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Homogeneous Reaction between a Water Soluble Vinyl Sulfonyl Reactive Dye and Methyl-α-D-glucoside. Part II. A Kinetic Study

Zhenghua Zhu & Xiaodong Zhang

East China University of Chemical Technology, Shanghai 200237, Peoples Republic of China

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ABSTRACT

The rate of reaction between a soluble vinyl sulfonyl reactive dye and methyl-α-D-glucoside has been studied. It was found that only two reaction products D_6 *and* D_4 *were formed; neither* D_2 *or* D_3 *was present. The rate constant* k_6 *was 9·38 times greater than* k_4 *at 50°C and the rate constant* k_6 *8·54 times greater than* k_4 *at 60°C. The rates of alkaline hydrolysis of* D_6 *and* D_4 *were also studied. The mechanism of hydrolysis of* D_6 *and* D_4 *follows an elimination route initially. The rate of hydrolysis of* D_6 *at pH 12·824 (*$k = 0{\cdot}1142\ \text{min}^{-1}$ *at 50°C,* $k = 0{\cdot}1149\ \text{min}^{-1}$ *at 60°C) is greater than that of* D_4 *at the same pH (*$k = 0{\cdot}0678\ \text{min}^{-1}$ *at 50°C,* $k = 0{\cdot}1092\ \text{min}^{-1}$ *at 60°C).*

1 INTRODUCTION

The rate of reaction between a model vinyl sulfonyl reactive dye and methyl-α-D-glucoside in dioxane–H_2O solution and the rate of hydrolysis of model dye-glucosides have been previously studied.[1,2]

In this paper, we study the influence of a sulfonic acid group, both on the rate of reaction between the soluble dye and methyl-α-D-glucoside in aqueous solution, and on the rate of hydrolysis of dye-glucosides.

2 DETERMINATION OF THE RATE OF REACTION BETWEEN THE SOLUBLE VINYL SULFONYL REACTIVE DYE AND METHYL-α-D-GLUCOSIDE IN AQUEOUS SOLUTION

Standard solution of dyes of concentration 0·1 mg/ml were obtained by dissolving 10 mg of dyes D, D_w, D_6 and D_4 respectively in distilled water

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(100 ml). Taking aliquot portions of these solution, further dilution gave a series of solutions of concentrations 1–7 mg/ml.

The samples were applied to chromatographic plates, developed and scanned. The peak areas of the spots were obtained and plots were produced for the peak areas versus corresponding dosage weights (Table 1 and Fig. 1).

The rate equations between the dye and methyl glucoside were similarly derived:[1]

$$\ln [D_o]/[D_t] = kt$$

where

$$k = k'_6 + k'_4 + k_w$$

$$k'_6/k_w = D_6/D_w; \quad k'_4/k_w = D_4/D_w$$

0·02 g Dye (4×19^{-5} mol), 0·18 g methyl glucoside ($9{\cdot}3 \times 10^{-4}$ mol) (dye: glucoside = 1:23) and 14·5 ml distilled water were added to a 50 ml flask, placed in a thermostat, and the mixture stirred for 1 h to dissolve the dye and glucoside completely. A solution of 0·5 ml of 2N NaOH was added to the reaction mixture (pH = 12·824) and after addition of the NaOH, samples (0·05 ml) were removed at intervals, cooled immediately and the pH adjusted to 7 by addition of dilute hydrochloric acid.

A Shimadzu CS-910 TLC-double scanning system was used to separate the reaction products. Using a microinjector, 1 ml of the reaction solution was dropped onto a chromatographic plate, made from silica gel G with 5% carboxymethyl cellulose solution. Four spots were apparent. The spots were air-dried and the chromatogram was developed as previously cited Ref. 1.

