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Study of Some Chemical Properties of Sulfonated Vinylsulfonyl Reactive Dyes

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ABSTRACT

The authors have synthesized a water-soluble vinylsulfonyl reactive dye and its alcoholysis products. Gel chromatography was used to separate and purify these compounds. The determination of the reaction rate constants of the alkaline hydrolysis and alcoholysis of the vinylsulfonyl reactive dye has been made by the ion-pair reversed-phase HPLC technique. The ratio of reaction rate constants of this reactive dye with n*-propanol, isopropanol and water is 1·00:0·19:0·52. The reaction rate constants of the alkaline hydrolysis of the model dye–fiber compounds have also been determined by the same method. The ratio of hydrolytic reaction rate constants of dye–primary ether bond to dye–secondary ether bond is 0·92:1·00.*

1 INTRODUCTION

The reactivity and the fastness to hydrolysis of the dye–fiber bond are important properties of reactive dyes and we have made previous studies of these properties.[1,2] There is no confirmatory evidence that the predominant reaction of vinylsulfonyl reactive dye with cellulose (**A**) occurs at the primary OH group or at the secondary OH groups. Stamm[3] found that the reaction of vinylsulfonyl reactive dye with cellulose occurs predominantly at the secondary OH group on C-2. Bullock & Rowland,[4,5] Chekalin,[6] Bahgwanth, Rama Rao & Venkataraman,[7] however, found that the reaction occurs predominantly at the primary OH group on C-6.

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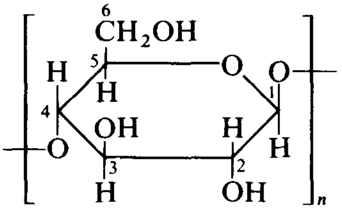
Yu Rong-Gen[8] synthesized a series of model vinylsulfonyl reactive dyes without a water-soluble group in the model dye molecule, and chose *n*-propanol and isopropanol to model the primary OH group and the secondary OH group of cellulose, respectively. The kinetics of the alcoholysis of the model dyes in organic solvents were determined. He found that the ratio of reaction rate constants of the model dyes with *n*-propanol to that with isopropanol, was between 4·02:1 and 4·86:1.



(**A**)

In this present paper, *n*-propanol and isopropanol are also chosen to model the primary OH group and secondary OH group of the cellulose (**A**), respectively. A water-soluble vinylsulfonyl reactive dye with a sulfonic acid group in the dye molecule and two corresponding model dye–fiber compounds have been synthesized. These compounds were purified by gel chromatography. The kinetics of the alkaline hydrolysis and alcoholysis of the dye and of the alkaline hydrolysis of the model dye–fiber compounds have been studied in aqueous medium by the ion-pair reversed-phase HPLC technique.

