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Study on the Hydrolysis Kinetics of Vinylsulfonyl Reactive Dye–Fiber Bond

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ABSTRACT

The alkaline hydrolysis rate constants k *of dyed cotton fiber were measured for a series of vinylsulfonyl reactive dyes and the alkaline hydrolysis rate constants* k′ *of corresponding model dye–fiber compounds were determined. The structure of the reactive dye largely determines the rate of hydrolysis of the dyed fiber. There is a good linear correlation between* k *and* k′ *for the same reactive groups. The hydrolytic behavior of the dyed cotton fiber can thus be explained by reference to the hydrolysis behavior of the corresponding model dye–fiber compounds, thus enabling studies on the mode of hydrolysis of the vinylsulfonyl reactive dye–fiber bond to be made, using MO theory.*

1 INTRODUCTION

The stability of the dye–fiber bond in dyeings of fiber reactive dye has been extensively studied[1–5] in particular with respect to the loss of color of the dyed fiber in aqueous alkaline or aqueous acidic medium, and to the determination of the quantity of hydrolyzed dye in this medium or of dye on the dyed fiber by spectrophotometric methods. The vinylsulfonyl dyes are an important class of reactive dyes and dyeings given by them are stable in aqueous acidic medium, but not in aqueous alkali. In this present paper we report a study of the kinetics of the alkaline hydrolysis and stability of the vinylsulfonyl dye–fiber bond using spectrophotometric and high-performance liquid chromatographic techniques.

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A series of reactive intermediates based on vinylsulfonyl-substituted anilines was synthesized, and these intermediates were diazotized and coupled with R-salt and β-naphthol to produce dyes containing different reactive groups and the corresponding model dyes. The dyes were applied to cellulose and the hydrolysis rate constants, k, of the dyed fiber were measured. In this way, relationships between the structure of the reactive dyes and the alkaline hydrolysis of reactive dye–fiber bonds can be made. The cellulose fiber is a polyhydroxyl compound, and combines with the reactive dye as a primary alcohol,[6] and thus, in a model system, the cotton can be replaced by methanol. The model dyes combine with methanol to produce model dye–fiber compounds. The rate constants of these model compounds, k', were measured and comparison of the k and k' values for the same reactive group showed that the hydrolysis behavior of the dyed fiber could be explained in terms of the hydrolysis behavior of the corresponding model dye–fiber compounds.

2 HYDROLYSIS KINETICS OF DYE–FIBER BOND

The processes involved in the hydrolysis of the dye–fiber bond in alkaline medium can be summarized as follows.

2.1 Diffusion of hydroxyl ion from medium to the surface of the dyed fiber

Fick's first law of diffusion shows that

$$J_{\mathrm{OH}^-} = -D(\mathrm{d}C_{\mathrm{OH}^-}/\mathrm{d}x) \tag{1}$$

where J_{OH^-} is the diffusion flux, which is the diffusion quantity of hydroxyl ion per unit time through unit area, D is the diffusion coefficient and $\mathrm{d}C_{\mathrm{OH}^-}/\mathrm{d}x$ is the concentration gradient of hydroxyl ion. Equation (1) shows that the difference of concentration is the diffusion motive force; that is to say, the substance diffuses always from high concentration to low until the concentrations are equal. The diffusion rate of the hydroxyl ion is in proportion to the difference between the hydroxyl ion concentration in the medium and on the dyed fiber surface, and this is given by eqn (2)

$$r_\mathrm{d} = k_\mathrm{d}([\mathrm{OH}^-]_\mathrm{l} - [\mathrm{OH}^-]_\mathrm{c}) \tag{2}$$

where r_d is the diffusion rate of hydroxyl ion from the medium to the dyed fiber surface; k_d is the corresponding diffusion rate constant; $[\mathrm{OH}^-]_\mathrm{l}$ and $[\mathrm{OH}^-]_\mathrm{c}$ are the hydroxyl ion concentrations in the medium and on the dyed fiber surface respectively.

2.2 Combination of hydroxyl ion with dyed fiber

The hydroxyl ion attacks the ether bond of the dyed fiber ($D—SO_2CH_2CH_2—O—Cell$) and the resulting hydrolysis process may be analyzed as follows:[8]

$$D—SO_2CH_2CH_2—O—Cell + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} D—SO_2CHCH_2—OCell + H_2O \tag{3}$$

$$D—SO_2\check{C}HCH_2—O—Cell \overset{k_2}{\rightleftharpoons} D—SO_2CH{=}CH_2 + CellO^- \tag{4}$$

$$D—SO_2CH{=}CH_2 + OH^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} D—SO_2\bar{C}HCH_2—OH \tag{5}$$

$$D—SO_2\bar{C}HCH_2OH + H_2O \xrightarrow{k_4} D—SO_2CH_2CH_2—OH + OH^- \tag{6}$$

In eqns (3)–(6), the $k_n (n = 1,2,3,4, -1, -3)$ are the reaction rate constants.

2.3 Diffusion of hydrolytic dye from the fiber surface to the medium

Using

$A = D—SO_2CH_2CH_2—OCell$	Dye–fiber compound
$B = D—SO_2\bar{C}HCH_2—OCell$	Hydrolysis intermediate of dye–fiber compound
$C = D—SO_2\bar{C}HCH_2—OH$	Hydrolysis intermediate of dye
$D = D—SO_2CH{=}CH_2$	Vinylsulfonyl dye
$E = D—SO_2CH_2CH_2OH$	Hydrolyzed dye

Then

$$r'_d = k'_d([E]_c - [E]_l) \tag{7}$$

In eqn (7), r'_d is the diffusion rate of hydrolyzed dye from the fiber surface to the medium; k'_d is the corresponding diffusion rate constant; $[E]_c$ and $[E]_l$ are the hydroxyl ion concentrations on the dyed fiber surface and in the medium respectively.