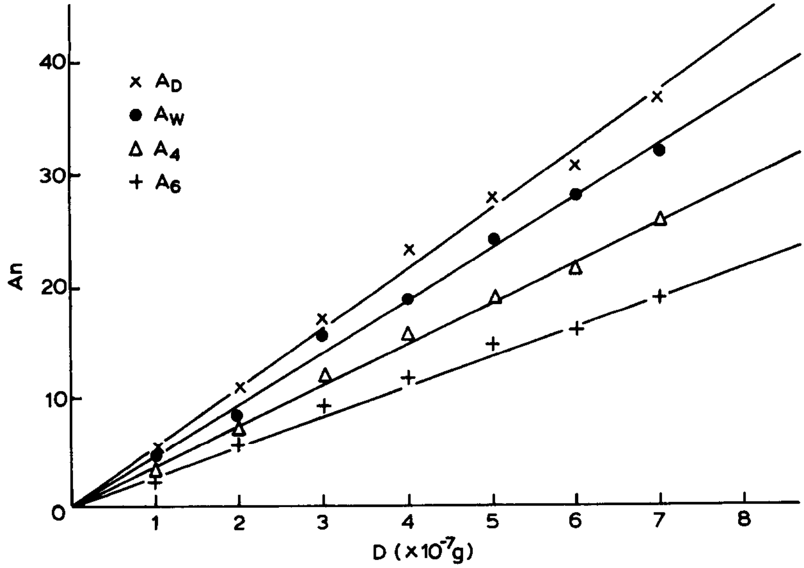


Fig. 1. Standard curves of D, D_w, D_6 and D_4.

TABLE 1

Peak Areas and Dosage Weights of Vinyl Sulfone Reactive Dye D, Hydrolysed Dye D_w and the Reaction Products D_6 and D_4

Dosage weight ($D_n \times 10^7$ g)	*0*	*1*	*2*	*3*	*4*	*5*	*6*	*7*
A_6	0	2 498·62	5 512·95	9 236·87	11 765·23	14 446·18	15 863·98	18 684·11
A_4	0	3 735·5	7 524·31	11 982·72	15 378·79	19 044·23	21 025·41	25 784·2
A_w	0	4 858·45	8 036·52	15 855·81	18 604·23	23 654·9	27 824·89	31 328·55
A_D	0	5 515·23	10 720·6	16 739·38	23 320·16	27 652·21	30 344·71	36 780·91

TABLE 2

Experimental Data and Calculated Results of the Reaction between the Dye and Methyl Glucoside at 50 ± 1°C and pH 12·824

Time (min)	*0*	*0·5*	*1·0*	*1·5*	*2*	*2·5*	*3·0*	*5·0*	*7·0*	*9·0*	*12·0*
A_6	0	6 240	12 110	16 122	19 110	20 095	20 095	20 704	27 041	29 023	26 928
A_4	0	890	1 840	2 294	2 548	2 943	3 114	4 823	5 569	6 531	5 183
A_w	0	2 490	5 130	62 331	73 312	7 865	8 223	12 160	14 299	17 751	17 058
A_D	108 871	95 224	82 908	66 839	48 771	40 791	30 826	24 679	18 365	15 707	11 453
D_6/D_w	—	0·242	3·995	4·378	4·422	4·323	4·466	4·424	3·205	2·767	2·671
D_4/D_w	—	0·454	0·455	0·467	0·442	0·459	0·480	0·5031	0·495	0·467	0·3856
$\ln(D_0/D_t)$	—	0·134	0·272	0·488	0·803	0·982	1·262	1·484	1·780	1·963	2·252

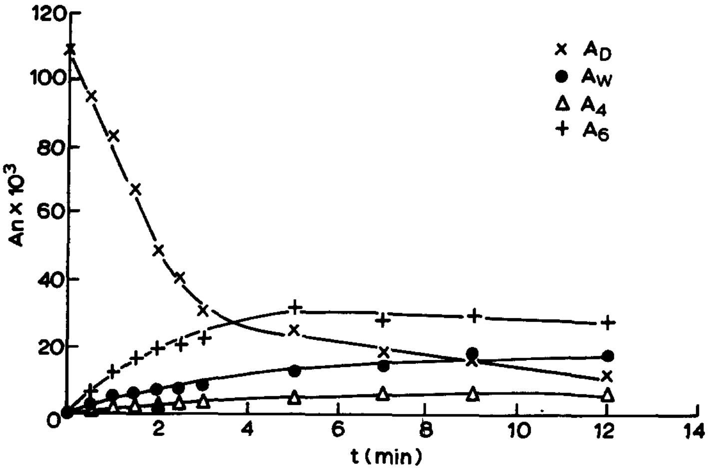


Fig. 2. Plots of peak areas versus reaction times (in minutes) of reaction 1 at 50°C ± 1°C and pH 12·824.

