Dyes and Pigments **19** (1992) 265–280

A Study of the Homogeneous Reaction Between a Model Cibacron Pront Reactive Dye and Methyl-α-D-glucoside

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(Received 5 February 1992; accepted 16 March 1992)

ABSTRACT

The reaction between a methoxy-triazinyl reactive dye and methyl-α-D-glucoside is studied in water-dioxane solution. The attacking site of different OH groups in the methyl-α-D-glucoside is determined by AM 600 ^1H *NMR spectroscopy and the reaction products are separated by thin-layer chromatography–double scanning. It is shown that only the* C_6 *and* C_4 *hydroxyl groups are involved. The relative rates of reaction (*$k_6/k_4 = 12$*) at 60 and 70°C are determined. The rate constants of the hydrolysis of the methoxytriazinyl dye-glucoside (for both* D_6 *and* D_4*) were measured kinetically. For* D_6 *the rate constants of hydrolysis at 80 and 90°C are 0·409 and 0·923 min*$^{-1}$*, respectively. For* D_4 *the rate constants of hydrolysis at 80 and 90°C are 0·0189 and 0·0433 min*$^{-1}$*, respectively.*

1 INTRODUCTION

The mechanism of the reaction between triazinyl reactive dyes and cellulose has not been completely resolved. One major factor is the determination of the glucoside OH groups at which the reaction takes place.

Dawson *et al.* used normal and isopropyl alcohols as model cellulose compounds and reached the conclusion that the ratio of the reaction rates of primary to secondary hydroxyl groups was between 13·4 and 15·2 for monochloro-triazine dyes.[1]

Baumgarte[2] used methyl-α-D-glucoside as a model cellulose compound. Paper chromatography was used to study the reaction between a dichloro-

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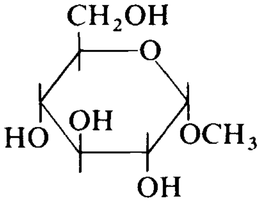
triazinyl dye and methyl-α-D-glucoside. The results of the chromatographic analysis were indeterminate, and only qualitative in nature.[2]

The present authors have previously studied the reaction between a vinyl sulphone reactive dye and methyl-α-D-glucoside using AM 400 ^1H NMR, and the reaction products were separated by TLC–double scanning.[3]

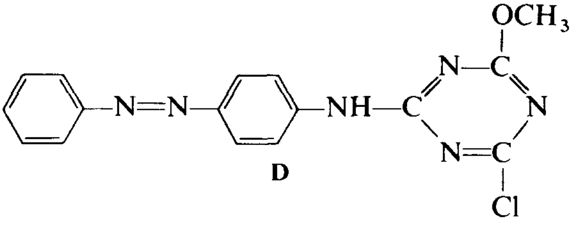
In this paper, a similar method was used for studying the reaction between a monochloro-methoxy-triazinyl dye (Cibacron Pront type) and methyl-α-D-glucoside. The products of the reaction were separated by TLC–double scanning, and the structures of reaction products, i.e. the attaching sites at the glucoside OH, were determined by ^1H NMR.

2 GENERAL DERIVATION OF RATE EQUATIONS

2.1 Structures of the monochloro-methoxy-triazinyl model reactive dye, methyl-α-D-glucoside and possible reaction products



(MOH)



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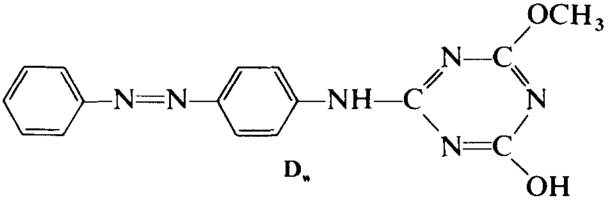

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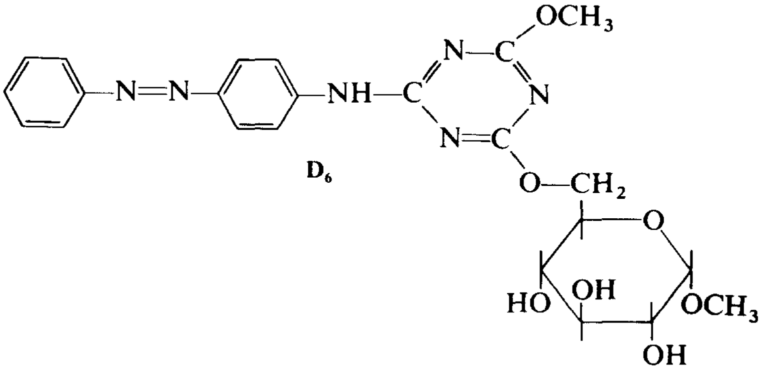
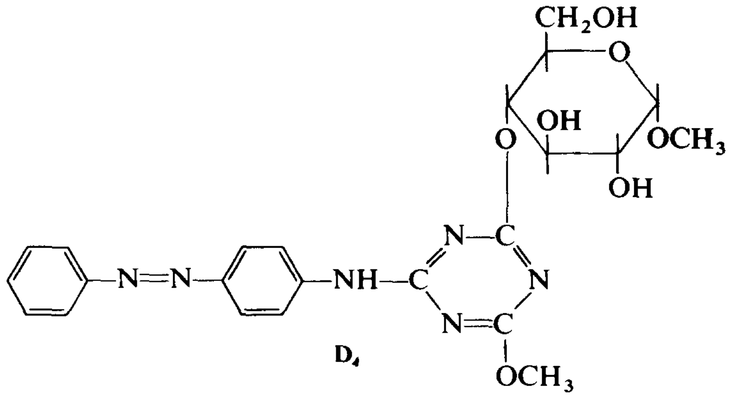
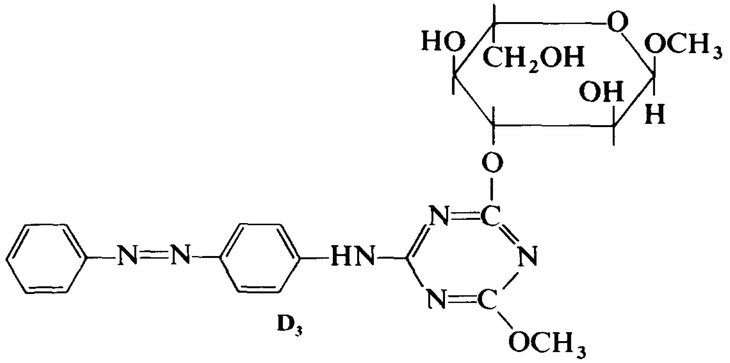