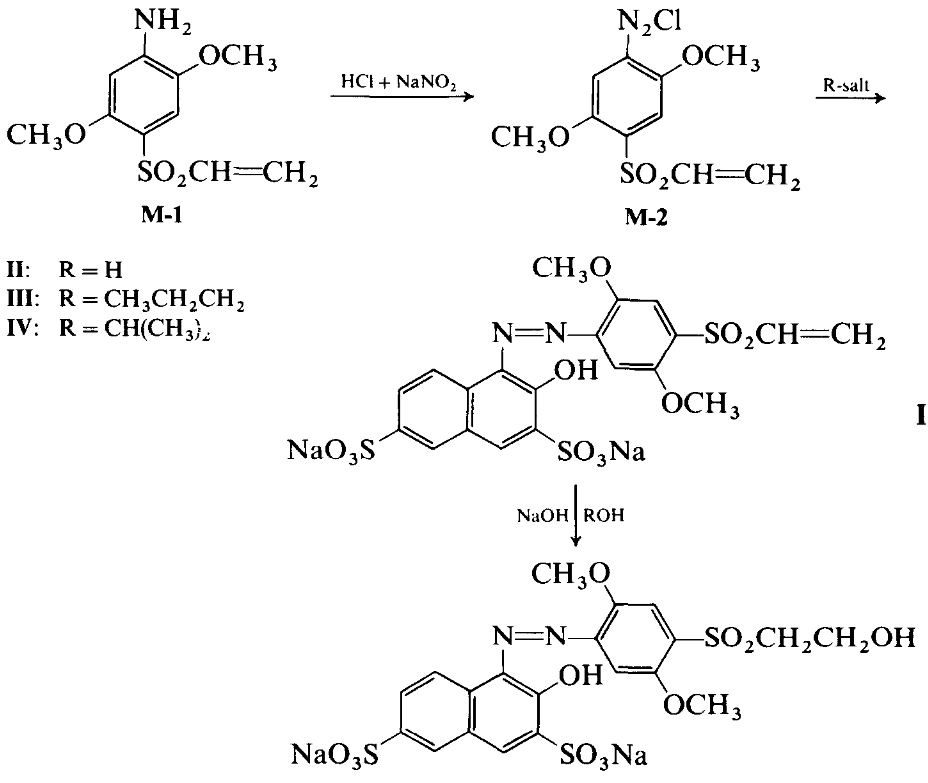
2 PREPARATION OF SAMPLES

2.1 Route of synthesis

Dyes **I–IV** were synthesized as indicated by Scheme 1.

TABLE 1
Elementary Analytical Data of Compounds **I–IV**

Compound	*Calculated (%)*				*Found (%)*			
	C	*H*	*N*	*S*	*C*	*H*	*N*	*S*
I	39·9	2·65	4·65	15·95	40·2	2·3	5·1	15·9
II	38·1	2·85	4·4	15·1	38·4	3·1	4·5	15·2
III	41·7	3·6	4·2	14·5	42·05	3·3	4·1	14·35
IV	41·7	3·6	4·2	14·5	41·3	4·1	3·9	14·4



Scheme 1

2.2 Preparation of samples

The vinylsulfonyl reactive dye (**I**) was obtained by diazotizing the vinylsulfonyl reactive intermediate (**M-1**) in HCl–$NaNO_2$ at 0–5°C, followed by coupling of **M-2** with R-salt at 5–8°C. Dye **I** was refluxed for 1 h in alkaline solution to obtain **II**, and 3 h in an alkaline solution of *n*-propanol (or isopropanol) to obtain **III** (or **IV**). The compounds **I**–**IV** were purified by gel chromatography. Characterization data are shown in Table 1.

3 STUDY OF THE KINETICS OF THE ALKALINE HYDROLYSIS AND ALCOHOLYSIS OF A VINYLSULFONYL REACTIVE DYE

3.1 Kinetic equation

In accordance with the nucleophilic addition mechanism, the alkaline hydrolysis of a vinylsulfonyl reactive dye may be expressed as follows.

3.1.1 Hydrolysis

$$\underset{(\mathrm{D})}{\mathrm{D{-}SO_2CH{=}CH_2}} + \mathrm{H_2O} \xrightarrow[\mathrm{OH^-}]{k'_{\mathrm{w}}} \underset{(\mathrm{D_w})}{\mathrm{D{-}SO_2CH_2CH_2OH}} \qquad (1)$$

The hydrolytic kinetic equation is:

$$-\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} = k'_{\mathrm{w}}[\mathrm{D}][\mathrm{OH}^-] \qquad (2)$$

where [D] and $[\mathrm{OH}^-]$ represent the corresponding mole concentrations of D and OH^-.

If the pH value of the reaction medium remains constant, $[\mathrm{OH}^-]$ may be included in k'_{w}. That is, $k_{\mathrm{w}} = k'_{\mathrm{w}}[\mathrm{OH}^-]$; k_{w} is the pseudo-order rate constant of hydrolysis of the dye. So,

$$-\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} = k_{\mathrm{w}}[\mathrm{D}] \qquad (3)$$

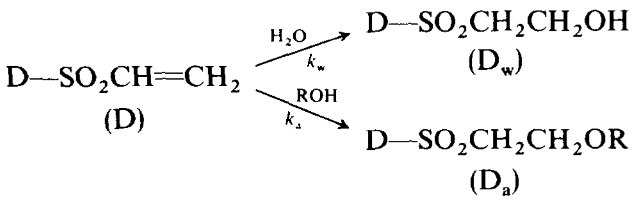
The integrated form of equation (3) is:

$$\ln\frac{[\mathrm{D}]_0}{[\mathrm{D}]_t} = k_{\mathrm{w}}t \qquad (4)$$

where $[\mathrm{D}]_0$ is the mole concentration of D at the time $t = 0$, and $[\mathrm{D}]_t$ is the mole concentration of D at time t.