For the reaction carried out at 50 ± 1°C and pH 12·824 (reaction 1), the results are shown in Table 2 (see also Figs 2 and 3). Since $A_D = K_D D$, $A_w = K_w D_w$, $A_6 = K_6 D_w$, $A_4 = K_4 D_4$, therefore

$$\ln(D_o D_t) = \ln(A_o/A_t)$$

The regression equation was:

$$\ln(D_o/D_t) = 0{\cdot}4076t - 0{\cdot}06, \quad r = 0{\cdot}989$$

and therefore, the rate of reaction (k) is equal to 0·4076 min^{-1}; k'_w, k'_6, k'_4 and $k'_6/(k'_6 + k'_4)$ can thus be calculated.

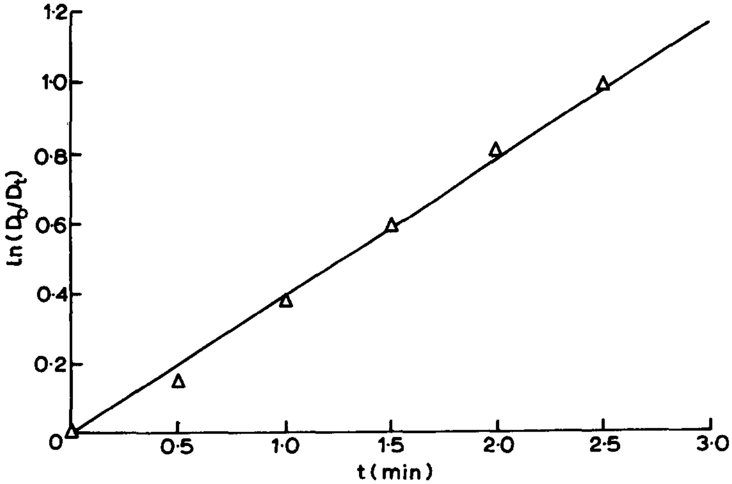


Fig. 3. Plots of $\ln(D_o/D_t)$ versus reaction time t (in minutes) of reaction 1 at 50 ± 1°C and pH 12·824.

TABLE 3
The Rate Constants of the Reaction between D and MOH

No.	*Reaction condition*	*ln*(D_o/D_t)	$\bar{k}_n$	k'_w	k'_6	k'_4	$k'_6/(k'_6+k'_4)$	*Reaction time*
1	50±1°C [GOH]:[D]=23:1 pH=12·824	$0{\cdot}4076t-0{\cdot}063$ $r=0{\cdot}989$	$\bar{k}_1=0{\cdot}4076$	0·0712	0·304	0·0324	0·904	2.3
2	60±1°C [GOH]:[D]=23:1 pH=12·824	$0{\cdot}5019t-0{\cdot}022$ $r=0{\cdot}9947$	$\bar{k}_2=0{\cdot}5119$	0·133	0·3568	0·0418	0·8952	2·5
3	60±1°C [GOH]:[D]=23:1 pH=12·824	$0{\cdot}2474t+0{\cdot}0456$ $r=0{\cdot}9859$	$\bar{k}_3=0{\cdot}2474$	0·0576	0·1694	0·243	0·8922	2·5
4	60±1°C [GOH]:[D]=46:1 pH=13·125	$0{\cdot}9727t+0{\cdot}052$ $r=0{\cdot}9921$	$\bar{k}_4=0{\cdot}9727$	0·1449	0·602	0·0809	0·9023	2
5	60±1°C [GOH]:[D]=46:1 pH=12·125	$0{\cdot}26133t+0{\cdot}07$ $r=0{\cdot}996$	$\bar{k}_5=0{\cdot}2613$	0·0325	0·2078	0·02078	0·9091	6