Thus, we may derive the kinetics equation for the alkaline hydrolysis of the dyed fiber and eqn (8) can be obtained from eqn (3).

$$-d[OH^-]/dt = k_1[A][OH^-] - k_{-1}[B][H_2O] \tag{8}$$

When the hydrolysis tends to stabilize, the rates of consecutive steps are equal to each other, so that

$$r_d = -d[OH^-]_c/dt \tag{9}$$

Combining eqns (2), (8) and (9) gives:

$$k_d([OH^-]_l - [OH^-]_c) = k_1[A][OH^-]_c - k_{-1}[B][H_2O]$$

$$[OH^-]_c = \frac{k_d[OH^-]_l + k'_{-1}[B]}{k_1[A] + k_d} \tag{10}$$

(where $k'_{-1} = k_{-1}[H_2O]$).

Compounds B, C, D may be considered to be intermediates in the reaction and if the reaction is steady, the concentrations of these compounds are independent of the reaction time in accord with the steady-state approximation.[9] Thus we may set out eqns (11)–(14) from eqns (3)–(6), viz.,

$$d[C]/dt = k_3[D][OH^-]_c - k_{-3}[C] - k'_4[C] = 0 \tag{11}$$

(where $k'_4 = k_4[H_2O]$).

$$d[D]/dt = k_2[B] - k_3[D][OH^-]_c + k_{-3}[C] = 0 \tag{12}$$

$$d[B]/dt = k_1[A][OH^-]_c - k'_{-1}[B] - k_2[B] = 0 \tag{13}$$

$$d[E]_c/dt = k'_4[C] \tag{14}$$

Combining eqns (11)–(14) and (10) gives

$$\begin{aligned} d[E]_c/dt &= \frac{k_1k_2}{k'_{-1} + k_2}[A][OH^-]_c \\ &= \frac{k_1k_2}{k'_{-1} + k_2} \cdot \frac{k_d[OH^-]_l + k'_{-1}[B]}{k_d + k_1[A]}[A] \end{aligned} \tag{15}$$

Since compound B is an intermediate, its concentration is very low and is negligible compared with $[OH^-]_c$, i.e., $[B] \rightarrow 0$ and hence eqn (15) may be approximated to give:

$$d[E]_c/dt = \frac{k_1k_2k_d}{(k'_{-1} + k_2)(k_d + k_1[A])}[A][OH^-]_l \tag{16}$$

Equation (16) is the alkaline hydrolysis kinetics equation of dyed fiber (dye–fiber bond).

The hydrolysis reaction of the dye-fiber link behaves as a pseudo-first-order reaction if the diffusion rate of hydroxyl ions into the fiber is large enough, i.e. $k_d \gg k_1[A]$, to keep $[OH^-]_c$ constant, and $[OH]_l$ is large and almost constant. In this extreme case, i.e. when the diffusion rate of hydroxyl ion from the medium to the dyed fiber surface greatly exceeds the rate of the hydrolysis reaction ($k_d \gg k_1[A]$), we may express the equation as follows:

$$d[E]_c/dt = [k_1k_2/(k'_{-1} + k_2)][A][OH^-]_l \tag{17}$$

Equation (17) may be simplified by supposing $k_a = k_1k_2/(k'_{-1} + k_2)$, the apparent hydrolysis rate constant, so that

$$d[E]_c/dt = k_a[A][OH^-]_l \tag{18}$$

When the alkaline hydrolysis is well stirred, we may also assume that the diffusion rate is larger than the reaction rate and the extreme condition may be achieved.

The alkaline hydrolysis of the model dye–fiber compounds ($D—SO_2—CH_2CH_2—OCH_3$) is a single-phase system and there is no diffusion problem when the reaction has achieved a stable condition.

Equations similar to (3) and (7) may be written for the model dye–fiber compound and a similar second-order reaction kinetics equation to eqn (17) may be given:

$$d[DOH]/dt = k_b[D—OCH][OH^-] \tag{19}$$

in which k_b is the apparent hydrolysis rate constant of the model dye–fiber compound.

If the alkaline hydrolysis is in excess alkali, we may assume the $[OH^-]$ is constant and the reaction behaves as a pseudo-first-order reaction. The rate constant of the pseudo-first-order reaction is a function of $[OH^-]$.

Given $k = k_a[OH^-]_1$, $k' = k_b[OH^-]$.

Equations (3)–(7) may be summarized and the total reaction equation represented as follows

$$D—OR + OH^- \longrightarrow D—OH + RO^- \tag{20}$$

($R = \text{Cell}, CH_3$)

$$-d[D—OR]/dt = -d[OH^-]/dt = d[E]_c/dt = d[D—OH]/dt$$

Hence eqns (18) and (19) may be rearranged to give:

$$-d[DOCell]/dt = k[DOCell] \tag{21}$$

$$-d[DOCH_3]/dt = k'[DOCH_3] \tag{22}$$

The integral forms of eqn (21) and eqn (22) are

$$\ln\frac{[DOCell]_0}{[DOCell]_t} = kt \tag{23}$$

$$\ln\frac{[DOCH_3]_0}{[DOCH]_t} = k't \tag{24}$$

Equations (21) and (24) are the kinetic equations for the alkaline hydrolysis which we have derived and eqn (16) may be rearranged to give:

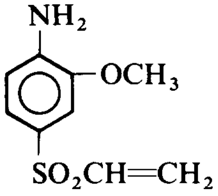
$$-\frac{\mathrm{d}[\mathrm{DOCell}]}{\mathrm{d}t}=\frac{k\,.\,k_{\mathrm{d}}[\mathrm{DOCell}]}{k_{\mathrm{d}}+k_{1}[\mathrm{DOCell}]} \tag{25}$$

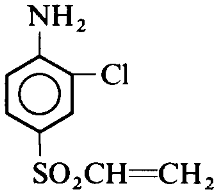
Equation (25) shows that, if the diffusion rate of OH^- into the fiber is slow, i.e. k_d is not much larger than $k_1[A]$, the reaction is not pseudo-first-order, though the hydrolysis is in a large excess of alkali.

