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Studies on Structural Effects of the Reaction Between Model Vinylsulfone Reactive Dyes and Methyl-α-D-Glucoside. Part II: Kinetic Studies

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ABSTRACT

The reactions between five vinylsulfone reactive dyes and methyl-α-D-glucoside have been studied in aqueous dioxan; the reaction products (D_6 *and* D_4*) were separated by TLC-double scanning. It is shown that only the* C_6 *and* C_4 *hydroxyl groups are involved, with neither* D_2 *nor* D_3 *being formed. The rates of 'model' dyeing reactions were determined. The rates of alkaline hydrolysis of the reaction products* D_6 *and* D_4 *were measured kinetically. It was found that when some substituents are present in the aromatic ring, the reactivity of the vinylsulfone group is varied. The rate constants of the model dyeing reaction and the alkaline hydrolysis of the model 'dye–fiber' compounds changed, while the ratio of primary product to secondary product (i.e.* k'_6/k'_4*) increased in the model 'dye–fiber' compound when a donor substituent, such as —*OCH_3*, was present* ortho- *and* para- *to the vinylsulfone group.*

1 INTRODUCTION

We have previously described the dyeing behavior of vinylsulfone reactive dyes with cellulose, and the hydrolysis behavior of the dyed cellulose fiber.[1,2,3] In these studies model vinylsulfone dyes and vinylsulfone dyes containing a sulfonic acid group were utilized.[4] The results showed that the vinylsulfone dyes, with or without sulfonic acid groups, reacted with methyl-α-D-glucoside mainly on —$CH_2OH(6)$, (*D6*) and only in smaller amount on —CHOH(4), (D_4); neither D_2 nor D_3 was formed. The relative amounts of D_6 to D_4 were almost the same at 50 or 60°C, but the presence of a sulfonic acid group rendered purification of the vinylsulfone dyes and dye-glucosides very difficult. In this present paper, the structural effect of the reactions between vinylsulfone dyes and methyl-α-D-glucoside is studied. Five model vinylsulfone dyes were synthesized and reacted with methyl-α-D-glucoside; the rates of formation and the rates of hydrolysis of the dye-glucosides were measured and compared.

2 EXPERIMENTAL

2.1 Determination of the yields of the reaction products by TLC-double scanning

The structure of the vinylsulfone dyes A, B, C, D, E and dye-glucosides DGA-6, DGA-4, DGB-6, DGB-4, DGC-6, DGC-4, DGD-6, DGE-6 and DGE-4 are listed in Part I of this paper.

A standard solution of the dye in acetone at a concentration of 5×10^{-3} g/ml was prepared. Aliquot portions of this solution were further diluted to give a series of solutions of concentration A_n. The samples were applied to chromatographic plates, developed and scanned. The peak areas of the spots were obtained and plots were made for the peak areas *versus* corresponding dosage weights. Standard curves for the hydrolyzed dyes, (spot 1 and spot 2) were obtained.

The reaction products in the above reaction are abbreviated using the following symbols:

	Dye A	Dye B	Dye C	Dye D	Dye E
Hydrolyzed	HDA	HDB	HDC	HDD	HDE
Spot 1	DGA-6	DGB-6	DGC-6	DGD-6	DGE-6
Spot 2	DGA-4	DGB-4	DGC-4	DGD-4	DGE-4

Taking dye A as an example, the standard curves of HDA, DGA-6 (spot 1) and DGA-4 (spot 2) are shown in Fig. 1.

2.2 Determination of the constants of the reactions between the vinylsulfone dyes and methyl-α-D-glucoside

From the standard curves of spot 1 and spot 2 (abbreviated as D_6 and D_4), the quantities of D_6 and D_4 after various reaction times (in minutes) can be determined, viz:

$$A_w = rwD_w, \qquad A_6 = r_6D_6, \qquad A_4 = R_4D_4$$

$$D_6/D_w = A_6r_w/A_wr_6, \qquad D_4/D_w = A_4r_w/A_wr_4, \qquad D_0/D_t = A_0/A_t$$

where r is the correlation coefficient and A the peak area.