3.1.2 Alcoholysis

The reaction of the vinylsulfonyl reactive dye in alkaline solution of an alcohol is, in fact, a parallel reaction of hydrolysis and alcoholysis, that is:



$$\underset{(\mathrm{D})}{\mathrm{D{-}SO_2CH{=}CH_2}} \begin{cases} \xrightarrow[k_{\mathrm{w}}]{\mathrm{H_2O}} \underset{(\mathrm{D_w})}{\mathrm{D{-}SO_2CH_2CH_2OH}} \\ \xrightarrow[k_{\mathrm{a}}]{\mathrm{ROH}} \underset{(\mathrm{D_a})}{\mathrm{D{-}SO_2CH_2CH_2OR}} \end{cases} \qquad (5)$$

From eqn (1), the following equation may be obtained.

$$\frac{\mathrm{d}[\mathrm{D_w}]}{\mathrm{d}t} = k_{\mathrm{w}}[\mathrm{D}] \quad \text{and} \quad \frac{\mathrm{d}[\mathrm{D_a}]}{\mathrm{d}t} = k_{\mathrm{a}}[\mathrm{D}]$$

So

$$\frac{\mathrm{d}[\mathrm{D_w}]}{\mathrm{d}[\mathrm{D_a}]} = \frac{k_{\mathrm{w}}}{k_{\mathrm{a}}} \quad \text{or} \quad \frac{[\mathrm{D_w}]_t}{[\mathrm{D_a}]_t} = \frac{k_{\mathrm{w}}}{k_{\mathrm{a}}} \qquad (6)$$

where [D], k_w have the same meaning as in eqn (1); k_a = pseudo-order rate constant of alcoholysis of the dye; $[D_w]_t$ = mole concentration of D_w at time t; $[D_a]_t$ = mole concentration of D_a at time t. Similarly, the total kinetic equation may also be obtained:

$$-\frac{d[D]}{dt} = (k_a + k_w)[D] = k[D] \tag{7}$$

where $k_a + k_w = k$, the total rate constant of hydrolysis and alcoholysis of the dye.

The integrated form of eqn (7) is:

$$\ln [D]_0/[D]_t = kt \tag{8}$$

From equations (6) and (8), k_w and k_a may be calculated.

3.2 Determination of rate constants k_w and k_a by ion-pair reversed-phase HPLC

3.2.1 Qualitative analysis of the components

A Waters model 510 HPLC instrument was used to separate and analyze the components of the hydrolysis and alcoholysis of vinylsulfonyl reactive dye. Column: Nova-Pak C18 (3·9 mm × 1·50 cm). Solvent system: $CH_3OH:H_2O$ (52:48, v/v) containing 0·0025 mol litre^{-1} tetrabutylammonium chloride as ion-pair reagent. The components were detected using a multiwavelength (190–600 nm) detector. The detected wavelength was 254 nm. The results of the separation are shown in Table 2 and Fig. 1.

3.2.2 Quantitative determination of components

The standard curve method utilizing HPLC may be used to determine the concentration of the components. A definite weight of the dye **I** corresponded to a definite peak area in the HPLC (see Table 3). On plotting the peak areas against the weights, the standard curve of the dye **I** may be obtained (see Fig. 2).

TABLE 2

t_R of Components

Component	t_R *(min)*
I	3·00
II	2·22
III	5·00
IV	4·15

Fig. 1. HPLC analysis of components.

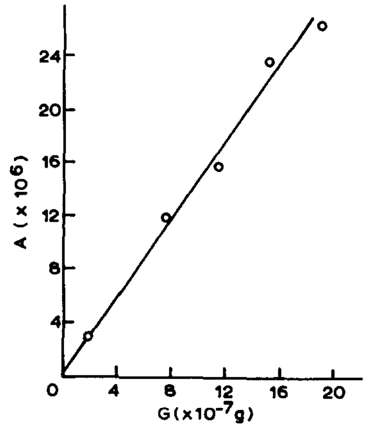


Fig. 2. Standard curve of dye **I**.