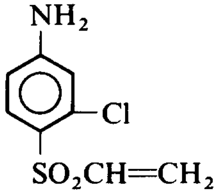
3 EXPERIMENTAL METHODS

3.1 Synthesis of reactive intermediates

Vinylsulfonyl-substituted anilines of formulae

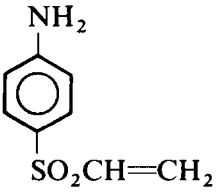


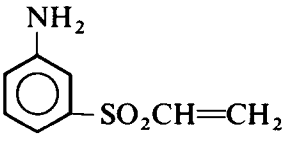




were synthesized using the general route shown in Scheme 1.

In addition, Shanghai Dyestuffs Chemical Plant No. 8 kindly supplied two further intermediates, viz.



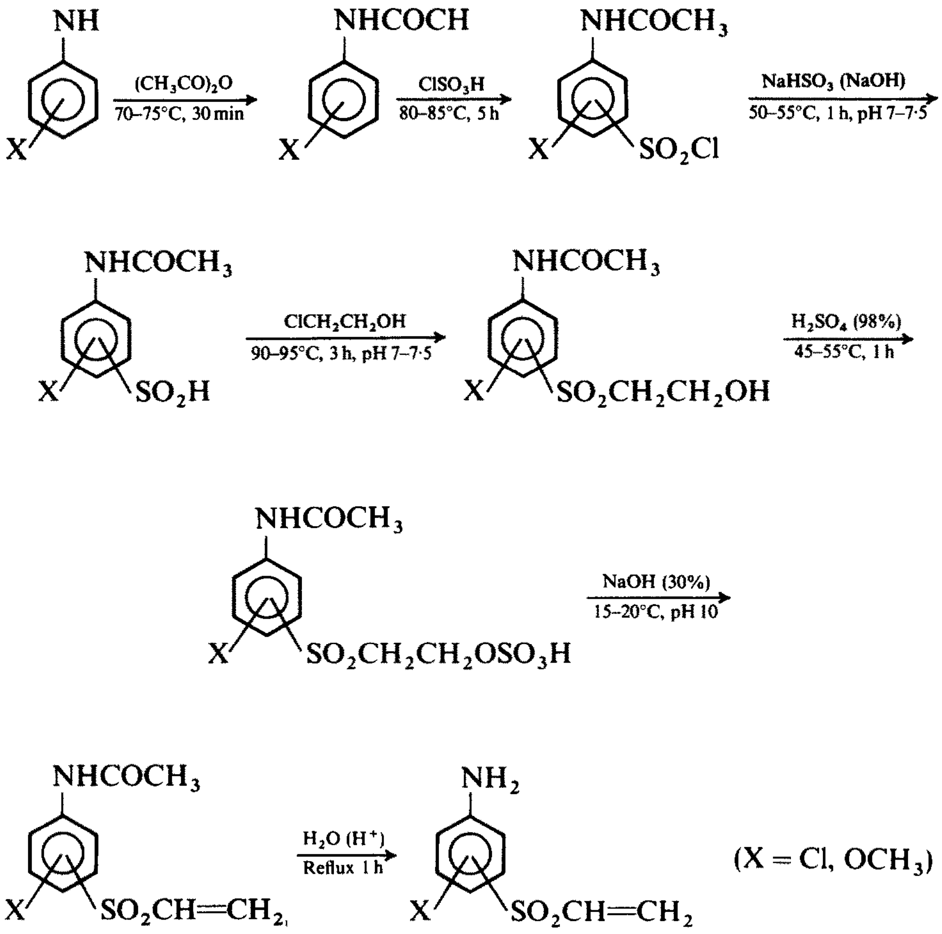


3.2 Synthesis of reactive and model reactive dyes

The above intermediates were diazotized and coupled at 5–8°C and pH 7–7·5 with R-salt and β-naphthol to produce reactive dyes and the corresponding model compounds shown in Table 1.

3.3 Dyeing of cotton fiber with reactive dye

Cotton cloth (2·00 ± 0·01 g/piece) was dyed with the five reactive dyes listed in Table 1 in a high-temperature and high-pressure laboratory dyeing machine



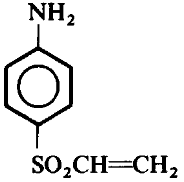
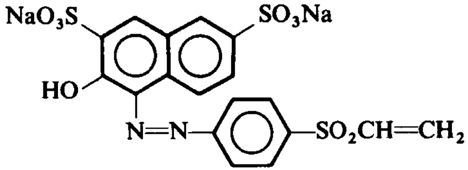
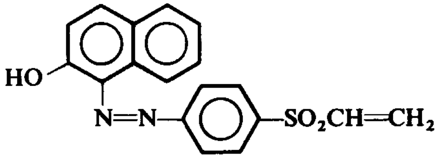
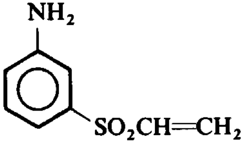
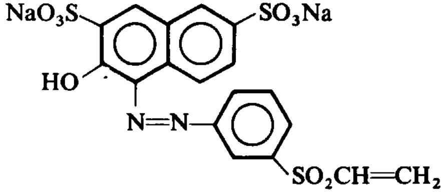
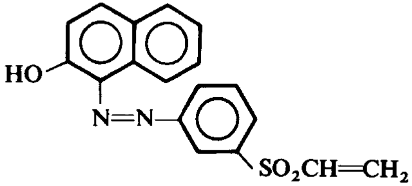
Scheme 1