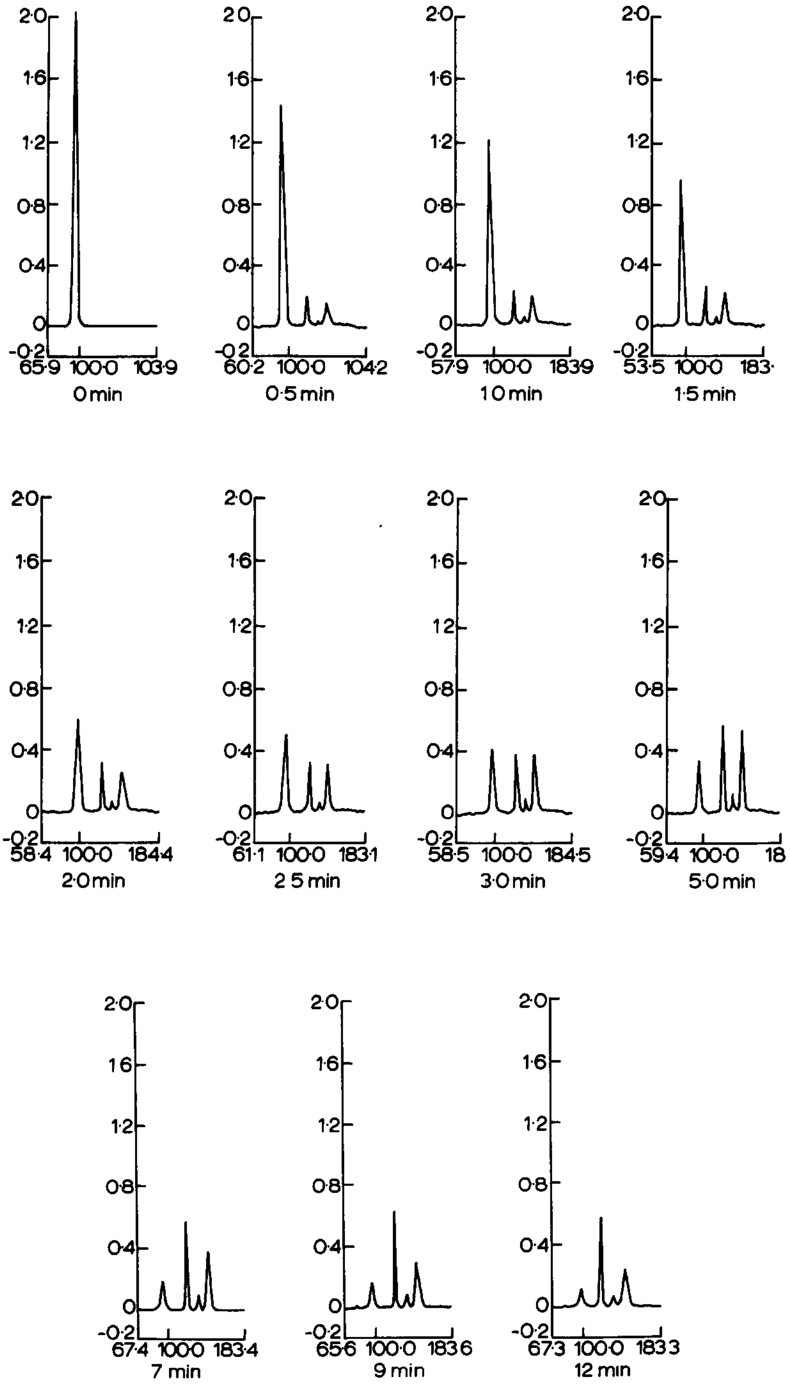


Fig. 4. Scanning diagram of chromatogram of reaction 1 at 50 ± 1°C.

For the reaction carried out at 60 ± 1°C and at different pH, similar results were obtained and these are summarized in Table 3.

