightarrow D\text{—}SO_2\text{—}CH_2CH_2\text{—}SCH_2COO^-$$

Scheme 2

2.2.5 *Iso-thiouronium-ethylsulphone dye (V)*

The vinylsulphone dye (**II**) ($9{\cdot}2 \times 10^{-3}$ moles: 5·0 g) and thiourea (0·015 moles: 1·13 g) were added to glacial acetic acid (200 ml) and the mixture refluxed for 12 h. The majority of the acetic acid (~190 ml) was then removed by vacuum distillation and the remaining reaction mixture was taken to pH 5–6 with 20% w/v aqueous sodium bicarbonate (~50 ml). The precipitated dye was filtered, washed with a minimum volume of water and then dried under vacuum. The yield was 4·4 g (77%).



$$D\text{—}SO_2\text{—}CH{=}CH_2 \xrightarrow[\text{HOAc}]{S{=}C(NH_2)_2} D\text{—}SO_2CH_2CH_2\text{—}S^+{=}C(NH_2)_2 \; OAc^-$$

Scheme 3

2.2.6 *S-thiosulphatoethylsulphone (Bunte salt) dye (VI)*[6]

The vinylsulphone dye (**II**) ($5{\cdot}5 \times 10^{-3}$ moles: 3·0 g) was dissolved in water (100 ml). The solution was saturated with carbon dioxide and sodium thiosulphate pentahydrate (0·012 moles: 3·0 g) added. The temperature was raised to 50°C and carbon dioxide bubbled in for a further 2 h to reduce the high pH generated by the NaOH produced in the reaction, otherwise the Bunte salt dye would decompose. Sodium chloride was then added and on cooling the precipitated dye was filtered, washed with saturated sodium chloride and dried. The yield was 2·7 g (73%).

$$D\text{—}SO_2\text{—}CH{=}CH_2 + Na_2S_2O_3 + H_2O \rightarrow D\text{—}SO_2\text{—}CH_2CH_2\text{—}SSO_3^-Na^+ + NaOH$$

Scheme 4

2.2.7 *Thioether dye (VII)*

This dye was prepared by adding a solution of vinylsulphone dye (**II**) (0·01 moles: 5 g) in water (100 ml) to sodium hydrosulphide (0·02 moles: 1·12 g) dissolved in water (150 ml), at 0–5°C under nitrogen. After 4 h the reaction mixture was adjusted to pH 5 with acetic acid. The resulting dye solution was raised to 50°C and sodium chloride (50 g) added. On cooling, the precipitate was filtered, washed with 10% (w/w) aqueous sodium chloride and dried. The yield was 2·2 g (43%).

$$D\text{—}SO_2\text{—}CH{=}CH_2 + NaSH \rightarrow D\text{—}SO_2\text{—}CH_2CH_2\text{—}S^-Na^+$$

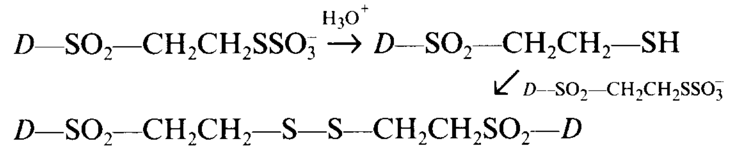
$$D\text{—}SO_2\text{—}CH_2CH_2\text{—}S^-Na^+ + D\text{—}SO_2\text{—}CH{=}CH_2$$

$$\xrightarrow{H_2O} D\text{—}SO_2\text{—}CH_2CH_2\text{—}S\text{—}CH_2CH_2\text{—}SO_2\text{—}D + NaOH$$

Scheme 5

2.2.8 *Disulphide dye (VIII)*

Route 1: The vinylsulphone dye (**II**) (0·02 moles: 10 g) was dissolved in water (400 ml). The solution was saturated with carbon dioxide and sodium thiosulphate pentahydrate (0·04 moles: 10 g) added. The temperature was raised to 50°C and carbon dioxide bubbled in for a further 2 h until conversion of the vinylsulphone to *S*-thiosulphatoethylsulphone (Bunte salt) was complete as shown by thin layer chromatography. The solution was adjusted to *c.* pH 2 with sulphuric acid (98% w/w) and refluxed for 7 days. The solution was then adjusted to pH 5 and sodium chloride (40 g) added. On cooling, the precipitated disulphide dye was filtered, washed with 10% aqueous sodium chloride and dried. The yield was 6·08 g (53%).



$$D\text{—}SO_2\text{—}CH_2CH_2SSO_3^- \xrightarrow{H_3O^+} D\text{—}SO_2\text{—}CH_2CH_2\text{—}SH$$

$$\swarrow D\text{—}SO_2\text{—}CH_2CH_2SSO_3^-$$

$$D\text{—}SO_2\text{—}CH_2CH_2\text{—}S\text{—}S\text{—}CH_2CH_2SO_2\text{—}D$$

Scheme 6

Route 2: The *S*-thiosulphatoethylsulphone dye solution was prepared as for Route 1. Thioglycolic acid (0·02 moles: 1·84 g) was then added and the solution adjusted to pH 7 with sodium carbonate. After 12 days at 25°C the pH was readjusted to pH 5. The solution was then heated to 50°C and sodium chloride (40 g) added. On cooling, the precipitated disulphide dye was filtered, washed with 10% aqueous sodium chloride and dried. The yield was 4·31 g (37%).

