Dyes and Pigments **17** (1991) 217–226

A Study of the Homogeneous Reaction Between a Vinyl Sulfone Reactive Dye and Methyl-α-D-glucoside. Part II: Mechanism of Hydrolysis of Vinyl Sulfone Dye–Glucosides

Zhu Zheng-Hua, Xia Jian-Mei & Chen Kong-Chang

East China University of Chemical Technology, Shanghai 200237,
People's Republic of China

(Received 21 November 1990; accepted 3 April 1991)

ABSTRACT

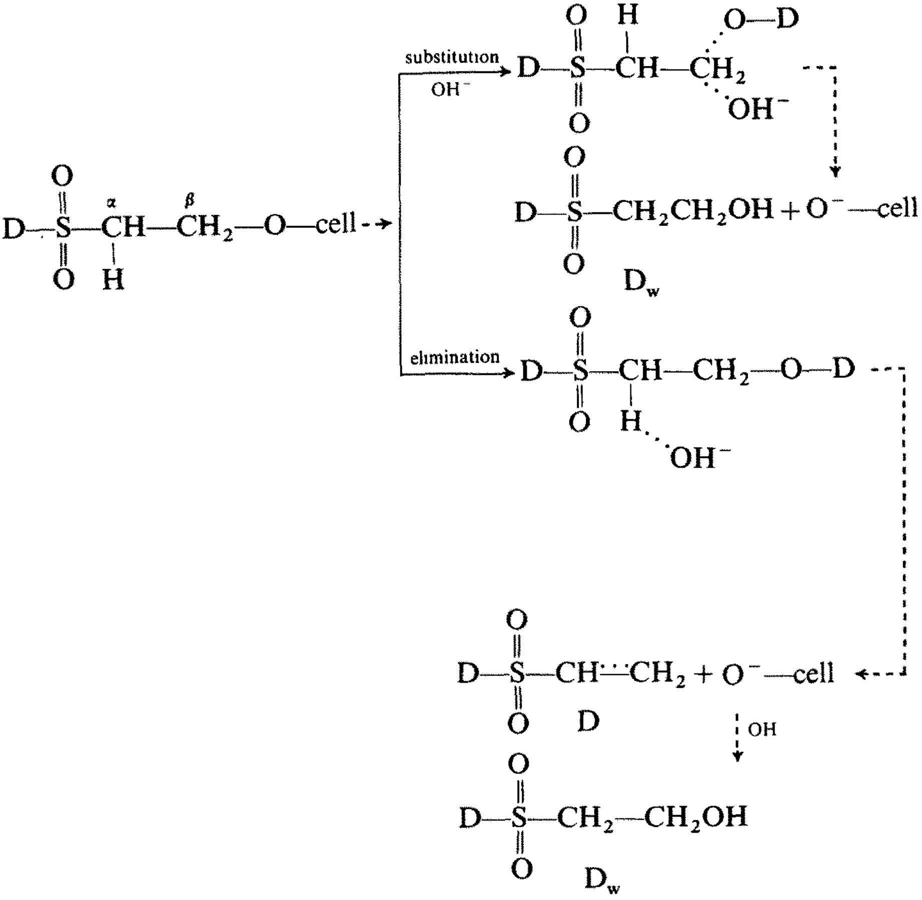
The rates of alkaline hydrolysis of the reaction products from a vinyl sulfone dye and methyl-α-D-glucoside (D_6 and D_4) have been measured kinetically. It was found that D_6 is hydrolysed 2·134 times faster than D_4. The mechanism of the hydrolysis of the dye–glucosides D_6 and D_4 is shown to involve predominately elimination in the first stage of the reaction.