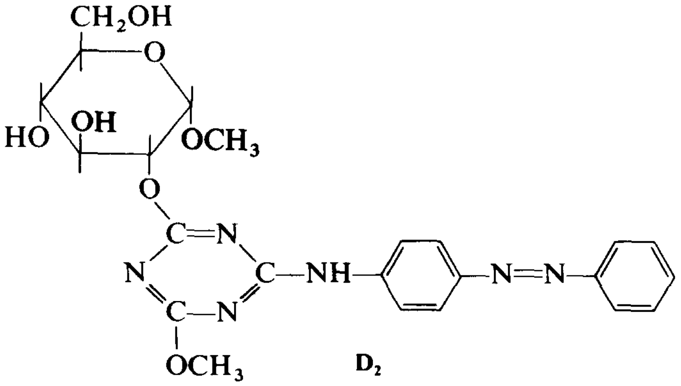
D₆



D₄



D₃



D₂

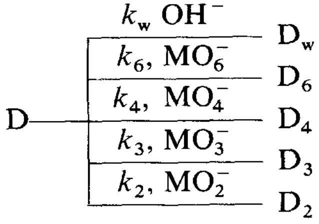
2.2 Derivation of rate equations

$$\begin{array}{rll} \mathrm{MOH} + \mathrm{OH}^- \rightleftharpoons & \mathrm{MO}_2^- + \mathrm{H_2O} & K_2 \\ & \mathrm{MO}_3^- + \mathrm{H_2O} & K_3 \\ & \mathrm{MO}_4^- + \mathrm{H_2O} & K_4 \\ & \mathrm{MO}_6^- + \mathrm{H_2O} & K_6 \end{array}$$

Therefore

$$K_2 = \frac{[\mathrm{MO}_2^-]}{[\mathrm{MOH}][\mathrm{OH}^-]} \qquad K_3 = \frac{[\mathrm{MO}_3^-]}{[\mathrm{MOH}][\mathrm{OH}^-]}$$

$$K_4 = \frac{[\mathrm{MO}_4^-]}{[\mathrm{MOH}][\mathrm{OH}^-]} \qquad K_6 = \frac{[\mathrm{MO}_6^-]}{[\mathrm{MOH}][\mathrm{OH}^-]}$$



$$-\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} = k_w[\mathrm{D}][\mathrm{OH}^-] + k_6[\mathrm{D}][\mathrm{MO}_6^-] + k_4[\mathrm{D}][\mathrm{MO}_4^-] + k_3[\mathrm{D}][\mathrm{MO}_3^-] + k_2[\mathrm{D}][\mathrm{MO}_2^-]$$

In the authors' experiments, a large excess of MOH and OH$^-$ was used:

$$\begin{aligned}-\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} = k_w[\mathrm{D}][\mathrm{OH}^-] &+ k_6K_6[\mathrm{D}][\mathrm{MOH}][\mathrm{OH}^-] \\ &+ k_4K_4[\mathrm{D}][\mathrm{MOH}][\mathrm{OH}^-] \\ &+ k_3K_3[\mathrm{D}][\mathrm{MOH}][\mathrm{OH}^-] \\ &+ k_2K_2[\mathrm{D}][\mathrm{MOH}][\mathrm{OH}^-] = k[\mathrm{D}]\end{aligned}$$

where

$$\begin{aligned}k = k_w[\mathrm{OH}^-] + k_6K_6[\mathrm{MOH}][\mathrm{OH}^-] + k_4K_4[\mathrm{MOH}][\mathrm{OH}^-] \\ + k_3K_3[\mathrm{MOH}][\mathrm{OH}^-] + k_2K_2[\mathrm{MOH}][\mathrm{OH}^-]\end{aligned}$$

By integrating

$$\ln\frac{\mathrm{D}_0}{\mathrm{D}_t} = kt$$

and

$$\frac{\mathrm{D}_w}{\mathrm{D}_6} = \frac{k_w}{k_6K_6\mathrm{MOH}} \qquad \frac{\mathrm{D}_w}{\mathrm{D}_4} = \frac{k_w}{k_4K_4\mathrm{MOH}} \qquad \text{etc.}$$

In the present case, it was found that only D_6 and D_4 were actually formed, viz:

$$\frac{\mathrm{D}_6}{\mathrm{D}_4} = \frac{k_6K_6}{k_4K_4}$$

Therefore, if the total rate constant k could be obtained experimentally, the relative rate constants k_6 and k_4 can then be calculated.

2.3 ^{1}H NMR of methyl-α-D-glucoside

The chemical shifts of the active hydrogen atoms in different glucoside OH groups are as follows:[3,4]

	Chemical shift (*δ ppm*)	*Peaks*	*Integral value* (*Hz*)
2-OH	4·68	Doublet	6·45
3-OH	4·74	Doublet	4·7
4-OH	4·84	Doublet	5·5
6-OH	4·45	Quartet	5·8 and 6·2

2.4 Reaction rate between monochloro-methoxy-triazinyl dye and methyl-α-D-glucoside

Dye (0·5 g, $1{\cdot}47 \times 10^{-3}$ mol) and glucoside (0·8 g, $4{\cdot}12 \times 10^{-3}$ mol) were added to water (4 ml) and dioxane (10 ml). The mixtures were maintained at 70 ± 1, 80 ± 1 and 90 ± 1°C, respectively; 10% NaOH solution (0·5 ml) was added and the pH maintained at 10. After 15 min, the reaction was stopped and the reaction mixture added to water (10 ml) and neutralized to pH 7.