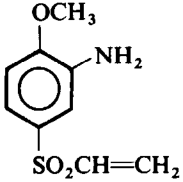
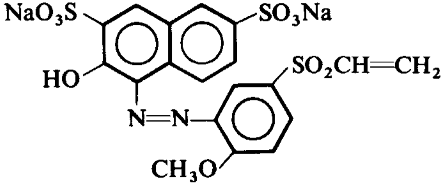
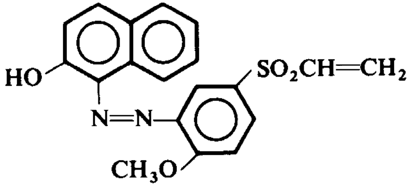
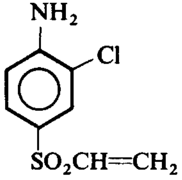
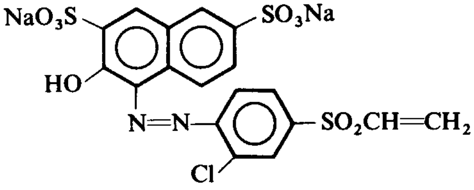
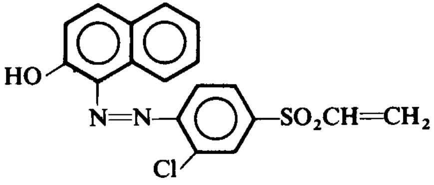
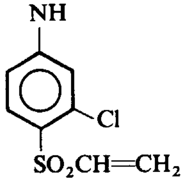
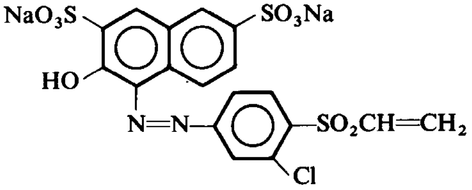
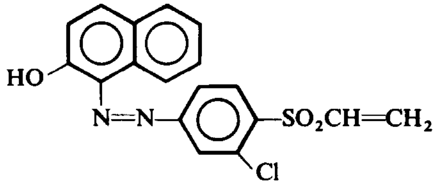
to give 10 dyed specimens for reactive dye, using the following conditions:

Depth of shade	3%
Liquor ratio	1:30
Glauber's salt, anhyd.	60 g litre^{-1}
Trisodium phosphate, cryst.	10 g litre^{-1}
Fixation temperature, time	60°C, 30 min
Dyeing temperature, time	60°C, 45 min

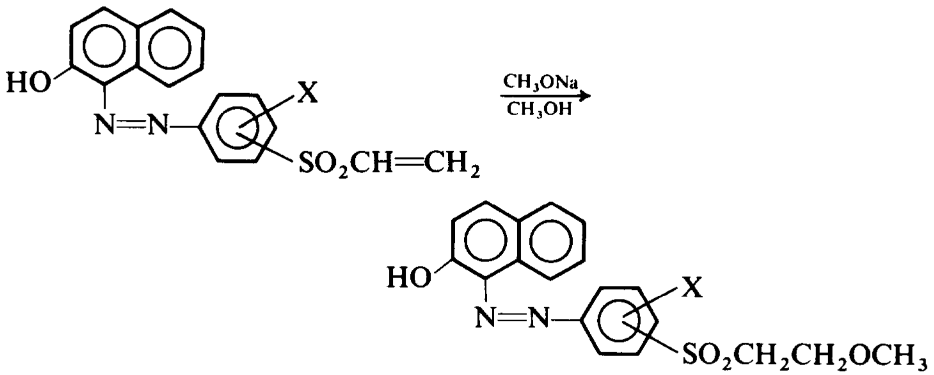
After dyeing, the dyed samples were washed with cold water and then heated in 3 g litre^{-1} neutral soap for 15 min at 95°C before washing with hot and cold water, and drying.

TABLE 1
Reactive Dyes and Model Reactive Dyes

Intermediates	*Reactive dyes*	*Model reactive dyes*
		
		

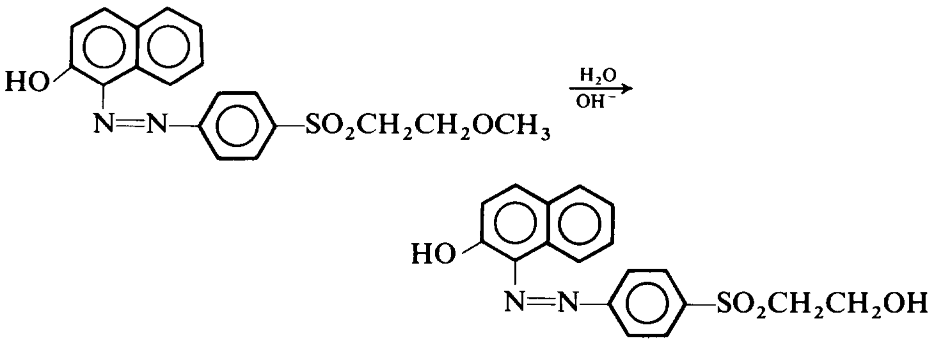
3.4 Synthesis and purification of model dye–fiber compounds



To a methanolic sodium methoxide solution prepared from methanol (60 ml) and sodium (0·69 g; 0·3 mol), was added at room temperature 0·3 mol of the model reactive dye, and the resulting solution was stirred while heating to reflux. After 1·5 h, the reaction was complete (TLC, using as developing solvent chloroform : acetone (10 : 1)). The cooled solution was poured onto ice–water slowly with stirring and the orange precipitate which separated was filtered, washed with water and dried.

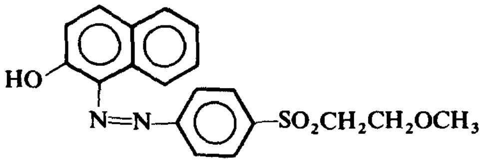
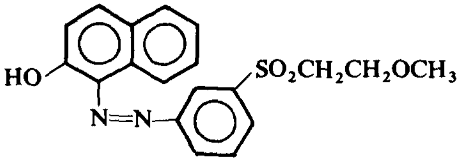
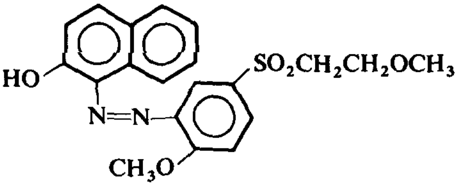
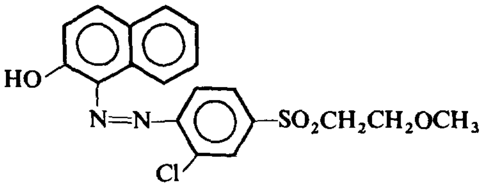
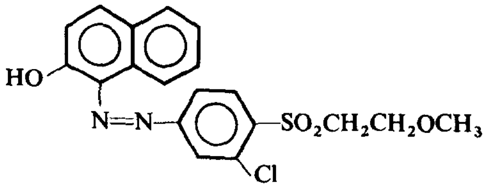
The product was recrystallized from methanol and chloroform, and purified by column chromatography [neutral alumina as fixed phase, chloroform : acetone (20 : 1) as developing solvent]. The melting points of the model compounds, elemental analysis and MS data are listed in Tables 2 and 3.