1 INTRODUCTION

The hydrolysis behavior of dyed cellulose fiber and model dye–fiber compounds has been studied.[1,2] Much information, such as the rates of the alkaline hydrolysis of dyed fiber, dye–fiber compounds and the hydrolytic stabilities of *n*- and iso-propyl ethers of some vinyl sulfone reactive dyes, has been obtained,[1,2] but the rate and mechanism of the hydrolysis of the dyed fiber are still not fully resolved. The crux of the matter is that two different kinds of dye–fiber compound are formed from the primary and secondary hydroxy groups in the cyclic glucosidic unit. The properties of *n*- and iso-propyl ethers of some vinyl sulfone dyes did not approximate to D_6 and D_4 directly. In the latter case not only are the electronic effects of the primary and secondary alkyl groups different but the steric environments of 6—CH_2—OD and 4—CH—OD are also dissimilar. Furthermore, the

Dyes and Pigments 0143-7208/91/$03·50

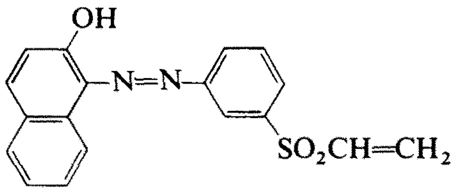
hydrolysis of the dyed fiber may proceed through different mechanisms, viz. the OH^- may attach to the β-carbon atom either by direct substitution or by elimination. The steric environments at the α- or β-carbon atoms in D_6 and D_4 are quite different.



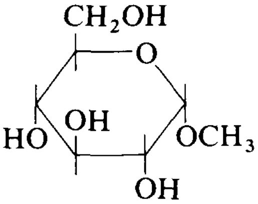
In this paper the rate of the alkaline hydrolysis of D_6 and D_4 are measured kinetically, and the mechanism of the hydrolysis of D_6 and D_4 is elucidated by TLC–double scanning plots.

The abbreviations D_6, D_4, D_w, D and MOH are represented by the following structures:

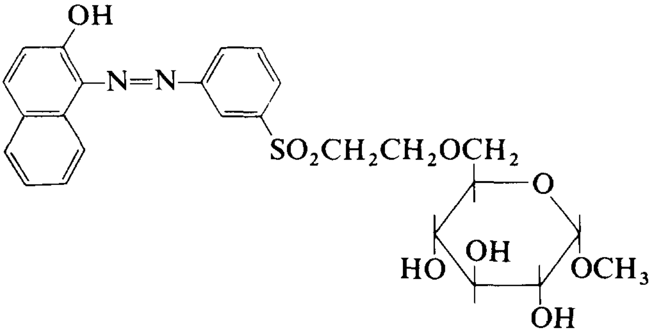
D:



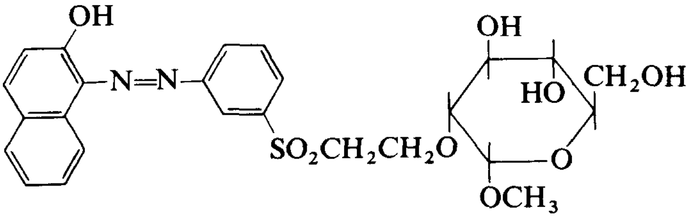
MOH:



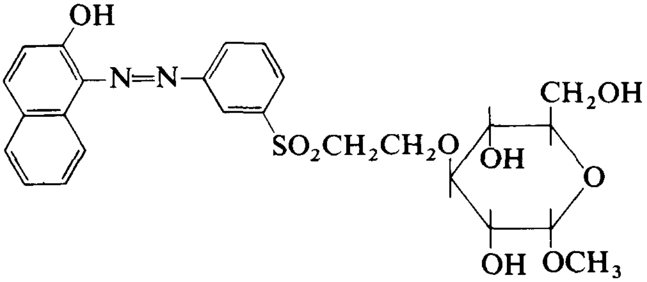
D_6:



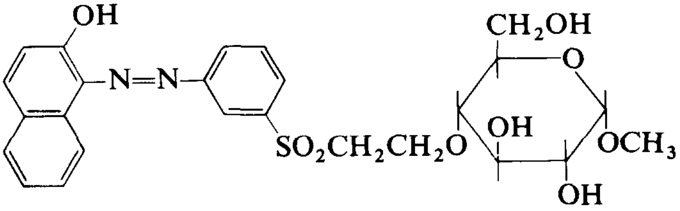
D_2:



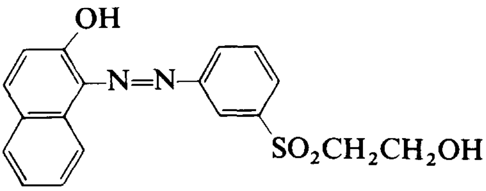
D_3:



D_4:



D_w:



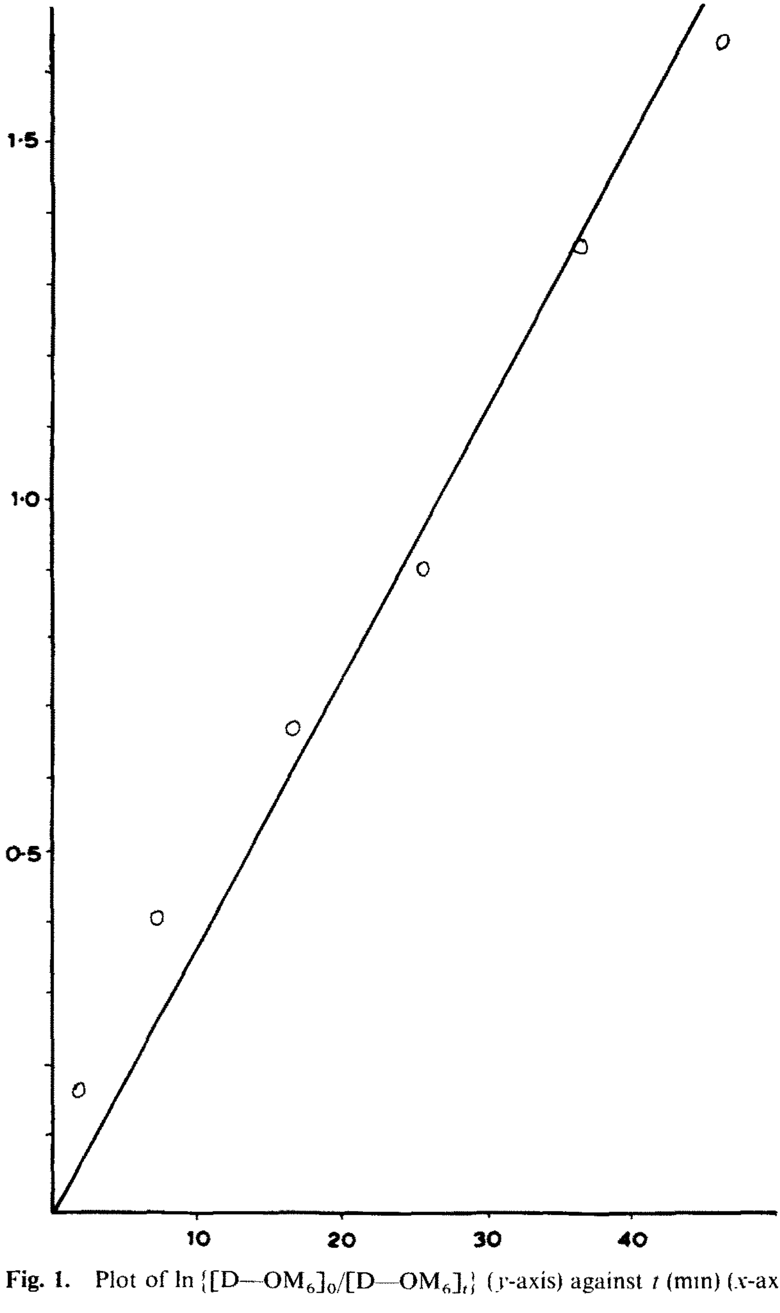


Fig. 1. Plot of $\ln\{[D\text{—}OM_6]_0/[D\text{—}OM_6]_t\}$ (y-axis) against t (min) (x-axis).