$$\begin{aligned}
&D\text{—}SO_2\text{—}CH_2CH_2SSO_3^- + {}^-SCH_2COO^- \\
&\qquad \rightarrow D\text{—}SO_2\text{—}CH_2CH_2\text{—}S\text{—}S\text{—}CH_2COO^- \\
&\qquad\qquad\qquad \swarrow \text{disulphide rearrangement} \\
&D\text{—}SO_2\text{—}CH_2CH_2\text{—}S\text{—}S\text{—}CH_2CH_2\text{—}SO_2\text{—}D \\
&\qquad + {}^-OOC\text{—}CH_2\text{—}S\text{—}S\text{—}CH_2COO^-
\end{aligned}$$

Scheme 7

2.3 Chromatography

2.3.1 *Thin layer chromatography (TLC)*

Silica gel was employed as the absorbent. The plates were developed in the following solvent mixture:

2-Methylpropan-2-ol:	4
Butan-1-ol:	3
Water:	3

2.3.2 *High performance liquid chromatography (HPLC)*

HPLC analysis was carried out using the Varian 5000 instrument.

Column:	Reverse Phase C-8 4·6 × 250 mm
Flow Rate:	2·0 ml min^{-1}
Detector:	480 nm and/or 254 nm
Temperature:	20°C
Conditions:	A = 0·001 M tetrabutylammonium bromide in HPLC grade water plus acetate buffer B = 0·001 M tetrabutylammonium bromide in HPLC grade methanol plus acetate buffer.

(i) Dyes **I–VI** were detected by elution in 65% eluent A: 35% eluent B

(ii) Dyes **VII** and **VIII** were detected by gradient elution as follows:

$T = 0$ min	65%A:	35%B
$T = 5$ min	65%A:	35%B
$T = 15$ min	0%A:	100%B

2.4 Application to wool

Dyeings on wool serge fabric (2·0% o.w.w.) with 1·0% Albegal B between pH 2 and pH 7 were produced for all dyes using a Zeltex Vistacolor dyeing machine. In each case the wool sample was introduced into the dyebath and the temperature raised to the boil over 30 min; dyeing at the boil was continued for a further 60 min. The dyebath pH was controlled by the use of the McIlvaine buffer system.[7]

Dyebath exhaustion (*E*) was determined by measuring the absorbance (at λ_{max}) of the dyebath at the beginning and at the end of dyeing, and expressed as a percentage.

2.4.1 Determination of fixation

A sample of each dyed fabric was repeatedly extracted with boiling 25% aqueous pyridine for 2-min periods until all the unreacted dye had been stripped. The extracts were combined and the amount of dye stripped determined spectrophotometrically. Fixation (*F*) was expressed as the percentage of dye removed from the fibre.

Visible spectra were recorded on Pye Unicam UV/VIS and Perkin Elmer Lambda 15 UV/VIS spectrophotometers.

Exhaustion versus pH and fixation versus pH profiles were obtained for each dye **I–VIII** on wool serge fabric.

2.5 Dye characterisation

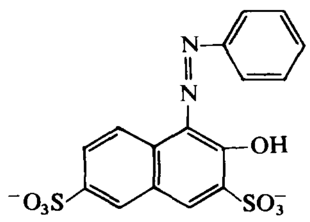
The synthesised compounds were recrystallised from a minimum amount of hot water. Care was taken with the reactive analogues to minimise β-elimination to vinylsulphone and subsequent hydrolysis to hydroxyethylsulphone. Dyes were characterised by infrared (IR) and/or elemental analysis and/or chromatographic (HPLC) analysis.

TABLE 1

Structure	*Dye*	*Type*
$D\text{—}SO_2CH_2CH_2\text{—}OSO_3H$	**I**	Reactive
$D\text{—}SO_2CH{=}CH_2$	**II**	Reactive
$D\text{—}SO_2CH_2CH_2\text{—}SO_3H$	**III**	Unreactive
$D\text{—}SO_2CH_2CH_2\text{—}S\text{—}CH_2COOH$	**IV**	Unreactive
$D\text{—}SO_2CH_2CH_2\text{—}S^+{=}C(NH_2)_2$	**V**	Reactive
$D\text{—}SO_2CH_2CH_2\text{—}SSO_3H$	**VI**	Reactive
$D\text{—}SO_2CH_2CH_2\text{—}S\text{—}CH_2CH_2SO_2\text{—}D$	**VII**	Unreactive
$D\text{—}SO_2CH_2CH_2\text{—}S\text{—}S\text{—}CH_2CH_2SO_2\text{—}D$	**VIII**	Reactive

D is the sulphonated chromophore

D =



3 RESULTS AND DISCUSSION

3.1 Structures of dyes

The structures and classification of dyes **I–VIII** are illustrated in Table 1.

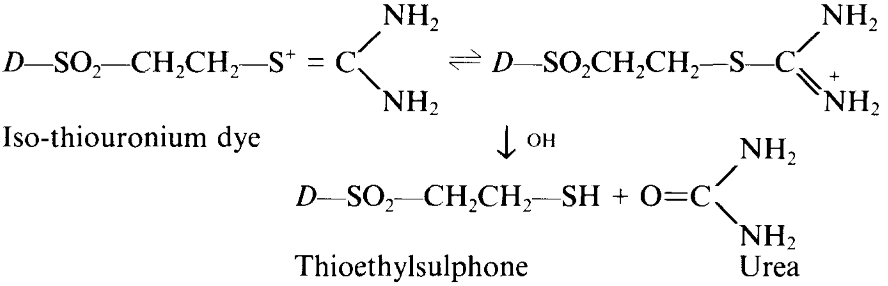
3.2 Identification of dyes I–VIII using HPLC

All the dyes were chromatographically pure, giving one band on HPLC. The vinylsulphone form (**II**) and the Bunte salt dye (**VI**) had the same retention time under the HPLC conditions employed but were well separated by TLC analyses (dye **II**, R_f value = 0·3; dye **VI**, R_f value = 0·5). Details are given in Table 2.