3.5 Synthesis and purification of the product of hydrolysis of model dye–fiber compounds



The model compound (0·01 mol) was added to sodium hydroxide (4 g) dissolved in water and dioxane (1 : 1) (100 ml) and the solution was then

TABLE 2
Structure and Melting Point of Model Dye–Fiber Compounds

No.	*Structure*	*M.p. (°C)*
M-1		191–192
M-2		136–137
M-3		183–184
M-4		184–185
M-5		158–159

heated to 60–65°C for 3 h. After cooling, solution was poured onto 100 ml of cold water and the orange precipitate filtered, washed and dried. It was recrystallized from chloroform, and purified by column chromatography [neutral alumina as fixed phase and chloroform:acetone (10:1) as developing solvent].

M.p. 223–224°C, p^+ at *m/e* 356. Calc.: C, 60·7; H, 4·5; N, 7·9. Found: C, 60·3; H, 4·5; N, 7·8%.

TABLE 3
Results of Elemental Analysis and MS Data

No.	*Calculated* (%)			*Observed* (%)			*Molecular ionic peak*
	C	*H*	*N*	*C*	*H*	*N*	
M-1	61·62	4·86	7·57	61·35	4·76	7·48	370
M-2	61·62	4·86	7·57	61·22	4·74	7·52	370
M-3	60·00	5·00	7·00	59·62	4·94	6·84	400
M-4	56·37	4·20	6·92	56·11	4·18	6·90	404
M-5	56·37	4·20	6·92	55·98	4·27	6·79	404

3.6 Alkaline hydrolysis kinetics of dyed fiber

Ten test-tubes containing 150 ml aqueous solution of 10 g liter^{-1} sodium hydroxide were heated to 60 ± 0·1°C in a high-temperature and high-pressure laboratory dyeing machine for 30 min, and ten dyed specimens added respectively. The dyed specimens were taken out at intervals of several minutes and immersed in cold water quickly to prevent hydrolysis. They were washed, heated in 3 g liter^{-1} neutral soap solution for 15 min, and washed again, dried, ironed, and the *K*/*S* values determined using the MIL TON ROY 350 Measure and Match System (USA).

3.7 Alkaline hydrolysis kinetics of model dye–fiber compounds

The model dye–fiber compound (0·000 125 mol) was dissolved in 20 ml dioxane:water (9:1), and heated to 60 ± 0·1°C for 30 min; 5 ml of 0·5% sodium hydroxide solution which had been preheated to 60 ± 0·1°C was then added with good stirring. Samples were taken at intervals and added to cold dilute hydrochloric acid, maintaining pH 5–6 to prevent hydrolysis. The samples are analyzed using the Shimadzu LC-6A system (Japan).

4 RESULTS AND DISCUSSION

4.1 Calculation of the basic hydrolysis rate constants of dyed fiber

A method involving the determination of the color strength was used to measure the alkaline hydrolysis rate constants of the dyed fiber.

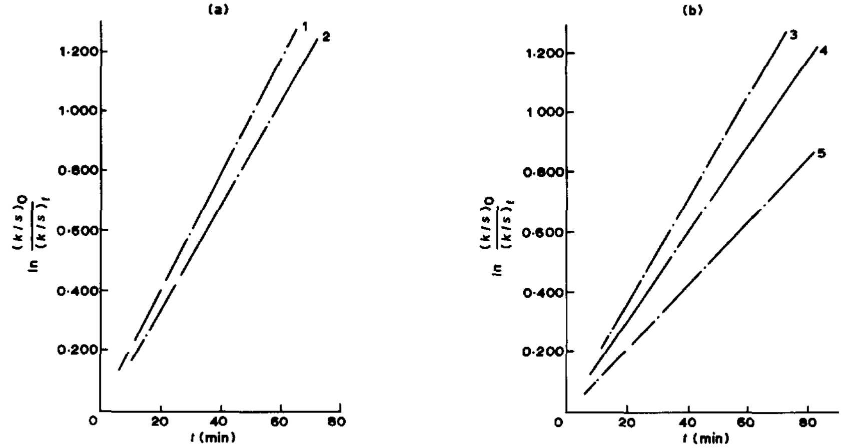
It is known that there is no linear relation between the reflection coefficient of dyed fiber and the dye content on fiber. The *K*/*S* value, which is in proportion to the dye content on fiber,[10] is defined by eqns (26) and (27):

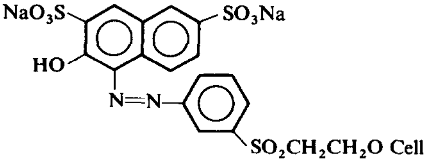
$$K/S=(1-R)^2/2R \tag{26}$$

$$(K/S)_1/(K/S)_2=C_1/C_2 \tag{27}$$

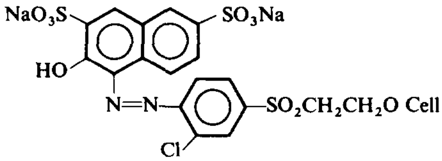
In eqns (26) and (27), R is the reflectance, K is the absorbance; and $(K/S)_1$ and $(K/S)_2$ are the K/S values of dyed fiber having dye concentrations of C_1 and C_2.