2 DETERMINATION OF THE SPECIFIC RATE CONSTANTS OF THE HYDROLYSIS OF THE VINYL SULFONE DYE–GLUCOSIDES D_6 AND D_4

D_6 (0·01 g, $1{\cdot}876 \times 10^{-5}$ mol) was dissolved in dioxan (5 ml) and water (2·5 ml). The solution was placed in a thermostat bath and stirred, while maintaining the temperature at 50 ± 1°C for 1 h and adding 10% NaOH solution (0·03 ml). Aliquots were removed at intervals, immediately cooled and dilute HCl acid was added to give a pH of 5 to 6. A microinjector was used to inject 1 ml 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, D_w and D. The peak areas of D_w, D and D_6 were measured quantitatively by TLC–double scanning, and the standard curves of D_6, D_w and D are illustrated in Part I of this investigation.[3] The concentrations of D_6, D_w and D after various times of hydrolysis are given in Table 1.

On plotting ln $\{[D—OM_6]_0/[D—OM_6]_t\}$ against time t a straight line was obtained (Fig. 1). The regression equation and regression coefficients were $y = 0{\cdot}031\,65x + 0{\cdot}13304$, $\gamma = 0{\cdot}9755$ and $k_6 = 0{\cdot}031\,65$.

The hydrolysis of D_4 was similarly effected. The plot of ln $\{[D—OM_4]_0/[D—MO_4]_t\}$ against time (t) is shown in Fig. 2. The regression equation and regression coefficients were found to be $y = 0{\cdot}014\,83x - 0{\cdot}118\,096$, $\gamma = 0{\cdot}921\,6$ and $k_4 = 0{\cdot}014\,83$.

When the kinetic data of the hydrolysis (k_6 and k_4) are compared, it is evident that D_6 is more easily hydrolyzed in alkaline medium than is D_4. The rate of hydrolysis of D_6 is 2·134 times that of D_4. It is interesting to compare

TABLE 1

Peak Areas A_6, A_w and A_D Formed During Hydrolysis

Time (*min*)	A_6	A_w	A_D	$\frac{[D-OM_6]_0}{[D-OM_6]_t}$[a]	$\ln\frac{[D-OM_6]_0}{[D-OM_6]_t}$
0	12 637·90	—	—	—	—
1	11 311·63	240·781	2 510·344	1·117 3	0·110 9
2	10 585·18	340·074	2 568·148	1·187 9	0·172 2
7	7 418·10	731·214	2 938·180	1·703 7	0·532 8
17	6 379·89	3 246·969	4 982·22	1·981 0	0·683 6
27	5 951·862	4 258·51	5 372·15	2·123 4	0·753 0
37	3 181·461	3 819·188	1 690·164	3·972 5	1·379 4
47	2 385	3 024	1 023	5·297	1·667

[a] M represents methyl-α-D-glucoside.