3.3 HPLC Investigation of the hydrolysis of dyes V and VIII

3.3.1 *Iso-thiouronium dye (V)*

Previous work has indicated that hydrolysis of iso-thiouronium dye derivatives would probably lead to the formation of thiol-terminated dyes as indicated in the following reaction scheme.[8]



Scheme 8. Hydrolysis of iso-thiouronium dyes

The synthesised iso-thiouronium dye (**V**) was dissolved in water at pH 8 (25°C). Samples were taken at various intervals in order to monitor iso-

TABLE 2
Chromatographic Retention Times of Dyes **I–VIII**

Dye	HPLC elution conditions	Column retention time (min)
I	Isocratic	5·1
II	Isocratic	7·2
III	Isocratic	4·8
IV	Isocratic	2·8
V	Isocratic	2·3
VI	Isocratic	7·2
VII	Gradient	9·4
VIII	Gradient	10·1

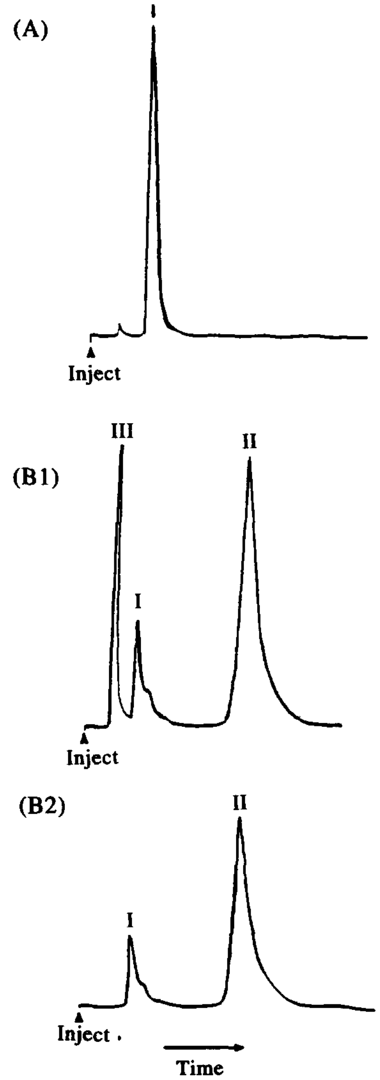
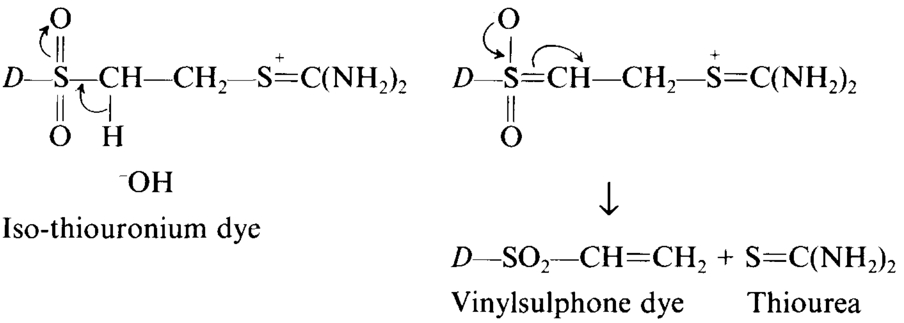


Fig. 1. Chromatographs from iso-thiouronium dye hydrolysis investigation: (A) Starting iso-thiouronium dye; (B1) Hydrolysed (pH 8, 24 h, 25°C) iso-thiouronium dye, detection wavelength = 254 nm; (B2) Detection wavelength = 480 nm.

thiouronium dye hydrolysis using HPLC. Figure 1 shows chromatographs of the starting dye (peak I) (detection wavelength = 254 nm) and the hydrolysed dye solution (detection wavelength = 254 and 480 nm) after 24 h at pH 8 (25°C).