For each of the reactive dyes shown in Table 1 were drawn hydrolysis kinetics plots of the dyed fiber (see Figs 1(a) and (b)). These show that there is a good relationship between $\ln[(K/S)_0/(K/S)_t]$ and the hydrolysis reaction





(1)



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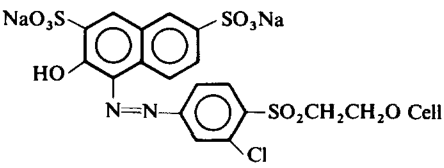
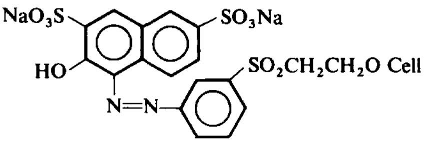
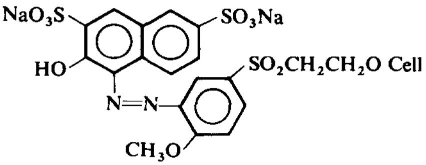


(2)



(4)



(5)

Fig. 1. Hydrolysis kinetics plots of dyed fiber.

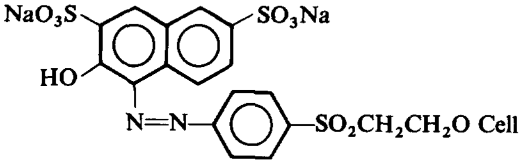
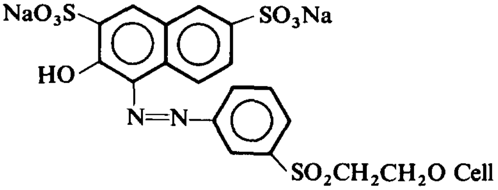
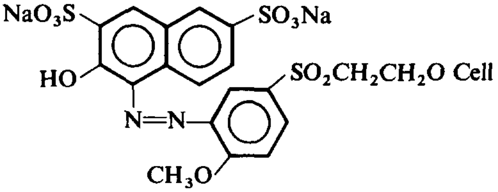
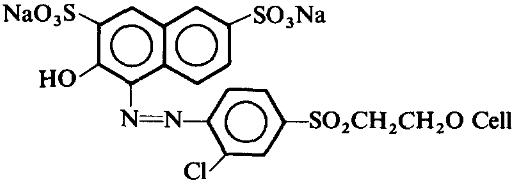
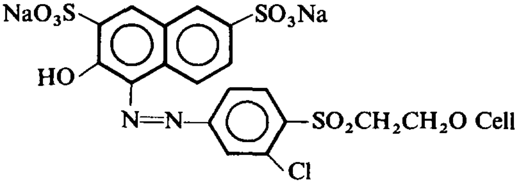
time t, and the slopes of the plots express the alkaline hydrolysis rate constants of the dyed fiber under the conditions used, i.e. with good stirring and in excess alkali.

Combining eqns (22) and (27) gives

$$\ln[(K/S)_0/(K/S)_t] = kt \tag{28}$$

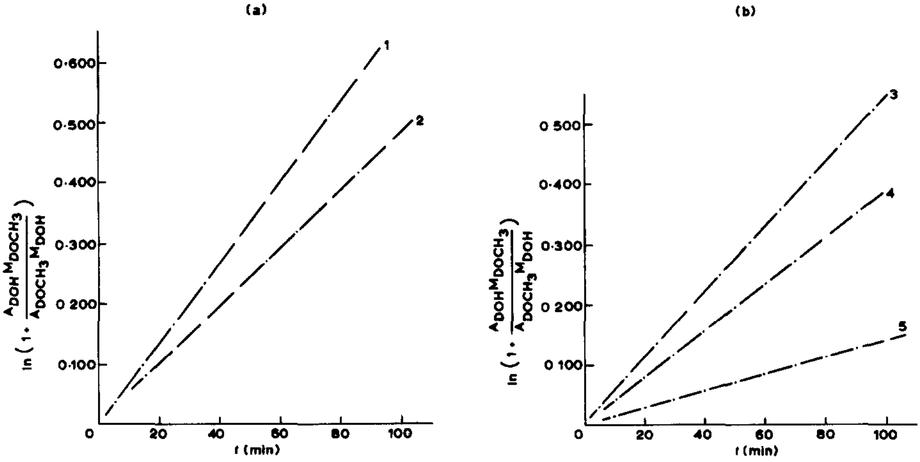
Regression analysis of the data was used and the slopes of the line regression equations (k) and the correlation coefficients (γ) are shown in Table 4.

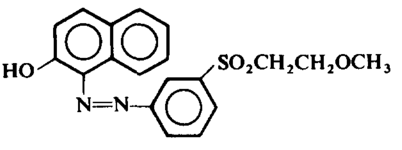
TABLE 4
Hydrolysis Rate Constants and Correlation Coefficients of Dyed Fiber

Structure	k (*min*)	γ
	0·0146	0·9984
	0·01961	0·9992
	0·01035	0·9985
	0·01755	0·9991
	0·01718	0·9987

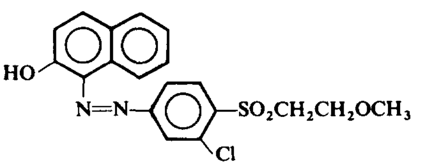
4.2 Calculation of the alkaline hydrolysis rate constants of model dye–fiber compounds

The model dye–fiber compound and its hydrolysis product were separated by HPLC to measure the alkaline hydrolysis rate constants of the model compounds. Methanol was used as the mobile phase on an ODS packed column and a visible–ultraviolet light detector was used for estimations of the λ_{max} of the model compounds. Separation was good and there was no disturbance. The external-standard method was used to effect a quantitative analysis. The results showed that the ratio of the peak areas of the model