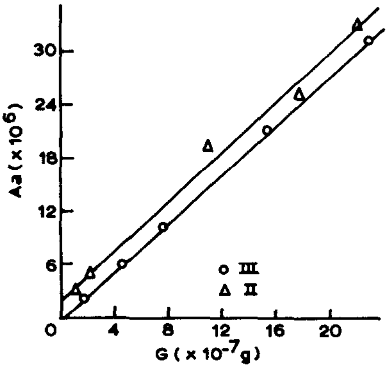


Fig. 3. Standard curves of model dye–fiber compounds.

TABLE 3

Vinsulfonyl Reactive Dye **I**: Weights and Areas in HPLC

G ($\times 10^{-7}$ g)	0	1·90	7·60	11·40	15·20	19·00
A (arbitrary units)	0	286 758	1 186 933	1 588 849	2 378 340	2 613 525

Similarly, the standard curves of the hydrolyzed vinylsulfonyl reactive dye **II** and the alcoholyzed **III** were also obtained (see Fig. 3).

The slopes of the standard curves were:

$$k_{\mathrm{I}} = 1{\cdot}43 \times 10^{12}\,\mathrm{g}^{-1}; \qquad k_{\mathrm{II}} = 1{\cdot}46 \times 10^{12}\,\mathrm{g}^{-1}; \qquad k_{\mathrm{III}} = 1{\cdot}41 \times 10^{12}\,\mathrm{g}^{-1}$$

The ratio of the slopes was:

$$k_{\mathrm{I}}:k_{\mathrm{II}}:k_{\mathrm{III}} = 1{\cdot}00:1{\cdot}02:0{\cdot}99 \simeq 1:1:1$$

So,

$$G_{\mathrm{I}}:G_{\mathrm{II}}:G_{\mathrm{III}}:G_{\mathrm{IV}} = A_{\mathrm{I}}:A_{\mathrm{II}}:A_{\mathrm{III}}:A_{\mathrm{IV}} \tag{9}$$

Thus the ratio of the weights of the different components was equal to the ratio of their peak areas in HPLC.

By eqn (9), eqn (4) may be rewritten:

$$\ln\frac{[\mathrm{D}]_0}{[\mathrm{D}]_t} = \ln\frac{[\mathrm{D}]_t + [\mathrm{D_w}]_t}{[\mathrm{D}]_t} = \ln\left(1 + \frac{G_{\mathrm{w}}M}{GM_{\mathrm{w}}}\right) = \ln\left(1 + \frac{A_{\mathrm{w}}M}{AM_{\mathrm{w}}}\right) = k_{\mathrm{w}}t$$

or

$$\ln\left\{\frac{A_{\mathrm{w}}M}{AM_{\mathrm{w}}} + 1\right\} = k_{\mathrm{w}}t \tag{10}$$

where A, A_{w} are the peak areas in HPLC of D and $\mathrm{D_w}$, respectively, and M, M_{w} are the molecular weights of D and $\mathrm{D_w}$, respectively.

Similarly, eqns (6) and (8) may also be rewritten:

$$\frac{A_{\mathrm{w}}M_{\mathrm{a}}}{A_{\mathrm{a}}M_{\mathrm{w}}} = \frac{k_{\mathrm{w}}}{k_{\mathrm{a}}} \tag{11}$$

$$\ln\left(1 + \frac{A_{\mathrm{w}}M}{AM_{\mathrm{w}}} + \frac{A_{\mathrm{a}}M}{AM_{\mathrm{a}}}\right) = kt \tag{12}$$

where A_{w}, A, M_{w} and M have the same meaning as in eqn (10); A_{a} = peak area in HPLC of $\mathrm{D_a}$; M_{a} = molecular weight of $\mathrm{D_a}$.

3.3 Experimental methods

3.3.1 Hydrolysis

Dye **I** (5·20 mg) was dissolved in de-ionized water (9·2 ml). The solution and 1% aqueous NaOH (0·8 ml) were preheated in a thermostat for 0·5 h at 50°C.