2.5 Separation of reaction products

The reaction products (in acetone) were separated on Silica Gel chromatographic plates. The spots were dried and developed with benzene/chloroform/ethylalcohol/dioxane (1:1:0·3:0·2).

Five spots were apparent, as shown:

Spot 1	unreacted dye, $R_f = 0{\cdot}867$
Spots 2, 3	hydrolysed dye, $R_f = 0{\cdot}521$, 0·518
Spot 4	reaction product 1, $R_f = 0{\cdot}459$
Spot 5	reaction product 2, $R_f = 0{\cdot}407$

2.6 Structural identification of reaction products

2.6.1 Elemental analysis

No. 2 (spot 4):	C%	55·02, 55·18 (55·42)
	H%	5·31, 5·36 (5·22)
	N%	16·53, 16·44 (16·87)
No. 1 (spot 5):	C%	55·11, 55·06 (55·42)
	H%	5·35, 5·44 (5·22)
	N%	16·28, 16·69 (16·87)

2.6.2 Mass spectra

No. 1: $M/e = 498$; No. 2: $M/e = 498$.

2.7 Identification of reaction products by ^{1}H NMR

Due to the shift effect of substitution (e.g. the presence of O-Alkyl), the δ values of the protons in the remaining OH are shifted toward high field. The presence of a 4-O-Alkyl substituent results in the proton signal for the remaining hydroxy group being shifted to lower field (Figs 1 and 2).

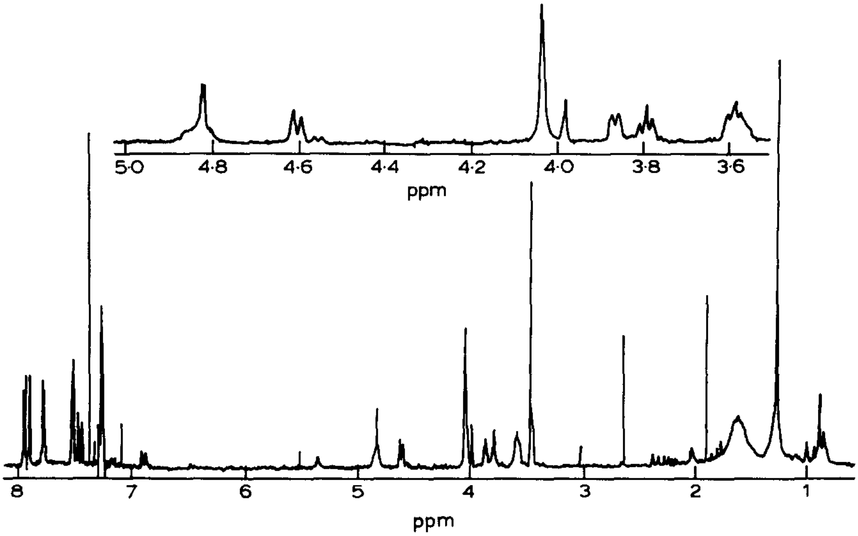


Fig. 1. ^{1}H NMR of D_6 in $CDCl_3$.

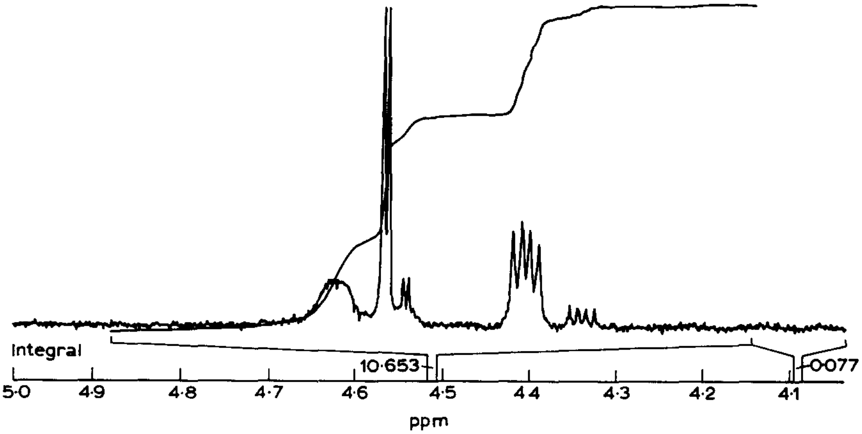


Fig. 2. ^{1}H NMR of D_6 in DMSO.

For spot 4 the observed δ values were:

	In unsubstituted MOH (ppm)	*In reacted product (ppm)*
2-OH	4·68	4·41
3-OH	4·74	4·54
4-OH	4·84	4·62

The ^1H NMR spectrum shows no signal for OH_6 in the reaction product (spot 4). If OH_6 were present, it would be shifted to 4·20 ppm approximately; spot 4 in the reaction product may therefore be identified as structure D_6.

For spot 5 the observed δ values were:

	In unsubstituted MOH (ppm in DMSO)	*In reacted product (ppm in DMSO ($CDCl_3$))*
2-OH	4·68	5·20 (4·70)
3-OH	4·74	5·28 (4·80)
6-OH	4·45	4·60 (4·50)

^1H NMR shows no OH_4 in the reaction product (spot 5); if OH_4 were present, it would be shifted to 5·3–5·4 ppm in DMSO or to 4·90 ppm in $CDCl_3$. The reaction product (spot 5) may therefore possibly be identified as structure D_4 (Figs 3 and 4).