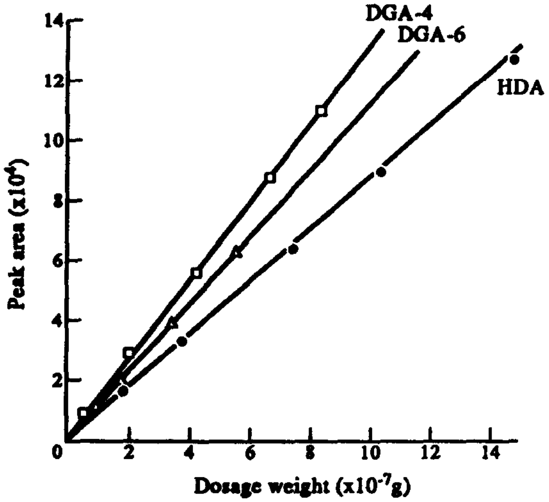


Fig. 1. Standard curves of HDA, DGA-6 and DGA-4.

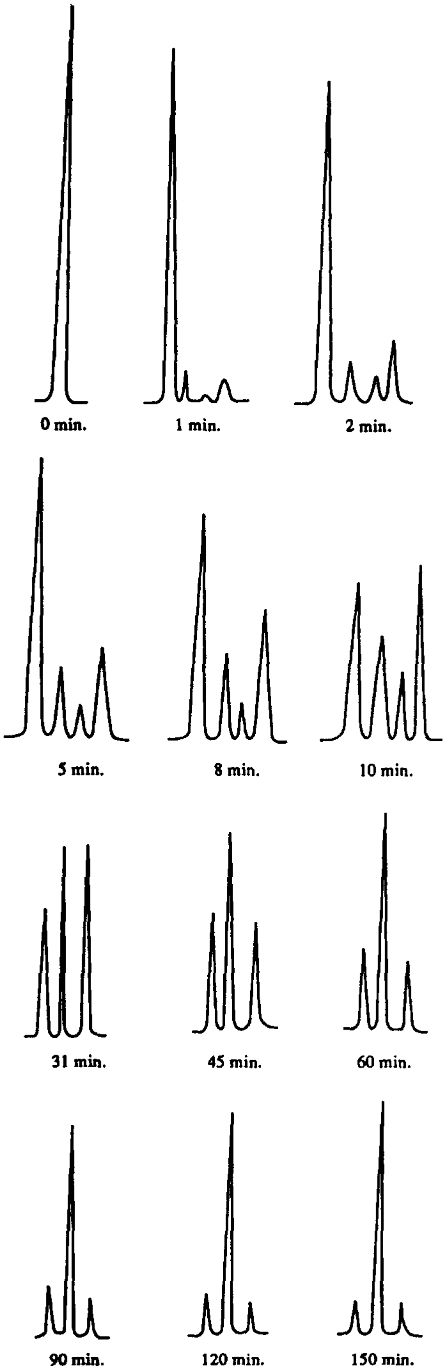
When the reaction proceeds over a period of 10 min, D_6/D_w and D_4/D_w may be considered as constant, because within this time limit, the 'dye–fiber' product is not undergoing any hydrolysis, i.e.

$$D_6/D_w = C_6 = \text{constant}, \qquad D_4/D_w = \text{constant}, \quad \text{and} \quad D_0/D_t = A_0/A_t$$

A mixture of 0·02 g (0·50 mmol) of dye and 0·18 g (0·92 mmol) of methyl-α-D-glucoside (dye : glucoside = 1:15) in distilled water (2 ml) and dioxane (10 ml) was heated at 50 ± 1°C; 10% NaOH solution (0·0736 ml, 1·84 mmol) was similarly maintained at 50°C for 1 h. After addition of the NaOH solution to the dye solution, samples (0·05 ml) were removed at intervals, cooled immediately and the pH adjusted to 7 by addition of dilute HCl. The samples were then applied to chromatographic plates, developed and scanned.