The solutions were then well mixed with good stirring to commence the reaction. Aliquot portions were taken at intervals of several minutes and neutralized immediately to pH 6–7 with dilute aqueous HCl. The peak areas of the components of the samples were determined by ion-pair reversed-phase HPLC.

3.3.2 Alcoholysis

Dye **I** (5·65 mg) and isopropanol (2·40 g) were dissolved in de-ionized water (10·7 ml). This mixture and 1% aqueous NaOH (1·2 ml) were preheated for 0·5 h at 50°C and the procedure outlined above was followed.

Similarly, the kinetics of the alcoholyses of **I** in *n*-propanol were also determined.

3.4 Results

3.4.1 Hydrolysis

From the peak areas in the HPLC of the components from the hydrolysis of dye **I** the corresponding $\ln(1 + MA_w/AM_w)$ may be obtained (see Table 4). By eqn (10), plotting $\ln(1 + MA_w/AM_w)$ against t, the hydrolytic kinetic curve of dye **I** is obtained (see Fig. 4). The slope of the kinetic curve is the hydrolytic rate constant of dye **I** (see Table 5).

3.4.2 Alcoholysis

From the peak areas in the HPLC of the components in the alcoholysis of dye **I** in isopropanol, the corresponding $\ln(1 + MA_w/AM_w + MA_a/AM_a)$ and A_wM_a/A_aM_w may be obtained (see Table 5). By eqn (12), plotting $\ln(1 + MA_w/AM_w + MA_a/AM_a)$ against t, the total kinetic curve of the hydrolysis and alcoholysis of dye **I** in *n*-propanol is obtained (see Fig. 5). The

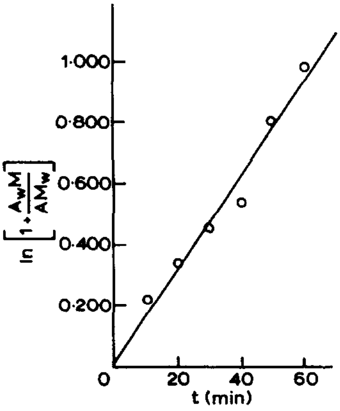


Fig. 4. Hydrolytic kinetic curve of dye **I**.

TABLE 4. Analytical Data of Components of Hydrolysis of Dye **I** by HPLC[a]

t (min)		*0*	*10*	*20*	*30*	*40*	*50*	*60*
A_w	1	0	209 749	385 347	918 026	886 453	804 177	524 134
	2	0	246 827	428 872	962 228	931 061	680 574	854 078
A	1	1 324 195	885 333	914 081	1 556 500	1 207 328	620 060	307 786
	2	1 421 902	985 353	1 071 683	1 646 193	1 270 187	468 486	489 637
$\ln\left(1+\frac{A_wM}{AM_w}\right)$	1	0	0·204	0·338	0·447	0·532	0·717	0·966
	2	0	0·214	0·324	0·443	0·532	0·871	0·981
	Average	0	0·209	0·331	0·445	0·532	0·794	0·973

[a] A, A_w are in arbitrary units.

slope of the total kinetic curve is the total rate constant k. From the total rate constant k and eqn (1), the alcoholytic rate constant k_a and the hydrolytic rate constant k_w of dye **I** in *n*-propanol were obtained (see Table 5).

Similarly, the total rate constant k, the alcoholytic rate constant k_a and the hydrolytic rate constant k_w of the dye **I** in *n*-propanol were also obtained (see Table 6).

3.5 Discussion

The reactivity of the vinylsulfonyl reactive dye with the primary alcohol is higher than that with the secondary alcohol. The ratio of reaction rate