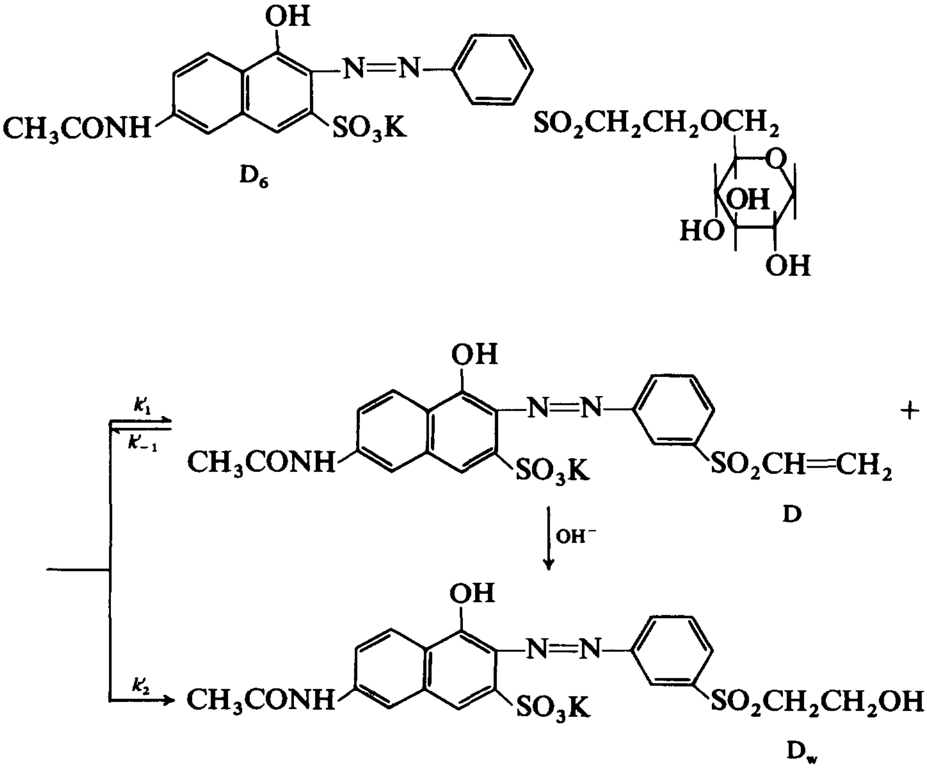
The double scanning diagrams of the TLC chromatogram of reaction 1 at 50 ± 1°C are shown in Fig. 4; scanning diagrams of the chromatograms of the other reactions were similarly obtained.

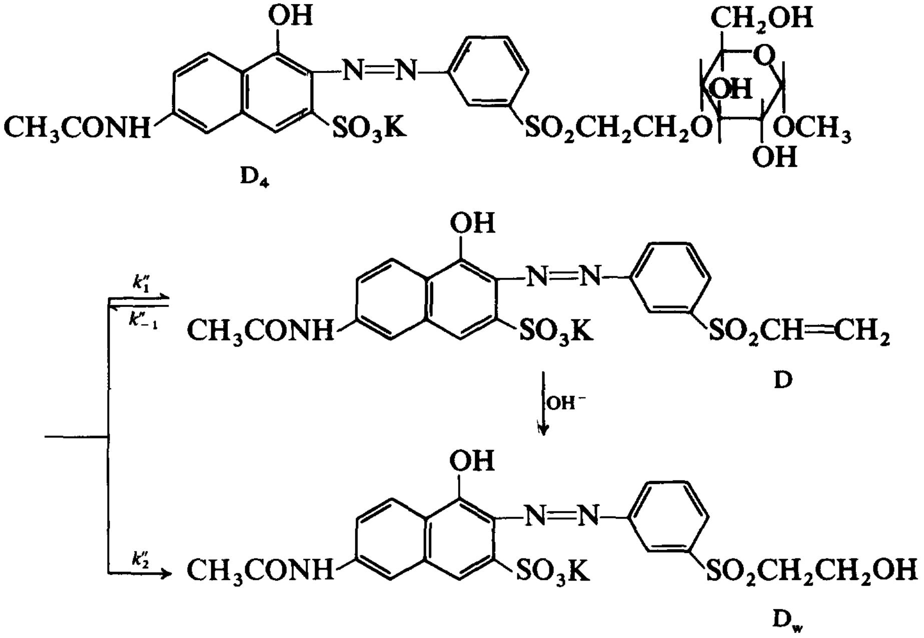
From these results, the rate of reaction between the soluble vinyl sulfonyl reactive dye and MOH is shown to be greater than that between MOH and the dye without a sulfonic acid group, as is apparent from Table 4.[1]

In the presence of the sulfonic acid group, the reaction rate at —CH_2OH (6) is greater than that of —CHOH(4) ($k'_6 > k'_w > k'_4$).