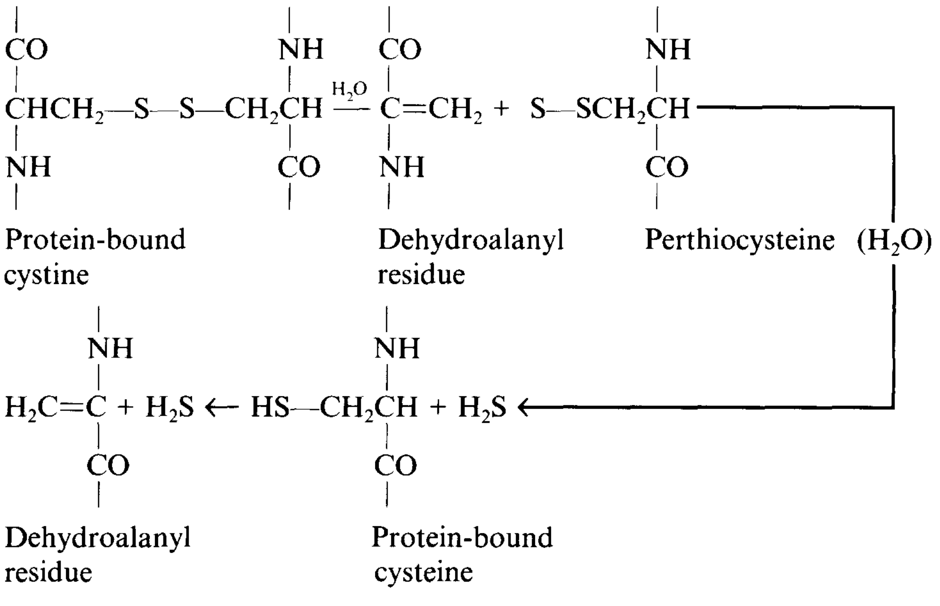
At 254 nm, the iso-thiouronium hydrolysate produced three peaks. However, on changing the detection wavelength to 480 nm, the peak at 1 min (i.e. peak III) disappeared indicating that its occurrence was due to a compound absorbing only in the UV. Cross-checking with standard thiourea and vinylsulphone dye solutions indicated that the two new major peaks arising were, in fact, due to the two starting reactants used in the synthesis of the iso-thiouronium dye (i.e. vinylsulphone dye (peak II) and thiourea (peak III)). This was probably due to ready β-elimination to the vinylsulphone brought about by the strong electron-withdrawing effect of the sulphone group coupled with the proximity of the cationic iso-thiouronium residue. The proposed mechanism is shown below:



Scheme 9. β-Elimination of the iso-thiouronium dye

*3.3.2 Disulphide dye (**VIII**)*

The nature of the disulphide bond of dye **VIII** is such that a β-elimination mechanism can occur which is similar to that in the hydrolysis of the cystine double bond in wool.



Scheme 10. Wool cystine hydrolysis reactions

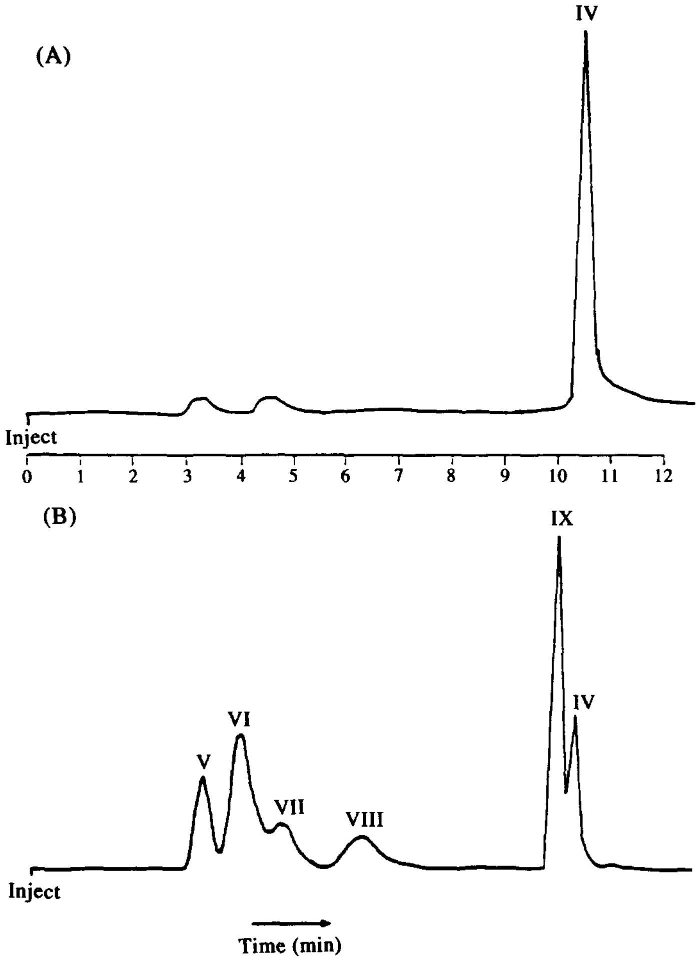
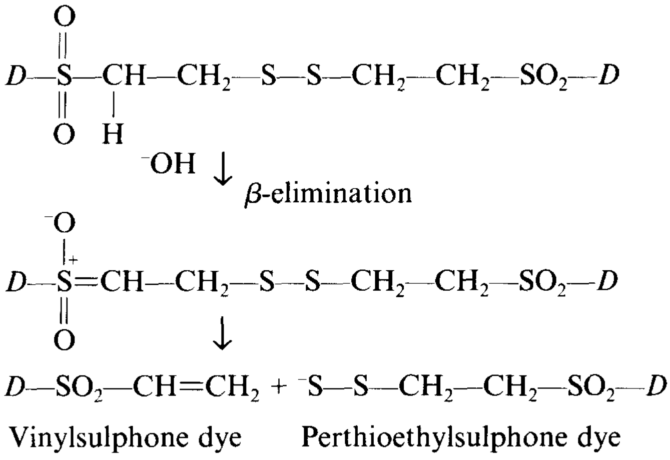


Fig. 2. Chromatographs from disulphide dye hydrolysis investigation: (A) Starting disulphide dye; (B) Hydrolysed (pH 9, 4 h, 50°C).

The synthesised disulphide dye was treated in an aqueous pH 9 solution at 50°C for 4 h. On cooling, a sample of the hydrolysate was analysed using gradient elution and a detection wavelength of 480 nm. Figure 2 shows chromatographs of the starting disulphide dye peak (**IV**) and the hydrolysed sample.