Taking dye A as an example, the formation of the reaction product DGA, using TLC-double scanning plots, at 50 ± 1°C, is shown in Fig. 2. The experimental data and calculated results of the reaction between dye A and methyl-α-D-glucoside DGA at 50 ± 1°C and 60 ± 1°C are shown in Tables 1 and 2; A_6 is the peak area of DGA-6 and A_4 is the peak area of DGA-4.

On plotting ln (D_0/D_t) of dye A against time t (in minutes) at 50 ± 1°C, a straight line was obtained (Fig. 3); the regression equation and correlation coefficient at 50 ± 1°C are $y = 0{\cdot}1074x - 0{\cdot}001\,588\,4$ and $r = 0{\cdot}9974$, respectively. The gradient of the line, k, i.e. the total rate constant of the reaction at 50 ± 1°C, is 0·1074 min^{-1}.



0 min. 1 min. 2 min.

5 min. 8 min. 10 min.

31 min. 45 min. 60 min.

90 min. 120 min. 150 min.

Fig. 2. The formation of the reaction products of DGA, plotted by TLC-double scanning at 50 ± 1°C.

TABLE 1
Experimental Data and Calculated Results of the Reaction Between Dye A and Methyl-α-D-Glucoside DGA at 50°C

	Time (min)						
	0	*1*	*2*	*5*	*8*	*10*	*Mean*
A_6	—	14 965	16 472	34 921	43 793	50 902	—
A_4	—	2 339	2 576	5 461	6 848	7 960	—
A_w	—	4 351	4 792	10 159	12 740	14 808	—
A_D	1·787 45	160 195	143 446	102 974	79 326	59 042	—
D_6/D_w	—	2·528	2·493	2·516	2·537	2·526	2·650
D_4/D_w	—	0·351	0·350	0·348	0·352	0·351	0·351
ln (D_D/D_t)	—	0·109 6	0·220 0	0·551 5	0·812 4	1·107 7	—

On plotting ln (D_0/D_t) of dye A against time (t) in minutes at 60 ± 1°C, a straight line was also obtained (Fig. 4); the regression equation and correlation coefficient at 60 ± 1°C are $y = 0{\cdot}1342x + 0{\cdot}0154$ and $r = 0{\cdot}9976$, respectively. The gradient of the line, k, i.e. the total rate constant of the reaction at 60 ± 1°C, is 0·1342 min^{-1}.

Since $k = k_w + k_6' + k_4'$, and $k_6'/k_w = D_6/D_w$. $k_4''/k_w = D_4/D_w$, k_w, k_6' and k_4' can be determined. It is interesting to note that the reaction between dye E and methyl-α-D-glucoside shows little reaction at 50 or 60°C. The experimental data and calculated results of the reaction between dye E and methyl-α-D-glucoside at 75 ± 1°C and 90 ± 1°C are shown in Tables 3 and 4.

On plotting ln (D_0/D_w) against time t (in minutes) at 75 ± 1°C, a

TABLE 2
Experimental Data and Calculated Results of the Reaction Between Dye A and Methyl-α-D-Glucoside DGA at 60°C

	Time (min)						
	0	*1*	*2*	*5*	*8*	*10*	*Mean*
A_6	—	12 260	23 769	59 815	104 441	153 133	—
A_4	—	1 846	3 580	9 008	15 729	23 061	—
A_w	—	4 315	8 366	21 053	36 760	53 989	—
A_D	192 863	163 643	146 338	96 310	68 682	48 085	—
D_6/D_w	—	2·539	2·591	2·547	2·479	2·518	2·540
D_4/D_w	—	0·357	0·348	0·349	0·352	0·343	0·350
ln (D_0/D_t)	—	0·164 1	0·276	0·694	1·032	1·398	—