3 DETERMINATION OF RATES OF ALKALINE HYDROLYSIS OF DYE-GLUCOSIDES

The alkaline hydrolysis of D_6 and D_4 may be represented by the following:





The rate equation of hydrolysis may be expressed as:

$$\ln [D_6]_D/[D_6]_t = k_6 t \quad \text{and} \quad \ln [D_4]_D/[D_4]_t = k'_4 t$$

where

$$k_6 = k'_1 + k'_2; \qquad k_4 = k''_1 + k''_2$$

0·02 g D_6 (or D_4) was dissolved in 30 ml distilled water; 7·5 ml of the dye solution was placed in a 50 ml conical flask and the flask placed in a thermostat, stirred and maintained at 50 ± 1°C for 1 h; 0·25 ml of 2N NaOH solution was added and the pH of the dye solution was 12·829 (by calculation). Aliquots were removed at intervals, immediately cooled and dilute HCl acid added to give a pH of 5–6. A microinjector was used to inject 1 ml onto a chromatographic plate, which was then developed and scanned. These reactions were similarly conducted using D_4, D_6 at different temperatures and at different pHs.

The chromatogram of D_6 and D_4 during the hydrolysis showed that there were two reaction products formed, D_w and D. The peak areas of D_w, D, D_6 or D_4 were measured quantitatively by TLC-double scanning, and the standard curves of D, D_w, D_6 or D_4 were illustrated in Section 2 of this investigation.

Taking the hydrolysis of D_4 at 50 ± 1°C, pH 12·826 as an example, the concentrations of D_4, D_w and D after various times of hydrolysis are given in Table 5.

TABLE 4

No. of reaction	*Reaction conditions*	$\bar{k}_n$	k'_w	k'_6	k'_r	$k'_6/(k'_6+k'_4)$
1	50±1°C [GOH]:[D]=4:1	0·141 1	0·016 74	0·108 1	0·016 28	0·869 1
2	60±1°C [GOH]:[D]=4 1	0·160 7	0·034 70	0·109 6	0·018 56	0·855 3

TABLE 5

Peak Areas of A_o, A_w and A_4 Formed during Hydrolysis

Time (min)	*0*	*2·5*	*5*	*10*	*15*	*20*	*30*	*40*	*60*
A_D	0	4 725·25	6 879·73	8 376·5	5 066·34	424·24	3 058·04	2 476·40	1 718·367
A_w	0	3 600·71	4 528·5	7 787·45	12 489·57	18 525·8	20 903·31	21 840·2	23 609·43
A_4	42 575·96	34 124·1	32 524·03	26 065·43	15 495·11	8 380·35	33 971·25	1 171·233	511·02
$\ln(D_{4o}/D_4t)$	0	0·221 3	0·269	0·491	1·0108	1·625	2·372	3·179 6	4·423

TABLE 6

Peak Areas of A_D, A_w and A_6 Formed during Hydrolysis

Time (min)	*0*	*3·0*	*5·0*	*10·0*	*15·0*	*20·0*	*30·0*
A_D	0	9 498·52	6 814·44	4 146·85	2 965·05	1 408·57	644·23
A_w	0	6 463·65	9 826·11	14 809·32	17 009·04	18 637·64	21 003·09
A_6	31 458·22	20 114·39	13 435·69	8 736·58	5 334·34	2 627·65	996·41
$\ln[D_6]_o/[D_6]_6$	0	0·447	0·850 7	1·281	1·601	2·483	3·452