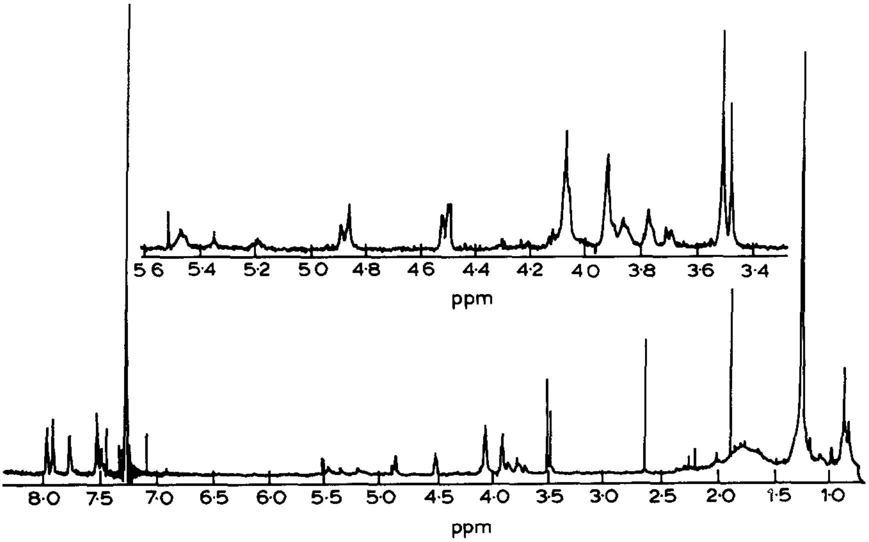


Fig. 3. ^1H NMR of D_4 in $CDCl_3$.

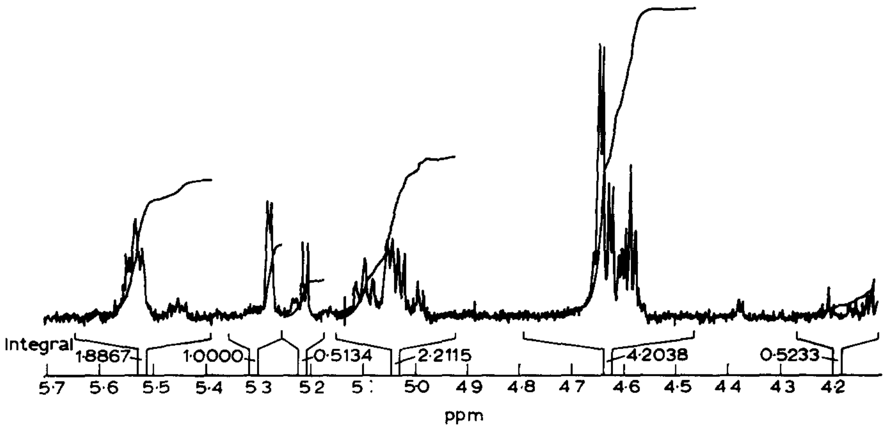


Fig. 4. ^{1}H NMR of D_4 in DMSO.

2.8 Determination of the rate constants for the reaction between the dye and MOH

The reaction was carried out as described above. At intervals 0·05 ml aliquots of the solution were taken, cooled and dilute HCl added to pH 7. Thin-layer chromatography with double scanning (using a Shimadzu-910) was used. The peak areas of D, D_6 and D_4 were experimentally determined. The standard curves plotted between D, D_6, D_4 and peak areas were thus obtained, respectively (Table 1).

TABLE 1
Peak Areas of D, D_w, D_6 and D_4 Against Time at 60°C

	t (min)						
	0	*4*	*8*	*16*	*24*	*32*	*43*
A_0	1·47	1·20	0·95	0·40	0·10	0·00	0·00
A_w	0	0·25	0·45	1·20	1·70	2·00	2·25
A_4	0	0·06	0·10	0·10	0·10	0·10	0·10
A_6	0	0·70	0·90	1·15	1·25	0·95	0·70
A_4/A_w	—	0·24	0·17	0·08	0·06	—	—
A_6/A_w	—	2·8	2·0	0·96	0·74	0·48	0·31

$$\frac{d[D]}{dt} = k[D] \quad \text{and} \quad [D] \propto A \quad \text{then} \quad \frac{d[A]}{dt} = k[A]$$

where $k = k_w + k_6K_6 + k_4K_4 = 0{\cdot}0526\ \text{min}^{-1}$ and $D_w\!:\!D_4\!:\!D_6 = k_w\!:\!k_4K_4\!:\!k_6K_6 = 2\!:\!0{\cdot}167\!:\!1$:

$$\frac{[D_6]}{[D_4]} = \frac{[A_6]}{[A_4]} \doteq \frac{k_6}{k_4} \doteq 12$$

TABLE 2
Plots of ln A_0 Versus Time at 70°C

	t (min)					
	0	*3*	*6*	*12*	*18*	*24*
A_0	3·31	2·30	1·55	0·55	0·20	0
ln A_0	1·197	0·833	−0·438	−0·598	−1·609	—
k	—	0·121 3	0·126 5	0·149 6	0·155 9	—

$k_{mean} = 0{\cdot}1383\ \text{min}^{-1}$ at 70°C.
$A_6:A_4:A_w = 7{\cdot}15:0{\cdot}60:2{\cdot}40 = 2{\cdot}98:0{\cdot}25:1$:

$$\frac{[D_6]}{[D_4]} = \frac{[A_6]}{[A_4]} \doteq \frac{k_6}{k_4} \doteq 12$$

From the plot of ln A_0 versus time (t) at 70°C, the total reaction rate constants at 70°C were obtained (Table 2). Similarly, ln A_0 versus time (t) at 80 and 90°C were obtained (Tables 3 and 4).