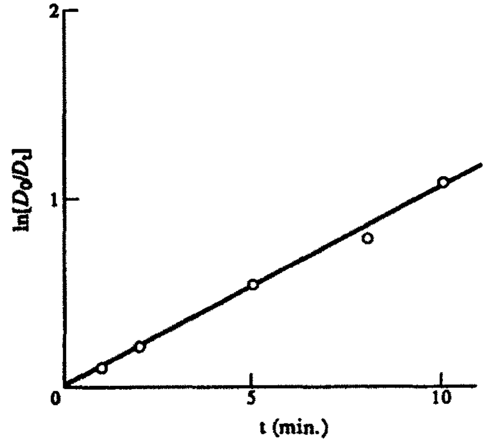


Fig. 3. Plot of ln (D_0/D_t) of dye A vs. time (t) at 50°C.

straight line was obtained; the regression equation and correlation coefficient at 75 ± 1°C are $y = 0{\cdot}0981x - 0{\cdot}0162$ and $r = 0{\cdot}988$, respectively. The gradient of the line, k, i.e. the total rate constant of the reaction at 75 ± 1°C, is 0·0981 min^{-1}.

On plotting ln (D_0/D_t) against time t (in minutes) at 90 ± 1°C, a straight line was also obtained; regression equation and the correlation coefficient at 90 ± 1°C are $y = 0{\cdot}285x + 0{\cdot}020$ and $r = 0{\cdot}987$, respectively. The gradient of the line, k, i.e. the total rate constant of the reaction at 90 ± 1°C, is 0·285 min^{-1}.

The kinetic data for the rates of formation, the total rates (k) between dyes A, B, C, D and E and methyl-α-D-glucoside, the rates (k_6') between

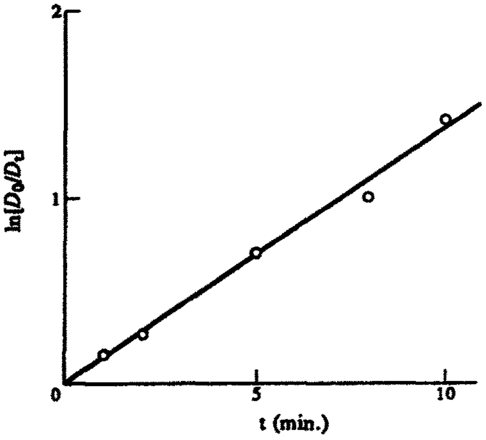


Fig. 4. Plot of ln (D_0/D_t) of dye A vs. time (t) at 60°C.

TABLE 3
Experimental Data and Calculated Results of the Reaction Between Dye E and Methyl-α-D-Glucoside at 75 ± 1°C

	Time (min)						
	0	*2·0*	*3·0*	*4·0*	*6·0*	*7·0*	*9·0*
A_6	0	5 018	10 896	14 290	21 130	22 480	20 494
A_4	0	1 175	2 390	3 263	4 684	5 344	6 485
A_w	0	1 855	3 823	5 151	7 320	8 671	10 661
A_D	53 304	46 544	41 315	34 536	29 267	28 200	24 126
D_6/D_w	—	5·310	5·549	5·446	5·667	5·28	3·773
D_4/D_w	—	1·046	1·387	1·406	1·420	1·367	1·350
ln (D_4/D_t)	—	0·135 6	0·254 8	0·434 0	0·599 0	0·636 7	0·792 7

—$CH_2OH(6)$ and MOH, and the rates of hydrolysis (k_w') are summarized in Table 5.

2.3 Determinations of the specific rate constants of the hydrolysis of the vinylsulfone dye-glucosides D_6 and D_4

D_6 (0·01 g, 1·876 × 10^{-5} mol) was dissolved in dioxane (5 ml) and water (2·5 ml). the solution was stirred, while maintaining a temperature of 50 ± 1°C for 1 h with addition of 10% NaOH solution (0·03 ml). Aliquots were removed at intervals, cooled immediately and dilute HCl added to give pH 5 ~ 6. One ml was injected onto a chromatographic plate, which was then developed and scanned.