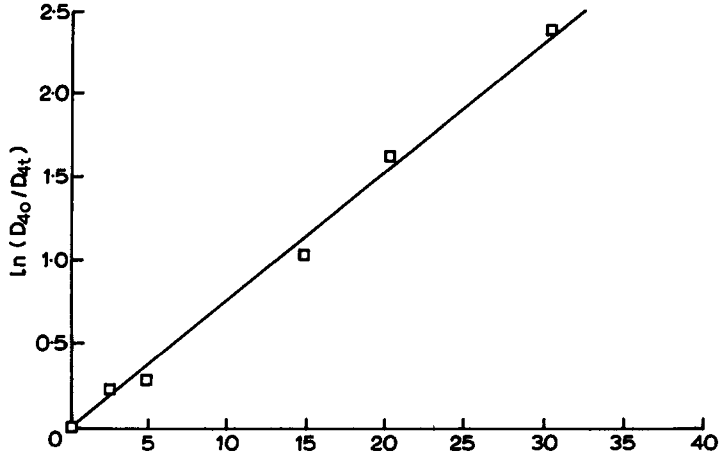


Fig. 5. Plots of ln $\{[D_4]_o/[D]t]$ against time *t* (in minutes).

On plotting ln $\{[D_4]_D/D_4]t\}$ against time *t*, a straight line was obtained (Fig. 5). The regression equation and coefficients were $y = 0·076\,77t - 0·0443$, $r = 0·9873$ and $k_6 = 0·114\,24\ \text{min}^{-1}$.

Figure 5 shows plots of ln $\{[D]_D/[D_4]t\}$ against time *t* in minutes.

The hydrolysis of D_6 at 50 ± 1°C, pH 12·824 was similarly effected. The peak areas of A_D, A_w and A_6 formed during hydrolysis were given in Table 6.

On plotting ln $\{[D_6]_D/[D_6]t\}$ against time *t*, a straight line was obtained (Fig. 6). The regression equation and coefficients were $y = 0·114\,24t + 0·013$, $r = 0·9873$ and $k_6 = 0·114\,24,\text{in}^{-1}$.

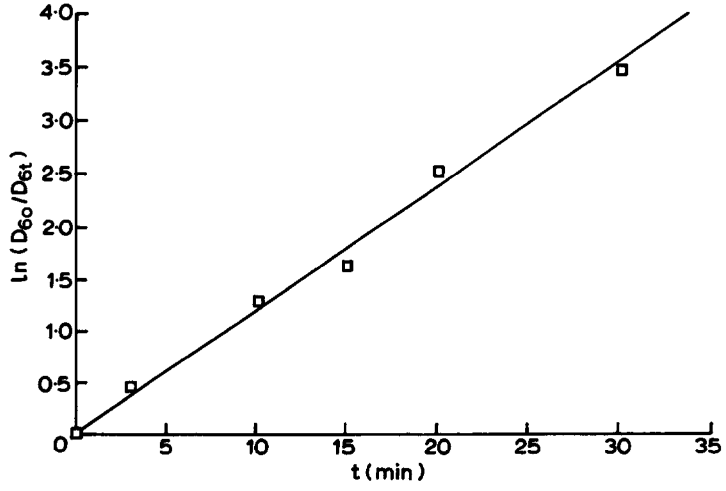


Fig. 6. Plots of ln $\{[D_6]_o/[D_6]t\}$ against time *t* (in minutes).