2.9 Calculation of relative reactivities of CH_2OH (6) and CHOH (4)

At 60°C

$$\frac{k_6K_6}{k_4K_4} = \frac{0{\cdot}0332}{0{\cdot}0028} \doteq 12$$

At 70°C

$$\frac{k_6K_6}{k_4K_4} = \frac{0{\cdot}0974}{0{\cdot}0082} \doteq 12$$

That is, the ratio of the reaction rate of primary to secondary hydroxyl groups is 12 for the monochloro-triazinyl reactive dye, both at 70 and 60°C. It is interesting to compare this result with the 13·4:15·2 given by Dawson

TABLE 3
Plot ln A_0 Versus Time at 80°C

	t (min)			
	0	*3*	*8*	*12*
A_0	2·8	1·5	0·5	0·06
ln A_0	1·029 6	0·405 5	−0·693 1	−2·813 4
k	—	0·208 0	0·215 3	0·320 2

$k = 0{\cdot}2478\ \text{min}^{-1}$ at 80°C.

TABLE 4

ln A_0 Versus Time at 90°C

	t (min)				
	0	*2·5*	*5*	*7·5*	*10*
A_0	3·00	1·50	0·60	0·30	0·06
ln A_0	1·986	0·4055	0·6108	−1·2040	−2·8134
k	—	0·2772	0·3219	0·3070	0·3912

$k = 0·3243\,\mathrm{min}^{-1}$ at 90°C.

et al.,[1] when primary and secondary aliphatic alcohols were used in the investigations.

2.10 Determination of rate constants of hydrolysis of methoxy-triazinyl dye-glucosides

The methoxy-triazinyl-glucosides (D_6 and D_4) were hydrolysed with aqueous NaOH at different temperatures.

2.10.1 *Hydrolysis of D_6*

TLC–double scanning diagrams for the hydrolysis of D_6 at 60°C were used to determine the concentration of D_6 at various times of reaction (Fig. 5).

The various peak areas of A_6 against time t in minutes are shown in Table 5, and a plot of ln $[A_6]_0/[A_6]_t$ versus time (t) gave a straight line, the slope of which is the specific rate constant k for the hydrolysis of D_6 at 60°C.

Similarly, the specific rate constants of hydrolysis of D_6 at 70, 80 and 90°C were determined, viz:

$$k_6 = 0·1837\,\mathrm{min}^{-1} \text{ at } 70°\mathrm{C}$$
$$k_6 = 0·409\,\mathrm{min}^{-1} \text{ at } 80°\mathrm{C}$$
$$k_6 = 0·923\,\mathrm{min}^{-1} \text{ at } 90°\mathrm{C}$$

The plots of ln $[A_6]_0/[A_6]_t$ against time (t) are shown in Fig. 6.

2.10.2 *Hydrolysis of D_4*

The specific rate constants of the hydrolysis of D_4 were similarly determined (Table 6). TLC–double scanning diagrams for the hydrolysis of D_4 at 80°C are shown in Fig. 7 (various peak areas against time (t) at 80°C).

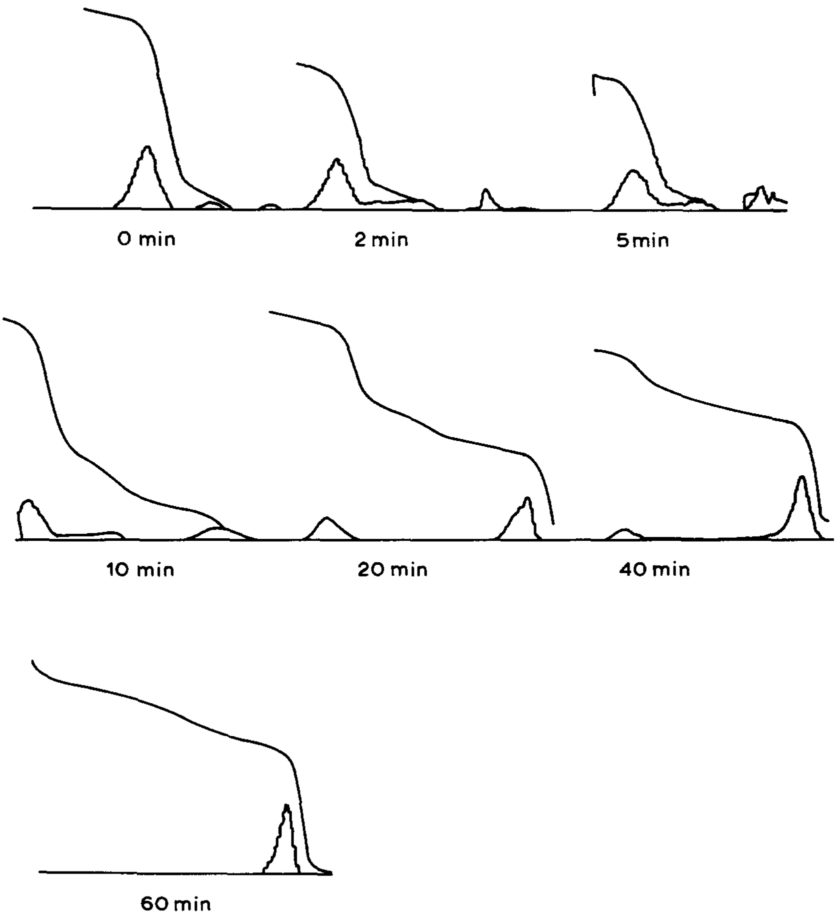


Fig. 5. TLC–double scanning diagram for the hydrolysis of D_6 at 60°C.