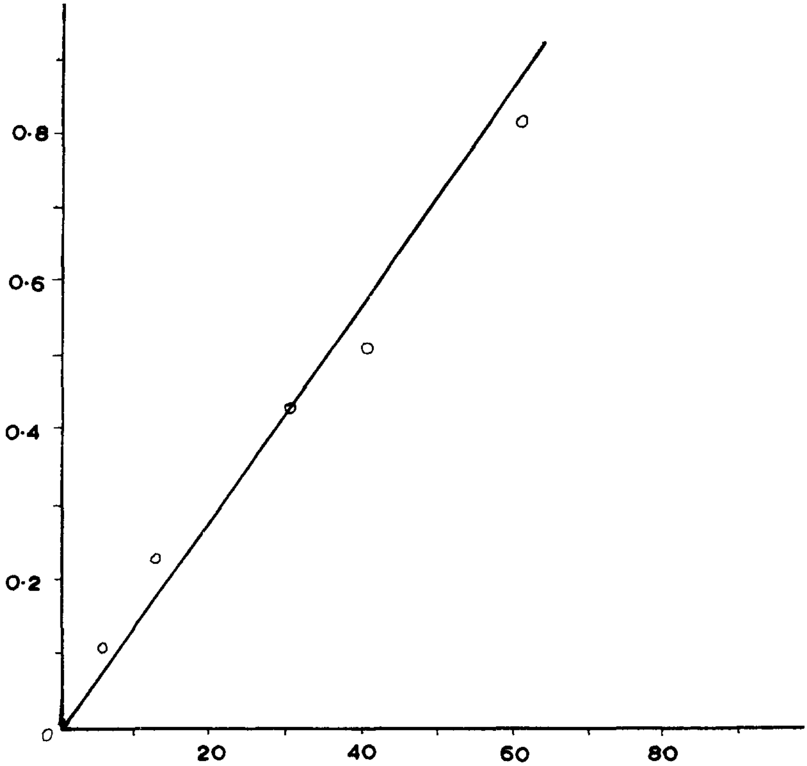


Fig. 2. Plot of $\ln\{[D—OM_4]_0/[D—OM_4]_t\}$ (y-axis) against t(min) (x-axis).

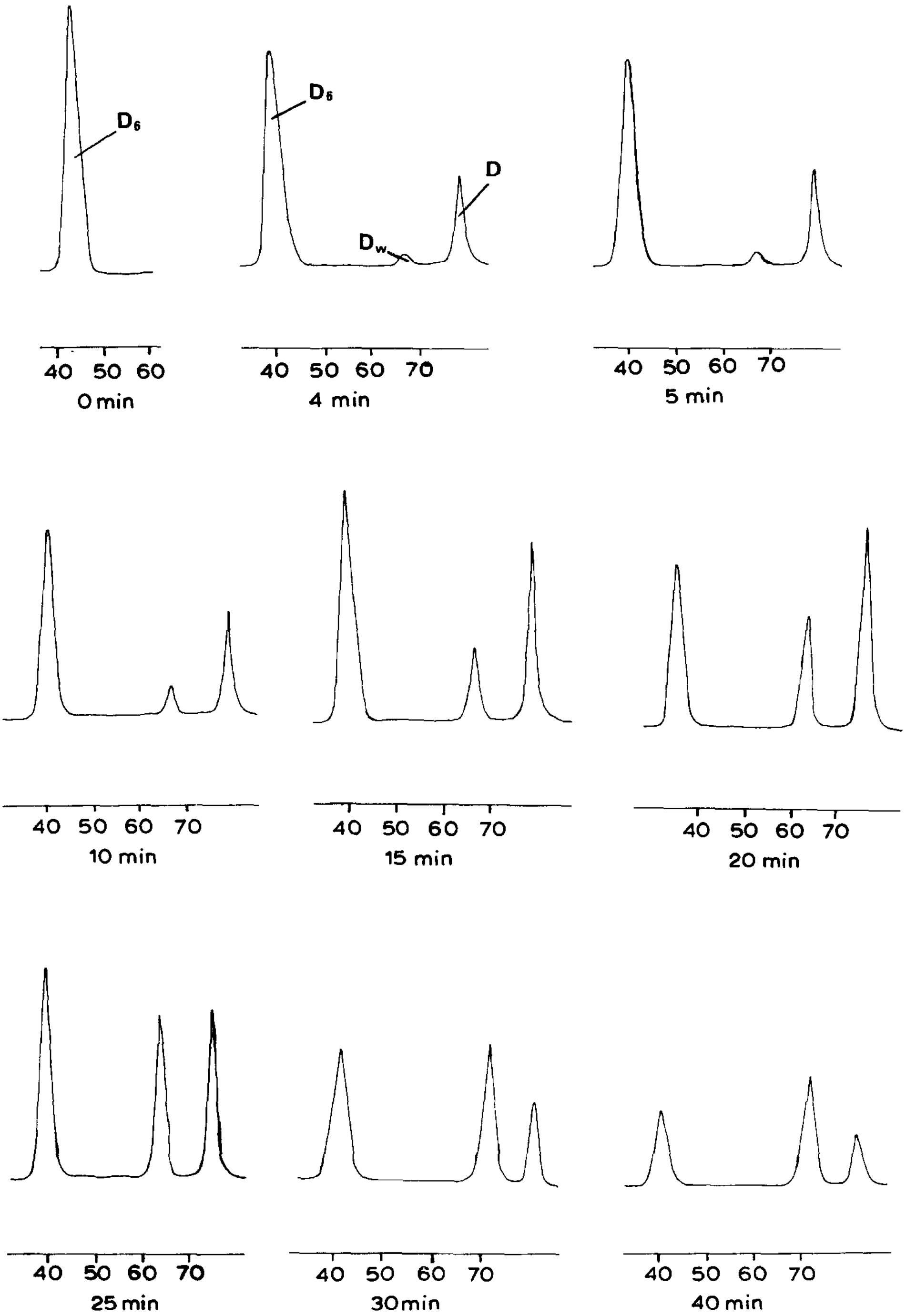
the results obtained from the hydrolytic stabilities of *n*- and iso-propyl ethers of some vinyl sulfone reactive dyes. In this present case it is evident that the steric environment of the C_6 carbon atom makes the attack of OH^- easier (when C_6 and C_4 are compared).