The chromatogram of D_6 during the hydrolysis showed that there were two reaction products formed, viz. D_w and D. The peak areas of D_w, D

TABLE 4
Experimental Data and Calculated Results of the Reaction Between Dye E and Methyl-α-D-Glucoside at 90 ± 1°C

	Time (min)						
	0	*1·5*	*2*	*3*	*3·5*	*4*	*6*
A_6	0	3 923	4 309	6 691	8 835	9 304	10 263
A_4	0	941	1 084	1 952	2 119	2 788	9 304
A_w	0	2 585	2 729	4 214	4 872	5 042	6 325
A_D	39 628	26 969	20 108	15 286	14 545	13 182	10 762
D_6/D_w	—	2·980	3·099	3·117	3·560	3·622	3·185
D_4/D_w	—	0·808	0·881	1·028	0·965	1·277	0·991
ln (D_0/D_t)	—	0·385	0·678	0·953	1·002	1·101	1·304

TABLE 5
Kinetic Data for the Rates of Formation of Dyes A, B, C, D, E and MOH and the Rates of Hydrolysis of the Dyes

Rate constant	*Temperature (°C)*	*Dye*				
		A	*B*	*C*	*D*	*E*
k (min^{-1})	50	0·107 4	0·141 1	0·113 8	0·161 8	0·098 (75°C)
	60	0·134 2	0·162 8	0·163 5	0·233 6	0·285 0 (90°C)
k'_6 (min^{-1})	50	0·069 9	0·108 1	0·076 5	0·085 1	0·068 0 (75°C)
	60	0·087 6	0·109 6	0·106 0	0·125 0	0·177 5 (90°C)
k'_4 (min^{-1})	50	0·009 74	0·016 3	0·011 5	0·015 0	0·017 5 (75°C)
	60	0·012 1	0·018 6	0·015 9	0·021 2	0·053 2 (90°C)
k'_w (min^{-1})	50	0·027 7	0·016 7	0·029 7	0·061 7	0·012 6 (75°C)
	60	0·034 5	0·034 7	0·041 3	0·087 3	0·054 2 (90°C)
k'_6/k'_4 (min^{-1})	50	7·177	6·640	6·652	5·673 3	3·878 (75°C)
	60	7·240	5·910	6·667	5·896	3·334 (90°C)

and D_D were measured quantitatively by TLC-double scanning. The concentrations of D_6, D_w and D after various hydrolysis times could thus be obtained. On plotting ln $\{[D_6]_0/[D_6]_t\}$ against time t, a straight line was obtained.

The hydrolysis of D_4 was similarly effected and an analogous plot of ln $\{[D_4]_0/[D_4]_t\}$ againt time (t) also obtained.

Taking the alkaline hydrolysis of DGD-6 as an example, the formation of the hydrolysis product plots by TLC-double scanning at 60 ± 1°C is shown in Fig. 5.

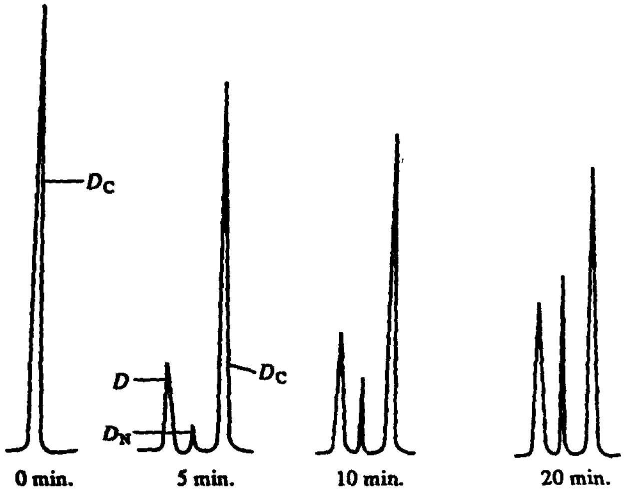


Fig. 5. Hydrolysis of DGD-6 (TLC-double scanning at 60 ± 1°C).