TABLE 5
Peak Area of A_6, $\ln\{[A_6]_0/[A_6]_t\}$ Versus Time at 60°C

	t (min)						
	0	*2*	*5*	*10*	*20*	*40*	*60*
A_6	1·40	1·25	1·02	0·81	0·48	0·20	0·05
$\ln [A_6]_0/[A_6]_t$	0	0·113 3	0·316 7	0·547 2	1·070	1·946	3·332
k	—	0·056 7	0·063 3	0·054 7	0·053 5	0·048 6	0·055 5

$k_6 = 0·0554\ \text{min}^{-1}$ at 60°C.
$r = 0·998$.

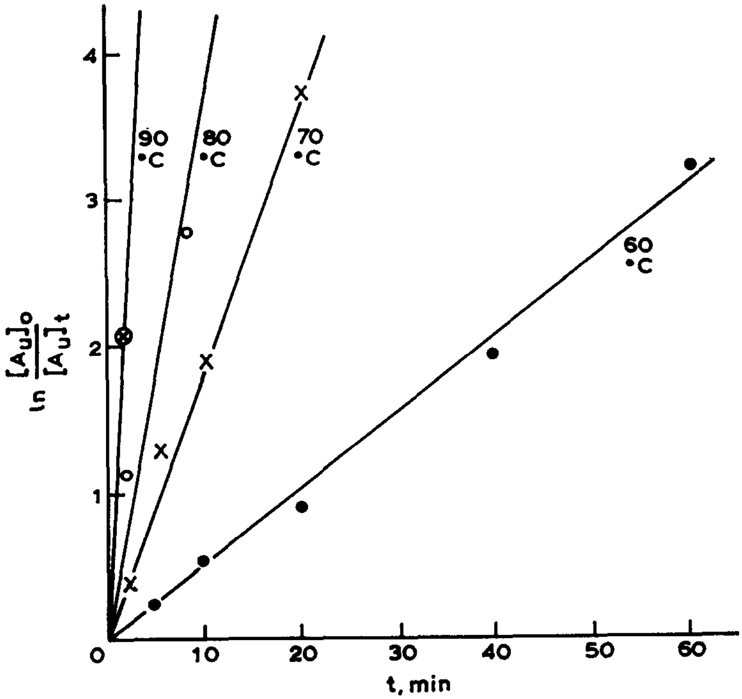


Fig. 6. Plots of ln $[A_6]_0/[A_6]_t$ versus time (t) at 60, 70, 80 and 90°C.

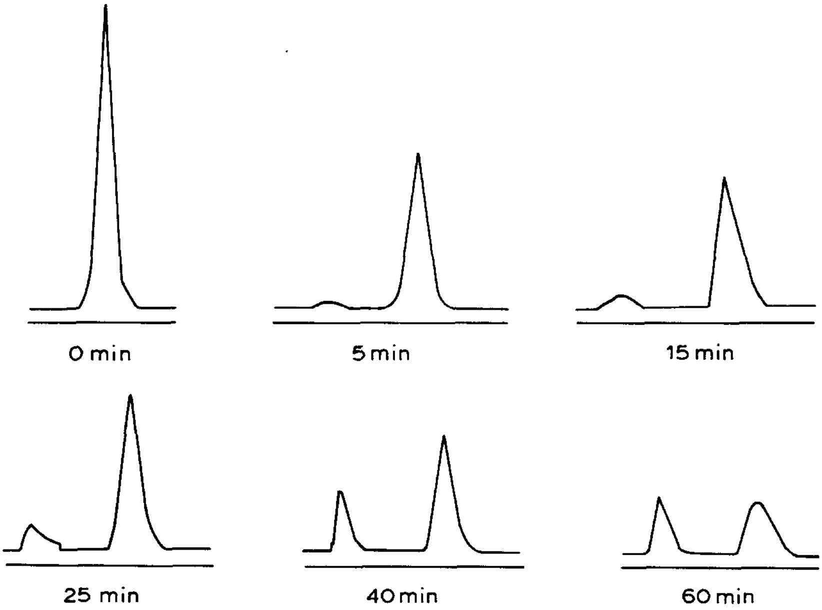


Fig. 7. TLC–double scanning diagrams for the hydrolysis of D_4 at 80°C.

TABLE 6

Peak Areas of A_4, $\ln [A_4]_0/[A_4]_t$ Versus Time at 80°C

	t (min)					
	0	*5*	*15*	*25*	*40*	*60*
A	2·90	2·60	2·25	1·80	1·36	1·60
$\ln [A_4]_0/[A_4]_t$	0	0·1092	0·2538	0·4769	0·7572	1·0647
k	—	0·0218	0·0169	0·0191	0·0189	0·0177

$k_4 = 0{\cdot}0189\ \text{min}^{-1}$ at 80°C.
$r = 0{\cdot}977$.

Similarly, the specific rate constant for the hydrolysis of D_4 at 90°C can also be determined:

$$k_4 = 0{\cdot}0433\ \text{min}^{-1} \text{ at } 90°\text{C}$$

Plots of $\ln [A_4]_0/[A_4]_t$ versus time *t* (in min) are shown in Fig. 8.

2.11 Hydrolysis of monochloro-methoxy-triazinyl reactive dye

In the chromatographic study of the hydrolysis products of the monochloro-triazine dye, the authors found that there was more than one spot on the TLC plate; ^{1}H NMR was used to study this.