3 MECHANISM OF HYDROLYSIS OF VINYL SULFONE DYE–GLUCOSIDES D_6 AND D_4

The mechanism of the hydrolysis of the vinyl sulfone dye–glucosides was studied by TLC–double scanning.

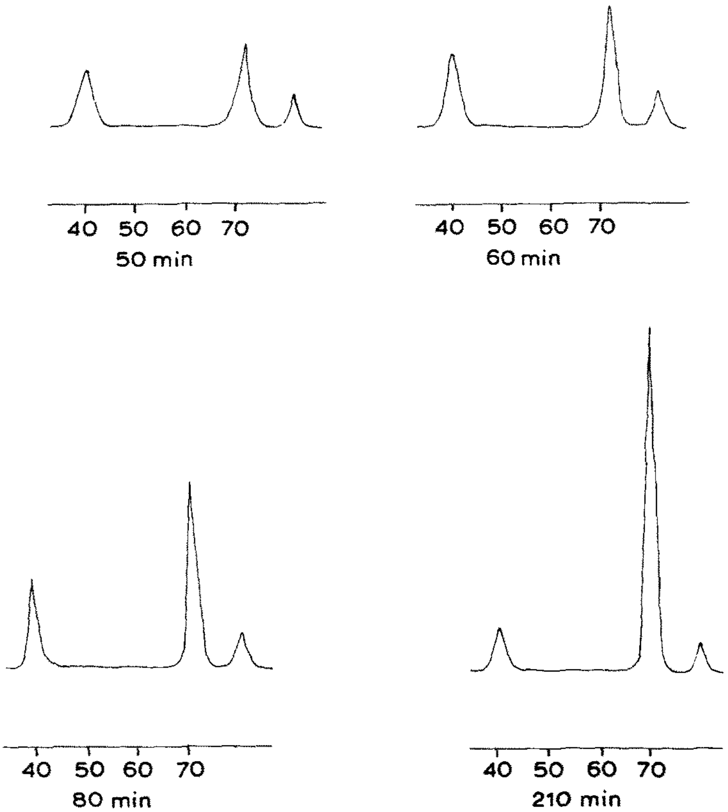
The scanning diagrams of D_6 during the hydrolysis are shown in Fig. 3.

From the scanning diagram of D_6 during alkaline hydrolysis it is evident that, in the initial stages of the hydrolysis, the hydrolytic product D, i.e. the vinyl sulfone dye, is in the larger amount and the hydrolyzed dye D_w is present only in a minor amount. In the later stages of the hydrolysis the



(*contd*)

Fig. 3. The hydrolysis of D_6 plots by TLC–double scanning at 50 ± 1°C.



50 min

60 min

80 min

210 min

Fig. 3—*contd.*

amount of hydrolyzed dye D_w gradually increases and the amount of the primary hydrolysis product, the vinyl sulfone dye D, gradually decreases. The scanning diagram of D_4 during alkaline hydrolysis shows a similar pattern (Fig. 4).

These results indicate that the course of the hydrolysis of the vinyl sulfone dye–glucosides is predominately via an elimination route.

4 CONCLUSION

The rates of hydrolysis of D_6 and D_4 in alkaline medium have been kinetically studied and compared. The results show that D_6 is more readily hydrolyzed than D_4.