TABLE 6

Experimental Data and Calculated Results of the Hydrolysis of DGD-6 at 60°

	Time (min)						
	0	*5*	*10*	*20*	*30*	*40*	*60*
A_0	—	10 280	14 398	20 590	20 109	17 260	14 707
A_w	—	3 614	6 304	17 426	25 671	31 034	35 779
A_6	89 937	77 409	65 135	19 845	34 019	25 651	13 790
$\ln [D_6]_0/[D_6]_t$	—	0·145 0	0·322 8	0·590 2	0·972 2	1·754 5	1·875 2

The experimental data and calculated results of the hydrolysis of DGD-6 at 60 ± 1°C are shown in Table 6.

On plotting $\ln [D_6]_0/[D_6]_t$ of dye DGD-6 against time t (in minutes) at 60 ± 1°C, a straight line was obtained (Fig. 6); the regression equation and correlation coefficient at 60 ± 1°C are $y = 0{\cdot}031\,248x - 5{\cdot}8389 \times 10^{-4}$ and $r = 0{\cdot}9994$, respectively.

The gradient of the line, k, i.e. the rate of hydrolysis of DGD-6, is 0·03148 min^{-1}.

The experimental data and calculated results of the hydrolysis of DGE-6 are shown in Table 7.

On plotting $\ln [D_6]_0/[D_6]_t$ of dye DGE-6 against time t (in minutes) at 50 ± 1°C, a straight line was obtained (Fig. 7); the regression equation and the correlation coefficient at 50 ± 1°C are $y = 0{\cdot}0051x - 0{\cdot}0113$ and $r = 0{\cdot}9220$, respectively.

The gradient of the line, k, i.e. the rate of hydrolysis of DGE-6 at 50 ± 1°C, is 0·0051 min^{-1}.

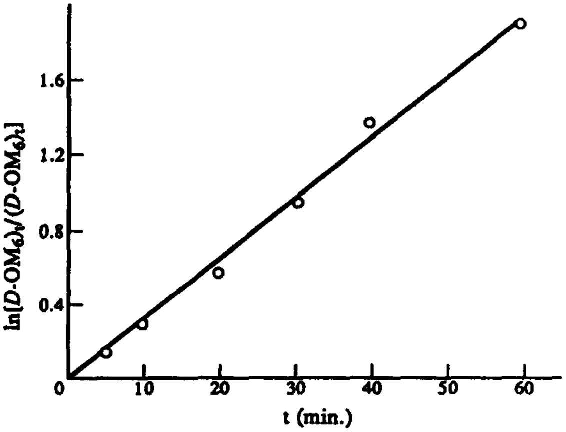


Fig. 6. Plot of ln $\{[D_6]_0/[D_6]_t\}$ of dye-glucoside DGD-6 vs. time (t) at 60 ± 1°C.

TABLE 7
Experimental Data and Calculated Results of the Hydrolysis of DGD-6 at 50°

	Time (min)							
	0	*5*	*10*	*20*	*30*	*40*	*50*	*60*
A_6	50 853	466 230	41 791	34 189	31 926	28 020	25 032	23 017
A_w	—	342·8	829·4	2 461	6 223	7 860	8 915	9 824
A_D	—	4 000	4 529	4 727	7 636	9 938	9 551	8 291
$\ln [D_6]_0/[D_6]_t$	0	0·087 6	0·199 63	0·397 0	0·465 5	0·596	0·708 8	0·792 7

The experimental data and calculated results of the hydrolysis of DGD-4 at 50°C are shown in Table 6.

On plotting $\ln [D_4]_0/[D_4]_t$ of DGE-4 against time t (in minutes) at 50 ± 1°C, a straight line was obtained (Fig. 8); the regression equation and the correlation coefficient at 50 ± 1°C are $y = 0{\cdot}151\,16x - 0{\cdot}011\,32$ and $r = 0{\cdot}9982$, respectively. The gradient of the line, k, i.e. the rate of hydrolysis of DGA-4 at 50 ± 1°C, is 0·015 16 min^{-1}.

Kinetic data for the rates of hydrolysis of DGA, DGB, DGC, DGD and DGE at 50 and 60°C are summarized in Table 9.