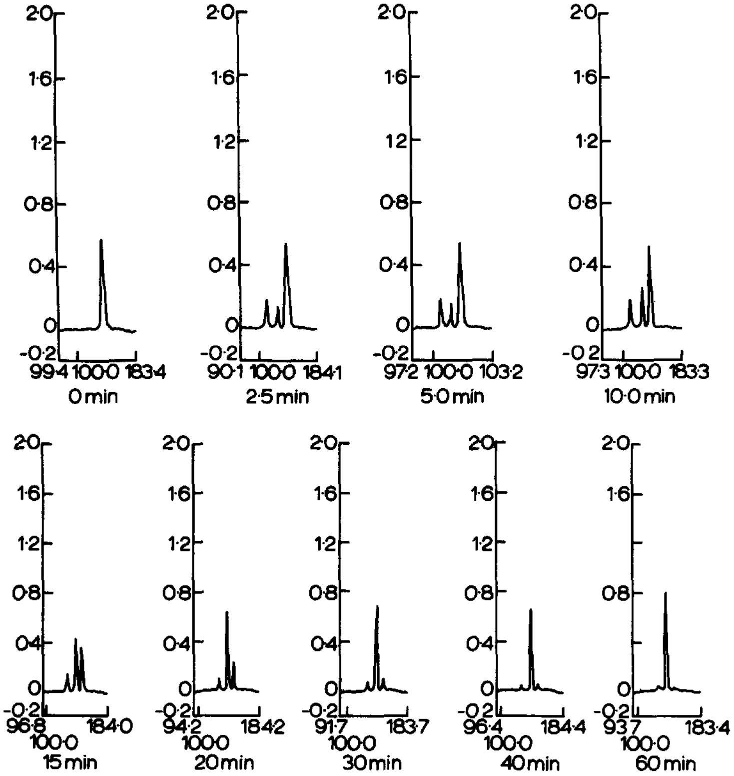


Fig. 7. The hydrolysis of D_6; plots by TLC-double scanning at 50 ± 1°C and pH 12·824.

TABLE 7
The Rates of Hydrolysis of D_4 and D_6

No.	*Reaction condition*	*Rate equations* $ln[D_o/D_t]=y$	*Rate constants* k (min^{-1})
1	D_4, 50 ± 1°C, pH = 12·824	$y=0{\cdot}076\,77t-0{\cdot}044\,3$ $r=0{\cdot}996\,08$	0·0768
2	D_6, 50 ± 1°C, pH = 12·824	$y=0{\cdot}114\,27t+0{\cdot}013$ $r=987\,3$	0·1142
3	D_4, 60 ± 1°C, pH = 12·824	$y=0{\cdot}109\,24t-0{\cdot}091$ $r=0{\cdot}996\,40$	0·1092
4	D_6, 60 ± 1°C, pH = 12·824	$y=0{\cdot}114\,89t-0{\cdot}045$ $r=0{\cdot}996\,7$	0·1149 0·1149
5	D_4, 50 ± 1°C, pH = 12·0	$y=7{\cdot}2\times10^{-3}t-4{\cdot}6\times10^{-3}$ $r=0{\cdot}996\,7$	0·0072
6	D_6, 50 ± 1°C, pH = 12·0	$y=0{\cdot}011\,6t+0{\cdot}037\,75$ $r=0{\cdot}996\,1$	0·0116
7	D_4, 60 ± 1°C, pH = 12·0	$y=0{\cdot}021\,18t-0{\cdot}005\,5$ $r=0{\cdot}999\,65$	0·0212
8	D_6, 60 ± 1°C, pH = 12·0	$y=0{\cdot}021\,94t+0{\cdot}014\,7$ $r=0{\cdot}996\,7$	0·0219

Figure 6 shows plots of ln $\{[D_6]_D/[D_6]t\}$ against time t in minutes, and the hydrolysis of D_6 plots by TLC-double scanning at 50 ± 1°C, pH 12·824 are shown in Fig. 7.

The hydrolysis of D_4, D_6 plots by TLC-double scanning at 50 ± 1°C, 60 ± 1°C were similarly conducted and the rates of hydrolysis of D_4 and D_6, for various reaction conditions are summarized in Table 7.

4 CONCLUSION

The homogeneous reaction between a soluble vinyl sulfonyl reactive dye and methyl-α-D-glucoside has been studied kinetically. The presence of a sulfonic group in the dye molecule had no effect on its reaction with methyl-α-D-glucoside; neither D_2 nor D_3 was formed. The relative rate of reaction was increased due to the fact that the reaction was carried out in aqueous medium, but the relative amount of D_6 formation was the same regardless of the presence or absence of a sulfonic acid group. The dye molecule reacted predominantly at the 6-CH_2OH group.

The rates of hydrolysis of D_6 and D_4 were also determined in alkaline medium. The mechanism of hydrolysis of D_6 and D_4 also followed an elimination route in the initial stage of the reaction; D_6 was hydrolysed more rapidly than D_4.

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1. Zhu Zhenghua, Xia Jianmei & Chen Kongchang, *Dyes and Pigments*, **17** (1991) 171–91.
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