The hydrolysate gave four new peaks. The peak corresponding to disulphide dye was still present indicating a reasonable stability to alkaline hydrolysis. Cross-checking with standard vinylsulphone and hydroxyethylsulphone (i.e. hydrolysed vinylsulphone) dye solutions indicated that peaks VIII and V were due to the presence of these compounds respectively. Peaks VI and VII could not be assigned to any of the standard dyes prepared. Peak IX was checked against a standard and found to be due to the formation of thioether dye during disulphide dye hydrolysis.

Further investigation confirmed the stability of the disulphide dye towards alkaline degradation. Figure 3 shows the chromatograph obtained after the alkaline disulphide dye solution was refluxed for 4 h at pH 9. Disulphide dye was still detectable; again peaks V, VIII and IX were found to be due to hydroxyethylsulphone, vinylsulphone and thioether, indicating that the dye disulphide undergoes alkaline hydrolysis via similar mechanisms to those well-documented for cystine hydrolysis.[9,10] These reactions are summarised in the following schemes which account for the presence of vinylsulphone, hydroxyethylsulphone and thioether in the disulphide hydrolysate:



$$D\text{—}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}\text{—}\underset{\underset{\displaystyle H}{|}}{CH}\text{—}CH_2\text{—}S\text{—}S\text{—}CH_2\text{—}CH_2\text{—}SO_2\text{—}D$$

$$\Big\downarrow {}^{-}OH \quad \beta\text{-elimination}$$

$$D\text{—}\overset{\overset{\displaystyle {}^{-}O}{|_{+}}}{\underset{\underset{\displaystyle O}{\|}}{S}}=CH\text{—}CH_2\text{—}S\text{—}S\text{—}CH_2\text{—}CH_2\text{—}SO_2\text{—}D$$

$$\Big\downarrow$$

$$D\text{—}SO_2\text{—}CH{=}CH_2 + {}^{-}S\text{—}S\text{—}CH_2\text{—}CH_2\text{—}SO_2\text{—}D$$

Vinylsulphone dye Perthioethylsulphone dye

Scheme 11. Mechanism for disulphide dye hydrolysis

$$D\text{—}SO_2\text{—}CH_2CH_2\text{—}SS^- + H_2O \rightarrow D\text{—}SO_2\text{—}CH_2CH_2SH + H_2S$$

Scheme 12. Perthioethylsulphone hydrolysis

$$D\text{—}SO_2\text{—}CH{=}CH_2 + D\text{—}SO_2CHCH_2SH$$
$$\rightarrow D\text{—}SO_2\text{—}CH_2CH_2\text{—}SCH_2CH_2SO_2\text{—}D$$

Scheme 13. Reaction of the vinylsulphone and thioethylsulphone dyes to give the thioether dye

$$D\text{—}SO_2\text{—}CH_2{=}CH_2 + {}^{-}OH \rightarrow D\text{—}SO_2\text{—}CH_2CH_2OH$$

Scheme 14. Vinylsulphone dye hydrolysis

Schemes 11–14 show that perthioethylsulphone and thioethylsulphone are probable intermediates produced during disulphide dye hydrolysis. This was confirmed by the presence of the thioether dye. Also, the thio-

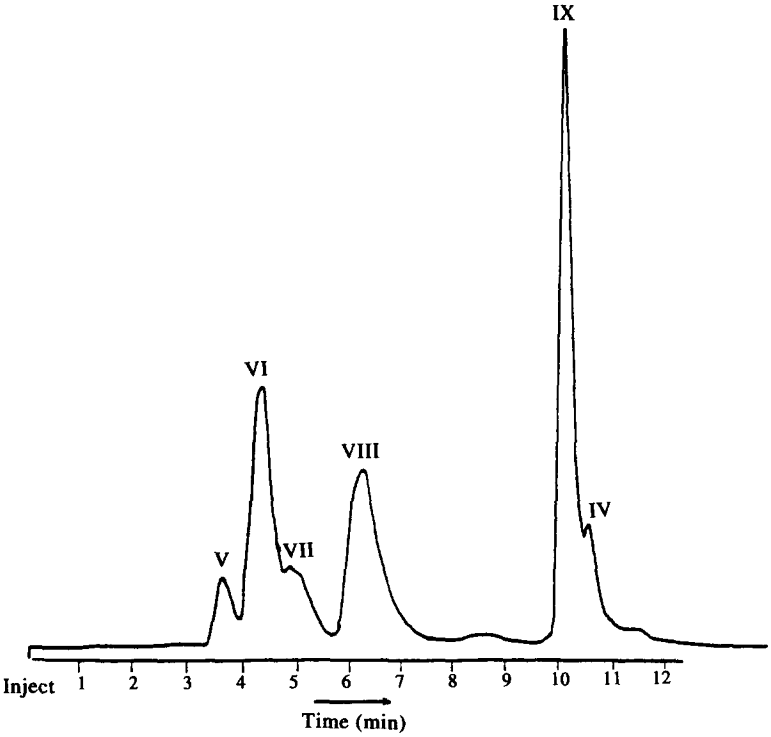


Fig. 3. Chromatograph of disulphide dye hydrolysis (pH 9, refluxed, 4 h).

ethylsulphone dye has a similar structure to the hydroxyethylsulphone and would therefore be expected to have a comparable HPLC retention time. A theoretical increase in retention time due to an increase in molecular weight would be observed. By the above arguments peak VI could have corresponded to thioethylsulphone dye formation during disulphide dye hydrolysis. Using the same arguments, peak VI could have corresponded to the perthioethylsulphone intermediate.