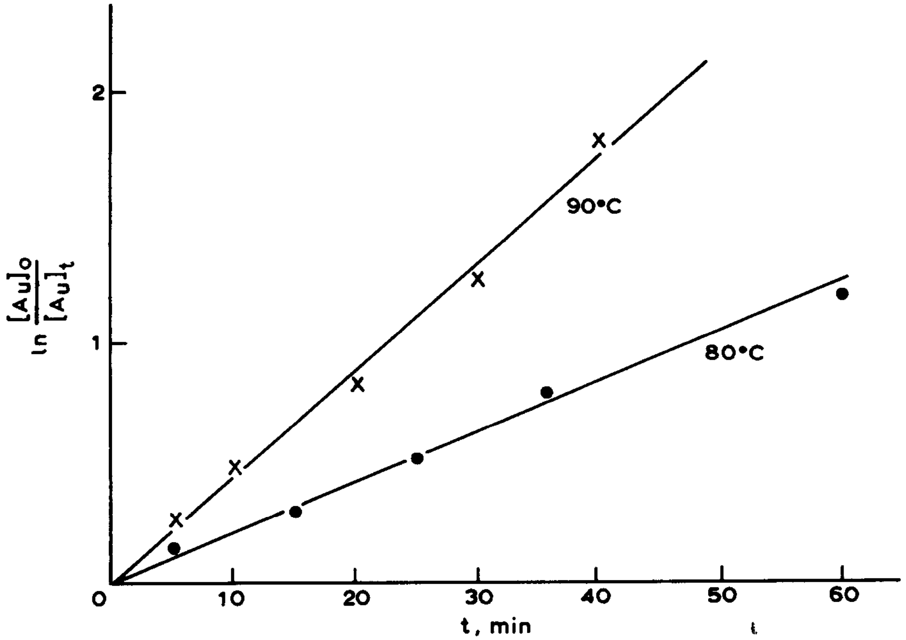


Fig. 8. Plots of $\ln [A_4]_0/[A_4]_t$ versus time (*t*) at 80 and 90°C.

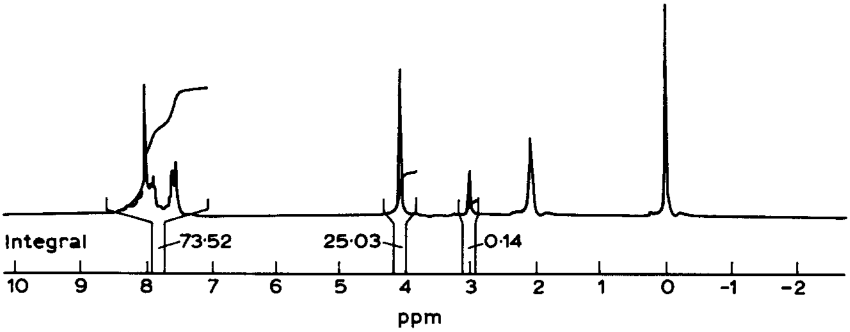


Fig. 9. ^{1}H NMR spectrum of D in CH_3COCH_3-d_6.

The ^{1}H NMR spectrum of the monochloro-methoxy-triazinyl reactive dye (in CH_3COCH_3-d_6) is shown in Fig. 9. In this figure the chemical shifts 7·5–8·5 ppm (δ_1) correspond to the hydrogen atoms in the benzene rings, the chemical shift at 4·1 ppm (δ_2) is due to the hydrogens of the OCH_3 group, and that at 3·0 ppm (δ_3) is due to hydrogen in the —NH— bridge. It was found that $\delta_1/\delta_2/\delta_3$ were in the ratio 9:3:1.

The ^{1}H NMR spectra of the monochloro-methoxy-triazinyl reactive dye after reaction with NaOH solution in CH_3COCH_3-d_6 at 67°C are shown in Fig. 10.

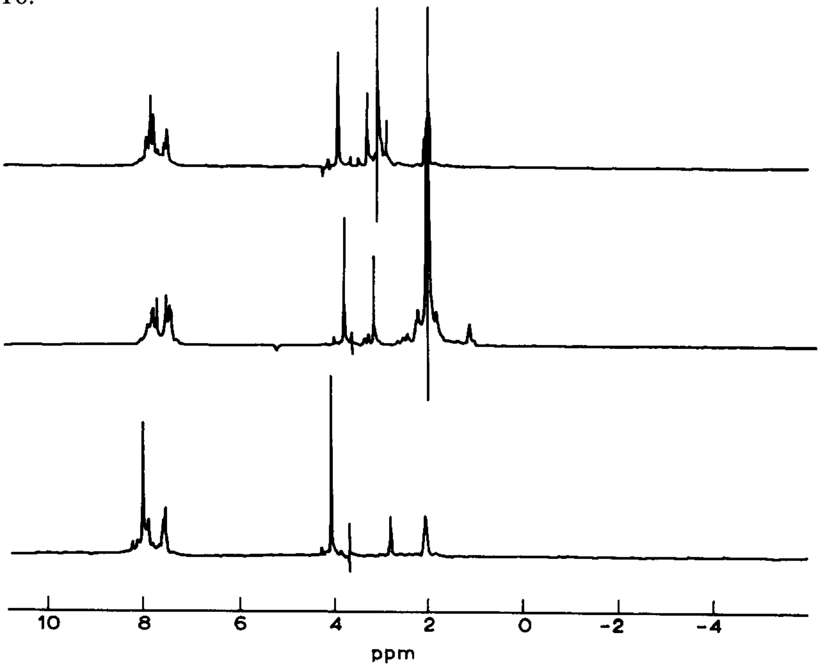
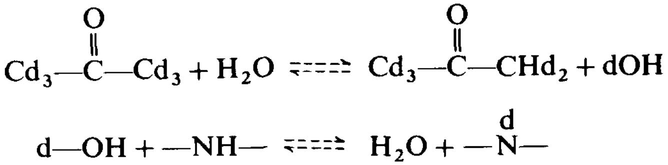


Fig. 10. ^{1}H NMR spectra of D after reaction with NaOH solution in CH_3COCH_3-d_6 at 67°C.