3 RESULTS AND DISCUSSIONS

3.1 Structures of dyes and rates of formation of dye-glucosides

From Table 5, it is evident that there is a structural effect of the dyes on the rate of the formation of dye-glucoside. Dyes B and C are isomeric, but the rate of formation of the dye-glucoside derived from C is much

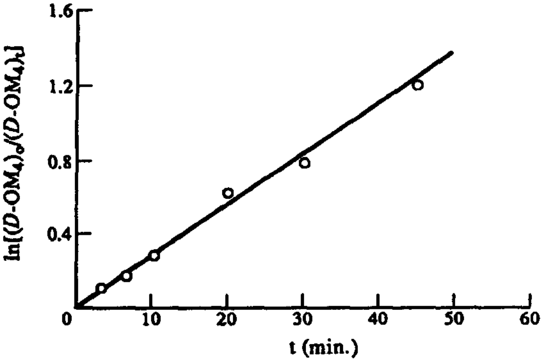


Fig. 7. Plot of $\ln \{[D_6]_0/[D_6]_t\}$ of dye-glucoside DGD-6 vs. time (t) at 50 ± 1°C.

TABLE 8
Experimental Data and Calculated Results of the Hydrolysis of DGA-4 at 50 ± 1°C

	Time (min)						
	0	*3*	*10*	*15*	*25*	*35*	*50*
A_0	—	5 722	12 644	14 870	19 293	26 580	237 944
A_w	—	1 405	3 114	5 732	7 424	12 611	18 477
A_D	71 144	68 090	62 298	57 146	48 948	43 522	33 168
$\ln [D_4]_0/[D_4]_t$	0	0·043 88	0·132 8	0·219 1	0·373 9	0·491 4	0·763 1

greater than that derived from B (0·1619 min^{-1}). Dyes A and D contain an electron-donating group (OCH_3), the presence of which decreases the electron-attracting capacity of the —SO_2—group, and thus the positive charge density at the β-carbon atoms is diminished.

Dye-glucoside formation involves a nucleophilic attack at the β-carbon atom of the vinyl double bond, and the rates k, k_6' and k_4' are therefore decreased. In dye E, in which two —OCH_3 groups present both *ortho-* and *para-* to the vinylsulfone group, the dye-glucoside formation rate is further decreased. The presence of electron-attracting groups in the phenyl ring, e.g. Cl, increases the hydrolysis rates (3, 6).

3.2 Structures of dye-glucosides and the rates of the alkaline hydrolysis

From Table 9 it is apparent that there is a relationship between the structure of the dye-glucoside and the rate of alkaline hydrolysis. Dye-glucosides having a slow rate of formation also hydrolyze slowly in an

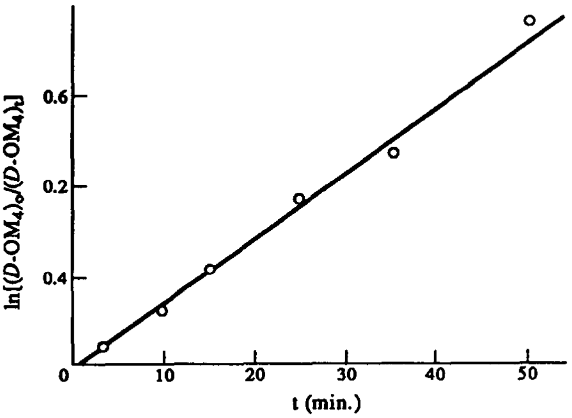


Fig. 8. Plot of ln $\{[D_6]_0/[D_6]_t\}$ of dye-glucoside DGA-4 vs. time (t) at 50 ± 1°C.