Ghadimi,[11] working with cysteine model compounds, found that perthiocysteine attacked the cystine disulphide bond forming a trisulphide bond. Close inspection of Figs 2 and 3 showed the possible presence of another peak at a retention time of *c.* 11·5 min. This peak was probably due to the presence of the trisulphide formed during disulphide hydrolysis as indicated below:

$$D\text{—}SO_2CH_2CH_2\text{—}S\text{—}S\text{—}CH_2CH_2SO_2\text{—}D + HS\text{—}S\text{—}CH_2CH_2\text{—}SO_2D$$
$$\downarrow$$
$$D\text{—}SO_2CH_2CH_2\text{—}S\text{—}S\text{—}S\text{—}CH_2CH_2SO_2D + HS\text{—}CH_2CH_2\text{—}SO_2\text{—}D$$

Scheme 15. Formation of trisulphide dye

TABLE 3
Elemental Analysis Results

Dye	*Required (%)*			*Found (%)*		
	C	*H*	*N*	*C*	*H*	*N*
I: $C_{18}H_{13}N_2O_{13}S_4Na_3$ (+3H_2O)	30·1	2·6	3·9	29·6	2·5	3·6
II: $C_{18}H_{12}N_2O_9S_3Na_2$ (+4H_2O)	35·3	3·1	4·7	35·2	3·2	4·6
V: $C_{19}H_{17}N_4O_9S_4Na_2$ (+3H_2O)	33·9	3·4	7·9	33·9	3·4	8·3
VI: $C_{18}H_{13}N_2O_{12}S_5Na_2$ (+5H_3O)	28·1	3·0	3·6	28·0	2·9	3·6
VII: $C_{36}H_{26}N_4O_{18}S_7Na_4$ (+6H_2O)	35·2	3·1	4·5	35·2	2·9	4·4
VIII: $C_{36}H_{26}N_4O_{18}S_8Na_4$ (+6H_2O)	34·3	3·0	4·4	34·4	2·8	4·3

3.4 Elemental and IR analyses

Elemental analysis of polysulphonated dyes may give misleading results since these dyes tend to crystallise with a varying number of water molecules in their crystal structure. The dangers of overdrying, leading to dyestuff decomposition, were considered to be very significant for many of the reactive and thiol derivatives synthesised in this work; thus the presence of water of crystallisation was unavoidable and CHN analysis results were adjusted accordingly.

Recrystallisation of the sulphoethylsulphone and *S*-thioglycolatoethylsulphone dyes from water was not possible since both dyes were highly soluble. The crude products in both cases contained a significantly high quantity of sodium chloride which led to poor colour yields on application

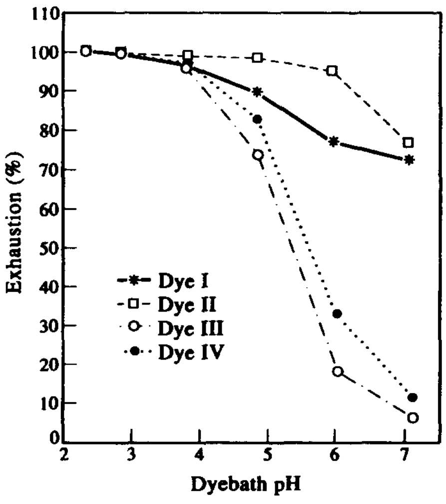


Fig. 4. pH v exhaustion profile for dyes I–IV.

to wool. To overcome this problem these dyes were not isolated from solution but were prepared *in situ* prior to dyeing. HPLC analysis of solutions of these dyes clearly indicated that the starting vinylsulphone had completely reacted with sodium sulphite (for dye **III**) and thioglycolic acid (for dye **IV**) giving one peak in each case.

The iso-thiouronium dye (**V**) was not recrystallised from hot water due to its high reactivity and ease of hydrolysis to the starting vinylsulphone and thiourea. The crude product was chromatographically pure by HPLC and gave the characteristic $(\text{—NH}_3)^+$ peak at 1666 cm^{-1} in IR spectroscopy. Elemental analysis of the crude product indicated a higher nitrogen content than expected. This was not an unexpected finding since the crude product will contain a small quantity of thiourea which is high in nitrogen. The *S*-thiosulphatoethylsulphone dye (**VI**) gave the characteristic $(\text{—S—SO}_3)^-$ peak at 1022 cm^{-1} in IR spectroscopy. Data are given in Table 3.

3.5 Application of dyes I–VIII to wool

The exhaustion and fixation data provided in this section characterise the dyeing properties possessed by each dye over the range of pH values examined. The pH versus exhaustion profiles are represented graphically for dyes **I–IV** in Fig. 4 and dyes **V–VIII** in Fig. 5. These show that dyes **I–VIII** had high substantivity for the fibre at low pH values (pH < 4). As the dyeing pH was increased the β-sulphatoethylsulphone (**I**) vinylsulphone (**II**), iso-thiouronium (**V**), *S*-thiosulphatoethylsulphone (**VI**) and disulphide (**VIII**) dyes still exhibited high substantivity ($E > 50\%$ at pH 7), whereas