TABLE 5

Analytical Data[a] of Components of Alcoholysis of Dye **I** in Isopropanol by HPLC

t (min)		*0*	*6*	*10*	*20*	*35*	*55*	*80*
A_w	1	0	47 543	136 484	266 534	446 735	469 105	674 823
	2	0	50 335	137 677	265 660	509 620	479 715	499 887
A_a	1	0	19 855	54 663	113 477	179 463	205 155	285 474
	2	0	20 482	54 852	105 512	210 165	229 415	206 980
A	1	2 119 730	916 640	879 433	680 611	507 754	277 947	246 405
	2	2 165 413	733 089	887 648	692 034	564 757	298 192	179 752
$\frac{k_w}{k_a}=\frac{A_wM_a}{A_aM_w}$	1	—	2·52	2·62	2·47	2·62	2·40	2·48
	2	—	2·58	2·64	2·65	2·55	2·17	2·53
	Average	—	2·55	2·63	2·56	2·58	2·29	2·51
$\ln\left(1+\frac{A_wM}{AM_w}+\frac{A_aM}{AM_a}\right)$	1	0	0·067 0	0·186	0·423	0·771	1·19	1·54
	2	0	0·087 1	0·186	0·409	0·789	1·17	1·55
	Average	0	0·077 1	0·186	0·416	0·780	1·18	1·54

[a] A_w, A_a, A are in arbitrary units.

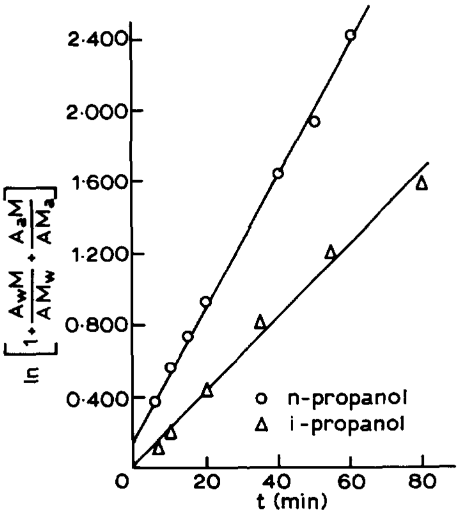


Fig. 5. Total kinetic curves of hydrolysis and alcoholysis of dye I.

constants of *n*-propanol to isopropanol is 1·00:0·19. This may be explained by the combined effect of the nucleophilicity, steric hindrance and dissociation ability of *n*-propanol and isopropanol, i.e.

Nucleophilicity:	*n*-Propanol < isopropanol
Steric hindrance:	*n*-Propanol < isopropanol
Ability to dissociate:	*n*-Propanol > isopropanol
pK_a:[9]	*n*-Propanol = 16·1; isopropanol = 17·1

The preference for model cellulose–dye reaction resultant from the higher nucleophilicity of isopropanol is offset by its larger steric hindrance and much lower ability to dissociate compared with *n*-propanol. Furthermore, the species entering into the reaction equation of the alcoholysis of the vinylsulfonyl reactive dye is the dissociated form of the alcohol. So the order of reactivity observed may be interpreted as a result of a higher

TABLE 6

Rate Constants of Hydrolysis and Alcoholysis of Dye I

Reaction medium	*Concentration of alcohol (mol litre^{-1})*	*Temperature (°C)*	*pH*	k_w/k_a	*k (min^{-1})*	*k_a (min^{-1})*	*k_w (min^{-1})*	*Regression coefficient (R)*
Water	—	50	12·3	—	—	—	$1·53 \times 10^{-2}$	0·990
n-Propanol–water	2·67	50	12·3	0·22	$3·60 \times 10^{-1}$	$2·95 \times 10^{-2}$	$6·49 \times 10^{-3}$	0·996
Isopropanol–water	2·67	50	12·3	2·52	$2·02 \times 10^{-2}$	$5·73 \times 10^{-3}$	$1·44 \times 10^{-2}$	0·996

concentration of $CH_3CH_2CH_2O^-$ compared with that of $(CH_3)_2CHO^-$, because of the higher dissociation coefficient for *n*-propanol relative to isopropanol.

In the parallel reaction of the hydrolysis and alcoholysis of the vinylsulfonyl reactive dye, the reactivity of *n*-propanol is greater than that of water in the *n*-propanol–water system; the ratio of reaction rate constants of *n*-propanol to water is 4·55:1·00. However, the reactivity of isopropanol is lower than that of water in the isopropanol–water system, the ratio of rate constants of isopropanol to water being 0·40:1·00. This may be explained as follows.