Figure 10 shows that during the hydrolysis of D with 30% NaOH, the δ 3·0 due to the bridged —NH— disappears. It may therefore be concluded that the following reactions occur:

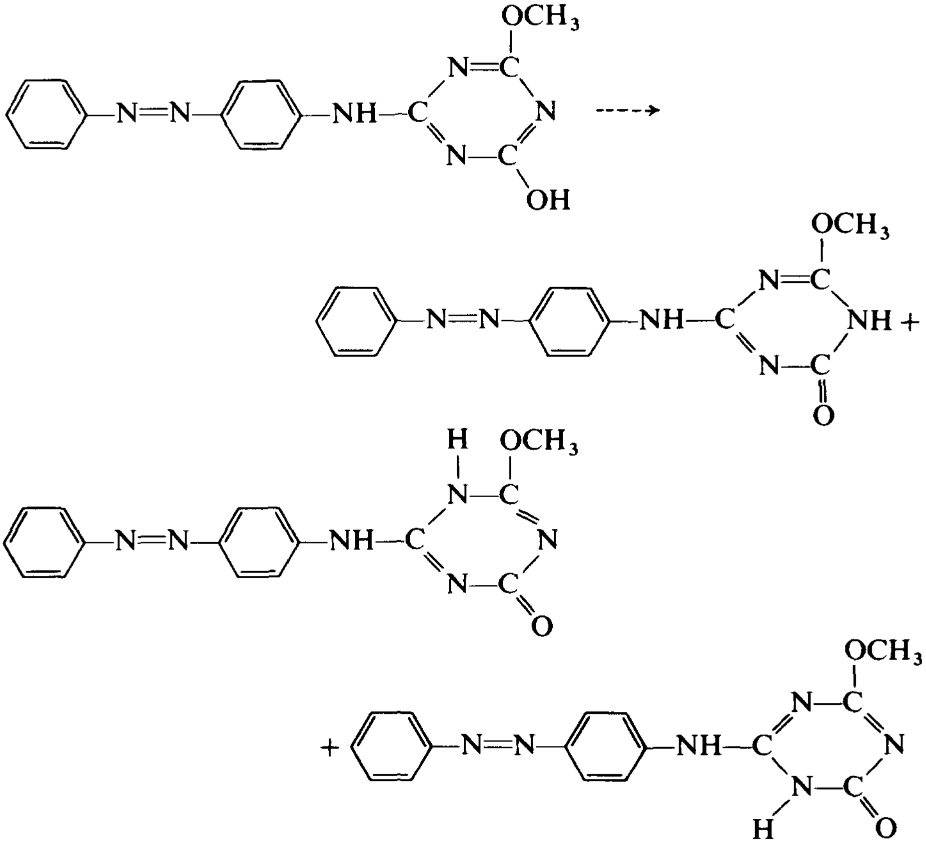


$$\mathrm{Cd_3{-}\overset{\overset{O}{\|}}{C}{-}Cd_3 + H_2O \rightleftharpoons Cd_3{-}\overset{\overset{O}{\|}}{C}{-}CHd_2 + dOH}$$

$$\mathrm{d{-}OH + {-}NH{-} \rightleftharpoons H_2O + {-}\overset{d}{N}{-}}$$

After a certain time of hydrolysis of D, new peaks at δ 1·1, 2·7 and 3·3 appear. These arise from the ring —NH— groups. The ^{1}H NMR spectrum is shown in Fig. 11.

It can thus be reasonably concluded that a number of isomers exist when the dye is hydrolysed:



Therefore, a single spot is not shown on TLC, but several products giving δ 1·1, 2·7 and 3·3 appear.

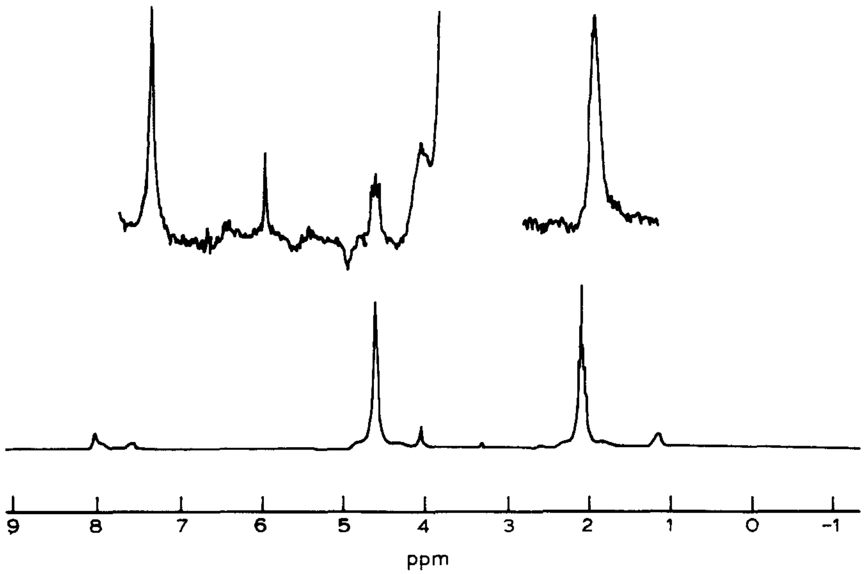


Fig. 11. ^{1}H NMR spectrum of D at the end of reaction in NaOH at 67°C.

3 CONCLUSIONS

The competitive reactions of different OH groups of methyl-α-D-glucoside with a model Cibacron Pront reactive dye have been studied. The reaction is carried out largely on the primary OH group, i.e. CH_2OH (6), but a small amount of —CHOH (4) is also formed. The relative reactivities of CH_2OH (6) to —CHOH (4) are 12:1 at both 60 and 70°C. The structures of D_6 and D_4 are confirmed by AM 600 MHz ^{1}H NMR, mass spectroscopy and elemental analysis. D_6 is more easily hydrolysed than D_4 (>20) at 80 and 90°C. The mechanism of hydrolysis of the model Cibacron Pront dye is also studied, using TLC–double scanning and 600 MHz ^{1}H NMR.

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