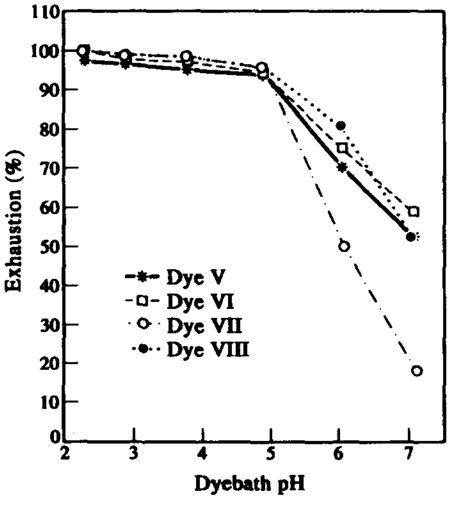


Fig. 5. pH v exhaustion profile for dyes V–VIII.

the sulphoethylsulphone (**III**), *S*-thioglycolatoethylsulphone (**IV**) and thioether (**VII**) dyes showed low substantivity ($E < 20\%$ at pH 7).

The synthesised compounds (**I–VIII**) were sulphonated anionic dyes and as such exhibited substantivity profiles comparable to acid dyes for wool. At low dyebath pH (pH < 4) the fibre acquired a strong overall positive potential, the acidic residues (aspartyl, glutamyl and C-terminal) being largely undissociated and the basic residues (arginyl, lysyl, histidinyl and N-terminal) being protonated. The high substantivity exhibited by these dyestuffs may be explained by the ionic attraction of sulphonated anions for protonated amino groups during dyeing, but hydrophobic and π–π interactions also play a role which may vary with dye structure. The increased number of protonated sites available for electrostatic dye–fibre interaction, brought about by the low dyeing pH, made the initial dye uptake (strike) very rapid and consequently unlevel. However, the relatively small size of the dye molecules facilitates dye migration as the temperature increases, giving dyeings of good levelness. As dyebath pH increases the overall positive potential of the wool decreases and protonation of the basic residues is significantly decreased, reducing the number of sites available for anionic dye–fibre electrostatic interaction. Consequently, those dyes which exhaust mainly by electrostatic interactions show much reduced exhaustion levels as the dyeing pH increases. This was found to be the case for the sulphoethylsulphone (**III**) and *S*-thioglycolatoethylsulphone (**IV**) dyes.

The thioether dye exhibited moderate substantivity for the fibre when dyeing at weakly acidic pH values ($E = 50\%$ at pH 6). Although electrostatic forces are partly responsible for the initial dye–fibre interaction

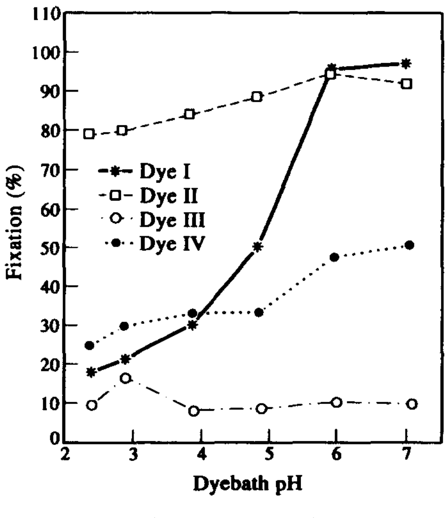


Fig. 6. pH v fixation profile for dyes **I–IV**.

(exhaustion), dye migration was reduced due to the hydrophobic Van der Waals forces operating between polar regions in the dye and in the fibre. The electrostatic and hydrophobic forces between the dye and wool imparted moderate substantivity and therefore moderate exhaustion at weakly acidic dyebath pH values. This behaviour is similar to that of an acid milling dye.

The β-sulphatoethylsulphone (I), vinylsulphone (II), iso-thiouronium (V) and *S*-thiosulphatoethylsulphone (VI) dyes exhibited high substantivity for wool at neutral to weakly acidic pH values. These dyes were able to react with lysine, cysteine, histidine and N-terminal side chains during dyeing and, therefore, are not solely dependent on non-covalent interactions to exhaust.

Under weakly acidic to neutral pH values non-covalent interactions enabled adsorption of the reactive dye anion to occur; the adsorbed dye was then able to react with any unprotonated lysine, histidine and N-terminal or cysteine residues.

The disulphide dye (VIII) exhibited a similar exhaustion profile to the reactive dyes **I**, **II**, **V** and **VI**. This dye was able to β-eliminate to produce reactive residues and its high molecular weight increased hydrophobic dye–fibre interactions in a similar way to the thioether dye.

The pH v fixation profiles for the dyes are represented graphically for dyes **I–IV** in Fig. 6 and dyes **V–VIII** in Fig. 7. Figure 6 shows that the fixation of the β-sulphatoethylsulphone dye (I) increased as the dyebath pH increased, reaching optimum values at pH 6–7. The fixation of the reactive vinylsulphone dye (II) was fairly high at all dyebath pH values ($F > 80\%$) reaching a maximum at pH 5·5–6·0. The fixation of the

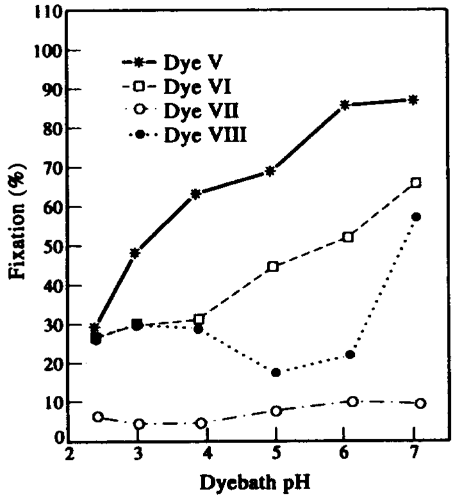


Fig. 7. pH v fixation profile for dyes V–VIII.

unreactive sulphoethylsulphone dye (**III**) was very low at all dyeing pH values ($2 < \mathrm{pH} < 7$). The fixation of the *S*-thioglycolatoethylsulphone (**IV**) was low over the pH range pH 2–5 and increased to optimum values at pH 6–7 ($F = 40$–50%).