The mechanism of the hydrolysis of the vinyl sulfone dye–glucosides may be by direct substitution or by elimination, but the latter mechanism is predominant in the initial stages of the hydrolysis.

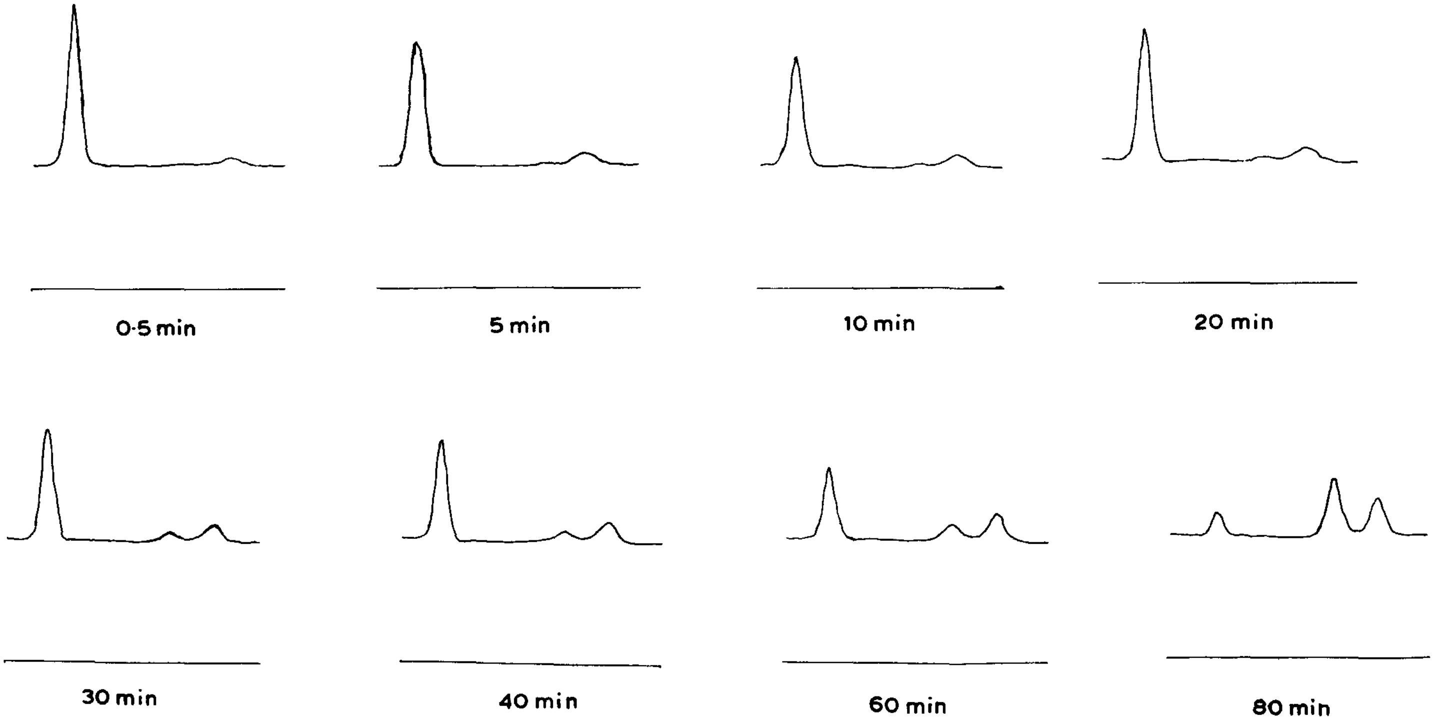


Fig. 4. The hydrolysis of D_4 plots by TLC–double scanning at 50 ± 1 C.

REFERENCES

1. Jiang Wen, Zhu Zheng-Hua & Chen Kong-Chang, *Dyes and Pigments*, **10** (1989) 217–237.
2. Zhu Zheng-Hua, Chen Kong-Chang & Yu Rong-Gen, *Dyes and Pigments*, **14** (1990) 129.
3. Zhu Zheng-Hua, Xia Jian-Mei & Chen Kong-Chang, *Dyes and Pigments*, **17** (1991) 171–191.