In the *n*-propanol–water system, the steric hindrance and dissociation coefficients of *n*-propanol and water ($pK_a = 15{\cdot}7$)[10] are similar. The higher nucleophilicity gives *n*-propanol a more favored model cellulose-dye reaction compared with water. In the isopropanol–water system, however, the decreased steric hindrance and higher dissociation coefficient result in water having a more favored model cellulose–dye reaction compared with isopropanol, although the nucleophilicity of isopropanol is higher than that of water.

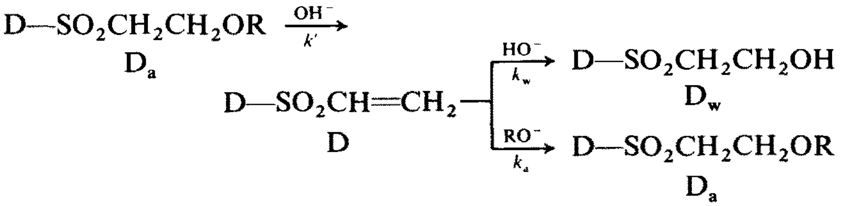
If the rate constant of hydrolysis of the vinylsulfonyl reactive dye **I** is used as the standard of reactivity for the hydrolysis of the dye, the ratio of the reactivities of the dye **I** with *n*-propanol, isopropanol and water is 1·00:0·19:0·52.

The results for reactivities of the hydrolysis of vinylsulfonyl reactive dye **I** in different reaction systems are conflicting, the ratio of reaction rate constants of the dye in water, the *n*-propanol–water system and the isopropanol–water system being 1·00:0·42:0·95. This may be caused by different chemical circumstances.

4 STUDY OF THE KINETICS OF THE ALKALINE HYDROLYSIS OF MODEL DYE–FIBER COMPOUNDS

4.1 Hydrolytic kinetic equation

In accordance with the nucleophilic elimination–addition mechanism, the hydrolysis of the model dye–fiber compounds may be expressed as follows.



$$\underset{D_a}{D{-}SO_2CH_2CH_2OR} \xrightarrow[k']{OH^-} \underset{D}{D{-}SO_2CH{=}CH_2} \begin{cases} \xrightarrow[k_w]{HO^-} \underset{D_w}{D{-}SO_2CH_2CH_2OH} \\ \xrightarrow[k_a]{RO^-} \underset{D_a}{D{-}SO_2CH_2CH_2OR} \end{cases} \tag{13}$$

From eqn (13),

$$-\frac{d[D_a]}{dt} = k'[D_a][OH^-] - k_a[D] \tag{14}$$

$$\frac{d[D]}{dt} = k'[D_a][OH^-] - (k_w + k_a)[D] \tag{15}$$

According to the stable-state theory, when the reaction arrives at a stable state, $d[D]/dt = 0$.

From eqn (15),

$$[D] = \frac{k'}{k_w + k_a}[D_a] \tag{16}$$

From eqn (14),

$$-\frac{d[D_a]}{dt} = \frac{(k'k_w + k'k_a)[OH^-] - k'k_a}{k_w + k_a}[D_a]$$

$$= k[D_a]$$

or

$$-\frac{d[D_a]}{dt} = k[D_a] \tag{17}$$

$$k = \frac{(k'k_w + k'k_a)[OH^-] - k'k_a}{k_w + k_a}$$

$$([OH^-] = \text{constant})$$

The integrated form of eqn (17) is:

$$\ln\frac{[D_a]_0}{[D_a]_t} = kt \tag{18}$$

where $[D_a]_0$ is the mole concentration of D_a at time $t = 0$; $[D_a]_t$ is the mole concentration of D_a at time t.

4.2 Determination of the hydrolytic kinetic rate constants of model dye–fiber compounds by ion-pair reversed-phase HPLC

4.2.1 Qualitative analysis of components

See Section 3.2.1.