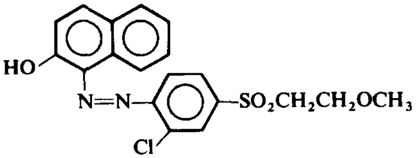




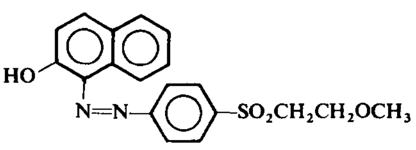
(1)



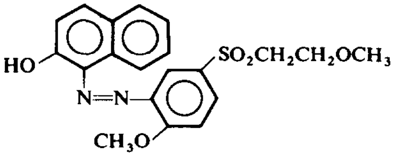
(2)



(3)



(4)



(5)

Fig. 2. Hydrolysis kinetics plots of model dye–fiber compounds.

compounds and the hydrolyzed compounds was equal to the ratio of their weights, so that

$$A_{\mathrm{DOCH_3}}/A_{\mathrm{DOH}} = W_{\mathrm{DOCH_3}}/W_{\mathrm{DOH}} \tag{29}$$

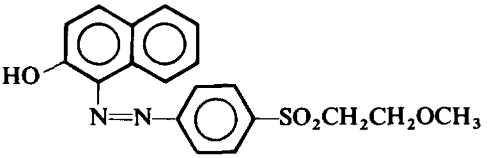
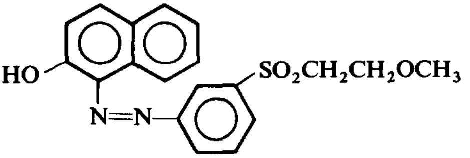
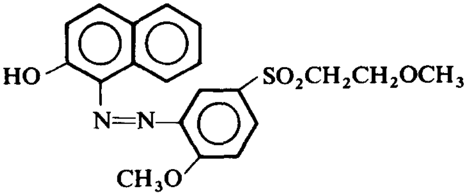
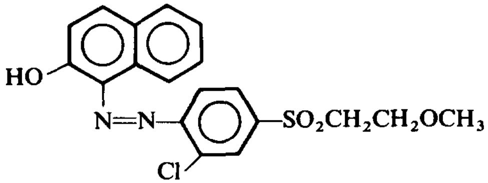
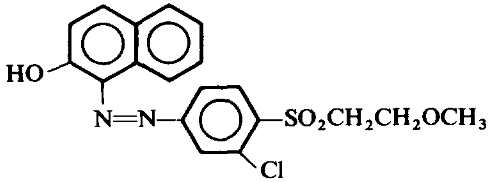
$$[\mathrm{DOCH_3}]/[\mathrm{DOH}] = (A_{\mathrm{DOCH_3}}/A_{\mathrm{DOH}})\cdot(M_{\mathrm{DOH}}/M_{\mathrm{DOCH_3}}) \tag{30}$$

In eqns (29) and (30) [ ] represents the mole concentration, A is the liquid-chromatographic peak area, W is weight and M is the molecular weight.

For each of the model compounds shown in Table 2, the hydrolysis

TABLE 5

Hydrolysis Rate Constants and Correlation Coefficients of Model Dye–Fiber Compounds

Structure	k′ (*min*$^{-1}$)	γ	$\lambda_{\max}$ (*nm*)
	$3{\cdot}843 \times 10^{-3}$	0·999 8	476
	$6{\cdot}825 \times 10^{-3}$	0·999 9	465
	$1{\cdot}343 \times 10^{-3}$	0·999 6	482
	$5{\cdot}439 \times 10^{-3}$	1·000 0	472
	$4{\cdot}899 \times 10^{-3}$	0·999 7	473

kinetics plots (see Figs 2(a) and (b)) show that there is a good linear relationship between $\ln[1+(A_{DOH}/A_{DOCH_3})(M_{DOCH_3}/M_{DOH})]$ and the hydrolysis reaction time t; the slopes of these plots express the alkaline hydrolysis rate constants of the dyed fiber (under conditions of good stirring and with a large excess of alkali).

The hydrolysis can be represented as follows:

$$DOCH_3 + H_2O \rightarrow DOH + CH_3OH$$

$$[DOCH_3]_0 = [DOCH_3]_t + [DOH]_t \tag{31}$$

Combining eqns (24), (30) and (31) gives

$$\ln[1+(A_{DOH}/A_{DOCH_3}).(M_{DOCH_3}/M_{DOH})] = k't \tag{32}$$

The resulting data were analyzed by regression analysis and the slopes of the line regression equations (k') and the correlation coefficients (γ) are shown in Table 5.

4.3 Comparison of the alkaline hydrolysis of dyed fiber and model dye–fiber compound

From the data in Tables 4 and 5, comparison can be made of the alkaline hydrolysis rate of the dyed fiber and of the model dye–fiber compounds, for the same reactive group. These comparisons are shown in Table 6 and in Fig. 3.

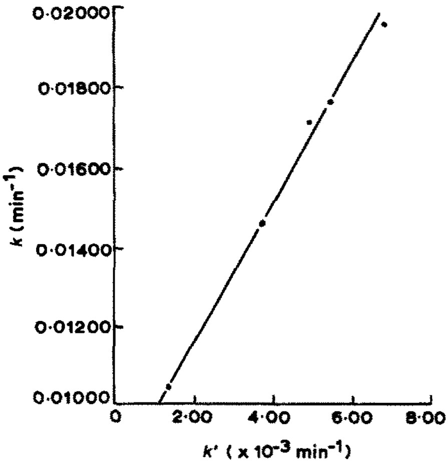
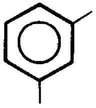
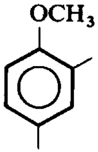
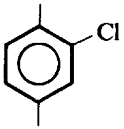
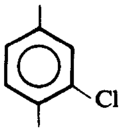


Fig. 3. Comparison between k and k'.