TABLE 9
Rates of Hydrolysis of DGA, DGC, DGD and DGE at 50° and 60°C

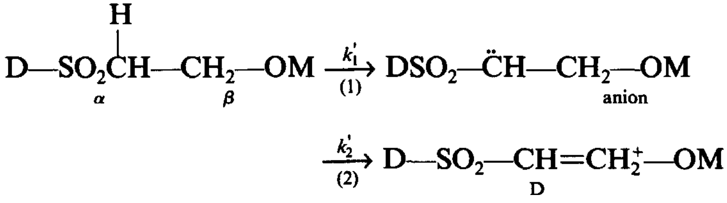
Temperature (°C)	*DGA*		*DGC*		*DGD*		*DGE*	
	6	*4*	*6*	*4*	*6*	*4*	*6*	*4*
50	0 014 45	0·015 45	0·024 26	0·023 84	0·025 95	0·025 99	0·005 1	0
60	0·019 47	0·019 62	0·028 46	0·025 48	0·031 48	0·027 76	0·013 1	0·010 2

alkaline medium, and dye-glucosides having a higher rate of formation hydrolyze more rapidly in an alkaline medium. When a donor group (OCH_3) is present *ortho* or *para* to the —$SO_2CH_2CH_2$—O— group, the rates of hydrolysis of the dye-glucoside, e.g. DGA or DGD, are decreased. In the case of DGE, where there were two OCH_3 groups *ortho* and *para* to the —SO_2CH_2CH—O— group, the rate of hydrolysis diminished even greater at 50 and 60°C.

3.3 Mechanism of hydrolysis of model 'dye–fiber' compounds

The mechanisms of hydrolysis of the vinylsulfone dye-glucosides can be directly shown by TLC-double scanning. The scanning diagrams for DGD-6 during hydrolysis are shown in Fig. 5. It is apparent that, in the initial stages of the hydrolysis, the hydrolysis product *D*, i.e. the vinylsulfone dye, is in greater amounts. In the later stages of the hydrolysis, the amount of hydrolyzed dye D_w gradually increases and the amount of the primary hydrolysis product (the vinylsulfone dye *D*), gradually decreases. The scanning diagram of DGD-4 during alkaline hydrolysis shows a similar pattern.

These results indicate that the course of the hydrolysis of the vinylsulfone dye-glucoside is predominantly via an elimination route. The first stage of the elimination is the formation of the anion at the conjugate base of dye-glucoside, which then further reacts unimolecularly to form the final vinylsulfone dye *D*, with —OM as a leaving group.



$$\mathrm{D{-}SO_2}\underset{\alpha}{\overset{\mathrm{H}}{\mathrm{C}}}\mathrm{H{-}}\underset{\beta}{\mathrm{CH_2}}\mathrm{{-}OM} \xrightarrow[(1)]{k_1'} \underset{\text{anion}}{\mathrm{DSO_2{-}\ddot{C}H{-}CH_2{-}OM}}$$

$$\xrightarrow[(2)]{k_2'} \underset{\mathrm{D}}{\mathrm{D{-}SO_2{-}CH{=}CH_2^{+}{-}OM}}$$

Therefore, if there is an electron-donating group present in the phenyl ring, the electron-attracting nature of the —SO_2— group is decreased, and, as a result, the acidic nature of the α-H atom is also decreased. Thus, the possibility of formation of the anion decreases, and the rate of hydrolysis of the dye-glucoside also decreases. Therefore, the alkaline hydrolysis of the dye-glucoside to the vinylsulfone dye follows an elimination unimolecular conjugate base mechanism (ELCB).[7]

4 CONCLUSIONS

Five different vinylsulfone reactive dyes were reacted with methyl-α-D-glucoside. The rates of formation of the dye-glucosides were measured and found to vary significantly with changes in the dye structure. In these studies, the rate constants varied from 1 to 1·5 at 50°C and from 1 to 1·76 at 60°C. In an extreme case, if two —OCH_3 groups were present, e.g. dye E, the rate constants decreased to 0·098 min^{-1} at 75°C, and 0·285 min^{-1} at 90°C, compared with the rate constants of dye B which were 0·1411 min^{-1} at 50° and 0·1628 min^{-1} at 60°.

Neither D_2 nor D_3 was observed in these studies, irrespective of the dye structure.

The rates of alkaline hydrolysis of the dye-glucosides changed with the structures of the dyes. When an electron donor group was present in the phenyl ring of the dye-glucoside, the rate of hydrolysis changed from 1 in the case of dye B to 0·16 in the case of dye E.

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