4.2.2 Quantitative determination of components

See Section 3.2.2

From eqn (9), eqn (18) may be rewritten:

$$\ln\left(1 + \frac{A_w M_a}{A_a M_w}\right) = kt \tag{19}$$

TABLE 7
Analytical Data[a] of Components of Hydrolysis of Model Dye–Fiber Compound **III**

t (*h*)		*0*	*10*	*16*	*24*	*40*
A_w	1	0	104 206	201 528	502 801	472 410
	2	0	166 128	272 608	319 660	557 222
A_a	1	1 031 994	3 015 292	2 839 255	4 771 574	2 398 757
	2	1 093 552	3 601 500	4 237 603	3 144 432	3 033 439
$\ln\left(1+\frac{A_wM_a}{A_aM_w}\right)$	1	0	0·0357	0·0719	0·105	0·188
	2	0	0·0473	0·0654	0·102	0·176
	Average	0	0·0415	0·0687	0·103	0·182

[a] A_w, A_a in arbitrary units.

4.2.3 Experimental method

Model dye–fiber compound **III** (12·12 mg) was dissolved in de-ionized water (13·8 ml). The solution and 1% aqueous NaOH (1·2 ml) were preheated for 0·5 h at 50°C and then mixed with good stirring to commence the reaction. Aliquot samples were taken at intervals of several hours and neutralized immediately to pH 6–7 with dilute HCl. The peak areas of the components of the samples were determined by ion-pair reversed-phase HPLC.

Similarly, the hydrolytic kinetics of the model dye–fiber compound **IV** were also determined.

4.3 Results

From the peak areas of the components determined by ion-pair reversed-phase HPLC, $\ln(1 + A_wM_a/A_aM_w)$ may be calculated (see Table 7). By eqn (19), plotting $\ln(1 + A_wM_a/A_aM_w)$ against t, the hydrolytic kinetic curve of model dye–fiber compound **III** is obtained (see Fig. 6). The slope of the kinetic curve is the hydrolytic rate constant of the model dye–fiber compound **III** (see Table 8).

Similarly, the hydrolytic kinetic curve and rate constant of model dye–fiber compound **IV** were also obtained (see Fig. 6 and Table 8).

TABLE 8
Rate Constants of Hydrolysis of Model Dye–Fiber Compounds (**III**, **IV**)

Model dye–fiber compound	*Temperature (°C)*	*pH*	*k (min^{-1})*	*Regression coefficient (R)*
III	50	12·3	$7{\cdot}60 \times 10^{-5}$	0·999
IV	50	12·3	$8{\cdot}23 \times 10^{-5}$	0·984

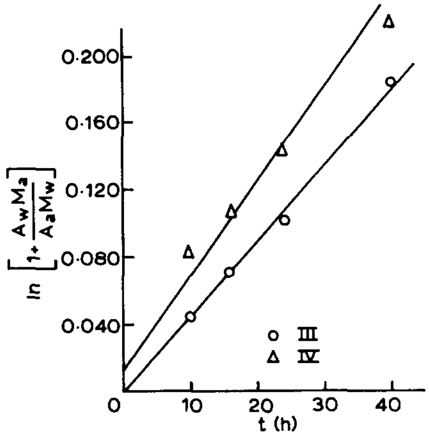


Fig. 6. Hydrolytic kinetic curves of model dye–fiber compounds.

4.4 Discussion

The results show that the hydrolytic reactivity of the model dye–fiber compound **IV** is higher than that of **III**. In other words, the fastness to hydrolysis of the model dye–primary ether bond is better than that of the model dye–secondary ether bond.

5 CONCLUSIONS

A water-soluble vinylsulfonyl reactive dye and two model dye–fiber compounds were synthesized and purified by gel chromatography. The kinetic rate constants of the alkaline hydrolysis and alcoholysis of the vinylsulfonyl reactive dye were determined by ion-pair reversed-phase HPLC. The ratio of the reactivities of the vinylsulfonyl reactive dye with *n*-propanol, isopropanol and water was 1·00:0·19:0·52. The kinetic rate constants of the alkaline hydrolysis of the model dye–fiber compounds were also determined by ion-pair reversed-phase HPLC. The ratio of the hydrolytic reactivities of the model dye–primary ether bond to the model dye–secondary ether bond was 0·92:1·00. The preference given to the combination of the vinylsulfonyl reactive dye with the primary alcohol compared with the secondary alcohol was not only because the reactivity of the dye with the primary alcohol was higher than that with the secondary alcohol, but also because the fastness to hydrolysis of the dye–primary ether bond was better than that of the dye–secondary ether bond.

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