TABLE 6
Comparison of Rate Constants k and k' (min^{-1})

	Reactive group				
	 $SO_2CH_2CH_2OR$	 $SO_2CH_2CH_2OR$	 $SO_2CH_2CH_2OR$	 $SO_2CH_2CH_2OR$	 $SO_2CH_2CH_2OR$
$DOCH_3$	$3{\cdot}843 \times 10^{-3}$	$6{\cdot}825 \times 10^{-3}$	$1{\cdot}343 \times 10^{-3}$	$5{\cdot}439 \times 10^{-3}$	$4{\cdot}899 \times 10^{-3}$
DOCell	0·014 60	0·019 61	0·010 35	0·017 55	0·017 18

$R = CH_3$, Cell

Treatment of the k and k' data by regression analysis gives the linear regression equation (33) and the correlation coefficients γ

$$k = 1{\cdot}726k' + 8{\cdot}143 \times 10^{-3} \tag{33}$$

$$\gamma = 0{\cdot}9955$$

It can be seen that there is a very good linear relationship between k and k' and thus the hydrolytic behavior of the dyed fiber can be fully explained in terms of the hydrolytic behavior of the corresponding model dye–fiber compound.

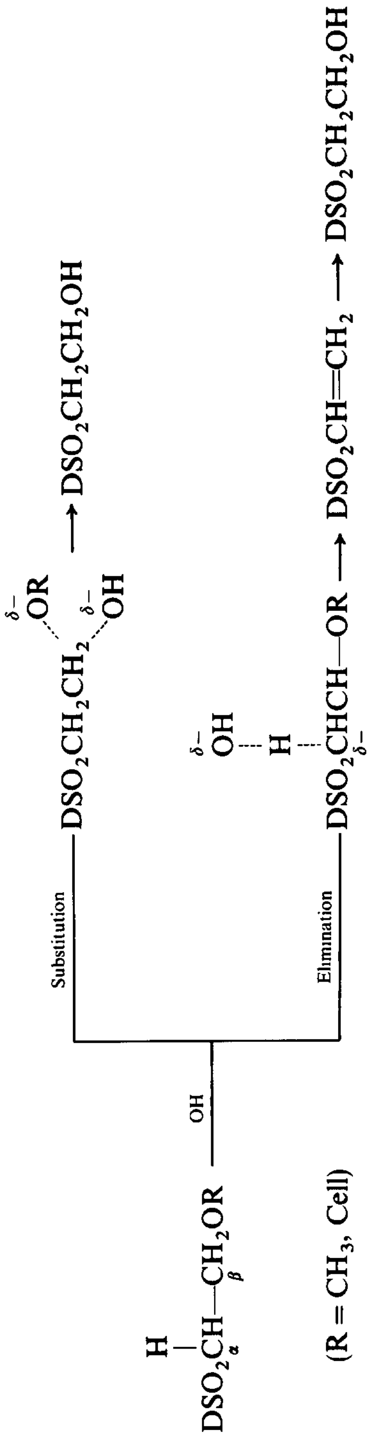
4.4 Reliability of the derivation of hydrolysis kinetics equation

Vinylsulfonyl reactive dyes combine with cellulose fiber to form the ether bond. Under alkaline conditions, when the nucleophilic reagent OH^- attacks the ether bond, both nucleophilic substitution and nucleophilic elimination occur almost simultaneously but in different relative proportions (Scheme 2).[11]

Nucleophilic substitution takes place when the nucleophile attacks the β-carbon atom, and the reaction rate depends on the nucleophilicity of the reagent. Nucleophilic elimination occurs when the nucleophile attacks the α-hydrogen atom, and the reaction rate is here dependent on the alkalinity of the reagent.

Steric effects also have a large influence on the reaction courses. The cellulose fiber is comparatively large and it is easier for OH^- to approach the α-hydrogen atom than the β-carbon atom when the OH^- attacks the dye–fiber bond. A strongly alkaline medium is necessary for the hydrolysis behavior of the model dye–fiber compound to approach the hydrolysis of the dyed fiber. Whilst the elimination reaction between OH^- and the dye–fiber bond produces the vinylsulfonyl dye, OH^- continuously attacks the vinylsulfonyl dye to produce the hydroxyethylsulfonyl dye.

Tables 4 and 5 show that the range of correlation coefficients is from 0·9984 to 0·9992 for dyed fiber, and from 0·9996 to 1·000 for model dye–fiber compounds and hence the linear relation is very good. Therefore, the alkaline hydrolysis both of the dyed fiber and of the model dye–fiber compounds proceeds strictly by pseudo-first-order reaction under the experimental conditions used. In Section 2 we have indicated under which conditions the alkaline hydrolysis of the dyed fiber deviates from the pseudo-first-order reaction, but such a case did not occur in our experiments, because the cotton fiber washed by soap was hydrophilic, the reaction was controlled by good stirring, and when the dyed fiber was placed in the alkaline solution we did not record the time immediately since the reaction has an unstable period at the beginning, especially in the non-homogeneous reaction medium.


DSO2CH(H)—CH2OR
α
β
OH
Substitution
Elimination
DSO2CH2CH2 δ−OR δ−OH
DSO2CH2CH2OH
δ−OH H DSO2CHCH—OR δ−
DSO2CH=CH2
DSO2CH2CH2OH
(R = CH3, Cell)

Scheme 2.

5 CONCLUSIONS

A series of vinylsulfonyl reactive dyes and model reactive dyes has been synthesized. Cellulose was dyed with the reactive dyes to produce the dyed fiber and the model reactive dyes were reacted with sodium methoxide to produce model dye–fiber compounds. The determination of the color strength of the dyed fiber was used to measure the alkaline hydrolysis rate constants, and HPLC was used to measure the alkaline hydrolysis rate constants of the model dye–fiber compounds.

Comparison of the hydrolysis behavior of both dyed fiber and model dye–fiber compounds shows that the hydrolysis behavior of dyed fiber can be fully explained by the hydrolysis behavior of model dye–fiber compounds. This enables a study to be made of the mode of hydrolysis of the vinylsulfonyl reactive dye–fiber bond using MO theory. The structures of the reactive dyes have an influence on the stability of the dye–fiber bond, and the results obtained provide a basis for investigation into the synthesis of reactive dyes having good fastness.

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