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Kinetic Study of Reaction of Vinylsulfonyl Aniline and Dichlorotriazinyl Group

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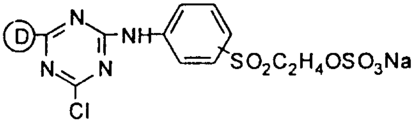
ABSTRACT

Two model bifunctional reactive dyes containing a vinylsufonyl group and a monochlorotriazinyl group were synthesized. The reactions between two kinds of vinylsulfonyl aniline and model dye in DMF have been studied and the rate constants of the reactions determined by the thin layer chromatograph (TLC) scanning method. It was found that the rate constant of the reaction of m-vinyl sulfonyl aniline with model dye was faster than that of p-vinyl sulfonyl aniline. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Since bifunctional reactive dyes containing a vinylsulfonyl group and a monochlorotriazinyl group initially reported in the 1980s, these dyes have developed rapidly and have recently become one of the most important types of reactive dyes. The general formula of such dyes is:



where D represents general chromophore group containing amino group.

The kinetic study of the hydrolysis of two reactive groups and reaction of the reactive groups with model cellulose has been extensively investigated by

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us [1–5], but kinetic study of syntheses of such dyes, especially the condensation reaction between the dichlorotriazinyl moiety and vinylsulfonyl aniline, which is a key aspect of the dye manufacture has not yet been evaluated. In this paper, the rate constant of the reaction of vinylsulfonyl aniline with the second chlorogroup of the dichlorotriazinyl ring was measured using the thin layer chromatograph (TLC) scanning method. 4-Aminoazobenzene was used as the chromophoric system, and an insoluble vinyl sulfonyl compound as model dye. The absence of sulfonic acid groups renders the purification, separation and structure determination of the model bifunctional dyes more facile.

EXPERIMENTAL

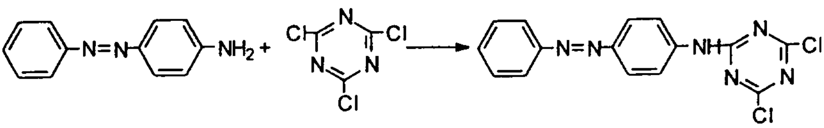
Mass spectra were measured on an HP 5989A spectrometer. ^{1}H NMR spectra were obtained on a Bruker AM300 spectrometer. Elemental analyses were performed using an EA-1106 instrument. TLC scanning was measured using the Shimadzu CS-930 double scanner.

Preparation of intermediates and model bifunctional reactive dyes

Syntheses of intermediates

m-Vinylsulfonyl aniline and *p*-vinylsulfonyl aniline were prepared by the literature method [6]. The model dye was prepared *via* the routes shown in Scheme 1.

19.7 parts of *p*-aminoazobenzene were dissolved in acetone at 0–5°C and reacted with 20.3 parts of cyanuric chloride at pH 3–4 for 1 h [2]. The model dye thus obtained was purified by recrystallization with ether. m.p. 202–203°C, MS (EI): m/e 345, ^{1}HNMR(CDCl$_3$, TMS): δ 8.02–7.25 (m, 9H), 1.57 (s, 1H). Calcd.: C, 52.19; H, 2.92; N, 24.35; Found: C, 52.36, H, 2.84; N, 24.62.

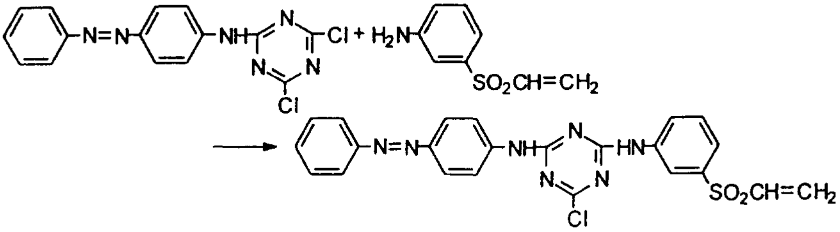


Scheme 1 Model dye.

Syntheses of model products

The structures of the model products are shown in Table 1.