Figure 7 shows that the fixation of the reactive iso-thiouronium dye (**V**) increased as the dyebath pH increased, reaching optimum values at pH 6–7. The fixation of the *S*-thiosulphatoethylsulphone dye (**VI**) increased steadily as the dyebath pH increased, reaching an optimum value of $F = 65\%$ at pH 7. The unreactive thioether dye (**VII**) exhibited very low fixation at all pH values ($2 < \mathrm{pH} < 7$). The disulphide dye (**VIII**) fixation was low over the pH range 2–6, but increased rapidly after $\mathrm{pH} > 6$ to approximately 60% at pH 7.

Dyes **I**, **V**, **VI** and **VIII** are able to covalently bond to the fibre due to their ability to β-eliminate to form the reactive vinylsulphone in the dyebath. The propensity for β-elimination leading to vinylsulphone formation and dye–fibre reaction increases with increasing pH.

The iso-thiouronium dye (**V**) β-eliminates more efficiently at lower pH values (pH 3–5) than the β-sulphatoethylsulphone dye ($F = 60$–65% at pH 4–5 compared with $F = 30$–50% at pH 4–5 respectively). As the dyebath pH was increased to pH 6–7 the fixation of both dyes and, therefore vinylsulphone formation, was similar ($F = 90\%$ at pH 6–7).

Dyes **I** and **V** clearly β-eliminate to the reactive vinylsulphone more efficiently than the disulphide dye since a number of side reactions occur folowing β-elimination of dye **VIII**.

The unreactive sulphoethylsulphone and thioether dyes were unable to β-eliminate to the reactive species at pH 2–7 and thus were readily stripped from the wool. The *S*-thioglycolatoethylsulphone was unable to β-eliminate and the moderate level of fixation (40–50%) at pH 6–7 should be placed in context with the low exhaustion (30–10%) and may be thus due to experimental error.

The dye chromophore present was stable to stripping with 25% aqueous pyridine. Those dyes able to β-eliminate tended to convert slowly to the vinylsulphone form during the stripping process but it was concluded that this reaction would have no effect on the fixation results since desorption is significantly more rapid than dye activation and subsequent reaction with the fibre.

4 CONCLUSIONS

The synthesis and characterisation (HPLV, IR and/or elemental analysis) of eight thiol derivatives of a model vinylsulphone dye have been carried

TABLE 4
β-Elimination Potential of the Dyes

Dye	*β-Elimination*
I	Yes
III	No
IV	No
V	Yes
VI	Yes
VII	No
VIII	Yes

out. The dyeing characteristics have been investigated and the dyestuffs classified in distinct groupings as determined by interpretation of the exhaustion and fixation profiles.

The pH versus exhaustion profile investigation grouped the synthesised dye compounds into four main different dyeing mechanism categories, as follows:

Dyes **I**, **II**, **V** and **VI**	Ionic/reactive
Dyes **III** and **IV**	Ionic
Dye **VII**	Ionic/hydrophobic
Dye **VIII**	Ionic/hydrophobic/reactive

The pH versus fixation profile investigation grouped the synthesised dye compounds into those able to β-eliminate to the vinylsulphone reactive species over the pH range ($2 < \mathrm{pH} < 7$) and those unable to β-eliminate as shown in Table 4.

The efficiency of β-elimination of dyes **I**, **V**, **VI** and **VIII** was also determined as indicated:

Iso-thiouronium (**V**)
β-Sulphatoethylsulphone (**I**)
S-thiosulphatoethylsulphone (**VII**)
Disulphide (**VIII**)

↑ Increasing ease of β-elimination to form the vinylsulphone reactive species.

ACKNOWLEDGEMENTS

The authors are grateful for the encouragement and financial support of the Wool Foundation (Ilkley).

REFERENCES

1. Caldwell, J. B. & Milligan, B., *Text. Res. J.*, **33** (1963) 481.
2. Von der Eltz, H. U., *Melliand Textilberichte*, **6** (1971) 687.
3. Lewis, D. M. & Smith, S. M., *J. Soc. Dyers & Col.*, **107** (1991) 357.
4. Heyna, J. & Schumacher, W., *German Patent* 966902 (1949).
5. Osterloh, F., *Textil Praxis*, **26** (1971) 164.
6. Caldwell, J. B. & Milligan, B., *Text. Res. J.*, **33** (1963) 481.
7. Vogel, A. I., *Textbook of Quantitative Inorganic Analysis*, 2nd edn. Longmans, London, 1951, p. 869.
8. Bell, V. A. & Lewis, D. M., *J. Soc. Dyers & Col.*, **93** (1977) 140.
9. Steenken, I. & Zahn, H., *J. Soc. Dyers & Col.*, **102** (1986) 269.
10. Milligan, B. & McClaren, J. A., *Wool Science—the Chemical Reactivity of the Wool Fibre*. Science Press, NSW, Australia, 1981.
11. Ghadimi, M., *PhD Thesis*, Open University, 1991.