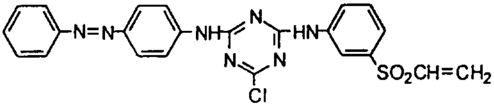
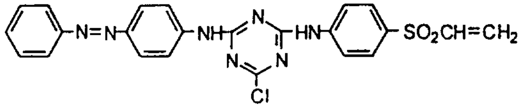
MP-1 were prepared via the route shown in Scheme 2.



MP-1

Scheme 2 MP-1.

TABLE 1
Structure of Model Products

Model product number	*Structure of model product*
MP-1	
MP-2	

After 8.6 parts of model dye and 5 parts of 3-vinyl sulfonyl aniline were dissolved in 1,4-dioxane, they were heated at 60°C for 1 h to give the crude model product MP-1 which was then purified by Al_2O_3 volume chromatography, using as developing solvents dichloroethane-ether (20:1 v/v). m.p. 104–106°C, MS (EI): m/e 492. ^{1}H NMR ($CDCl_3$, TMS): δ 7.98–7.49 (m, 13H), 6.65 (m, 1H), 6.49 (d, 1H), 6.07 (d, 1H), 2.70 (s,2H), Calcd.: C, 56.15; H, 3.66; N, 19.93; Found: C, 56.17; H, 3.72; N, 19.54.

MP-2 was prepared in an analogous manner m.p.184–185°C, MS(EI): m/e 492. ^{1}H NMR: δ 8.00–7.51 (m, 13 H), 6.66 (m, 1H), 6.47 (d, 1H), 6.04 (d, 1H), 1.64 (s, 2H). Calcd.: C, 56.15; H, 3.66; N, 19.93; Found: 56.40, H, 3.82; N, 19.77.

Kinetic study

Standard curve of model dye

A standard solution of model dye in acetone (1.08×10^{-2} mol l^{-1}) was prepared. Aliquot portions of this solution were further diluted to give a series of solutions of the model dye. The samples were applied to chromatographic plates, developed and scanned. The peak areas of the spots were obtained (see Table 2) and plots were made for the peak areas vs corresponding moles. The standard curve of the model dye is shown in Fig. 1.

The correlation coefficient was 0.998.

General derivation of rate equations

Because the reaction was carried out under an anhydrous condition, the reaction equation is

$$A + B \longrightarrow C + D$$

where A represents the model dye, B represents vinyl sulfonyl aniline, C represents the model product, and d represents HCl.

The rate equation is:

$$-\frac{\mathrm{d}[A]}{\mathrm{d}t} = k[A][B]$$

The result shows it is a two-order reaction, so the rate constant can be derived as below:

$$k = \frac{x}{t\mathrm{C}_0(\mathrm{C}_0 - x)} \tag{1}$$

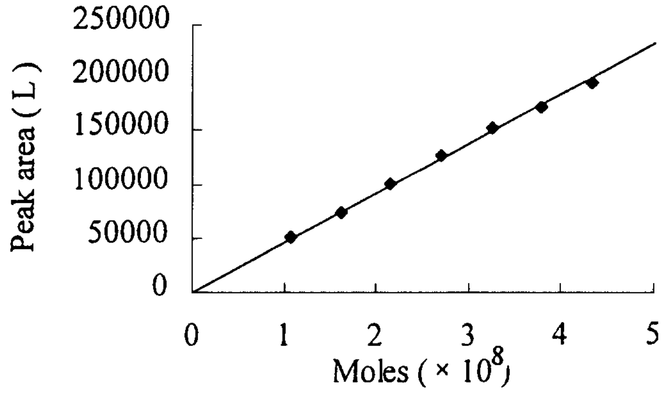


Fig. 1. Standard curve of model dye.

TABLE 2
Data of Standard Curve of Model Dye

Moles×10^8	*1.08*	*1.62*	*2.16*	*2.70*	*3.24*	*3.78*	*4.32*
Peak area	52143.16	74787.3	100405.3	128278.1	152823.1	170851.5	195286.3

Similar to what we have previously reported [6], the rate constant k is:

$$k = \frac{1}{tC_0} \cdot \frac{L_0 - L_t}{L_t} \tag{2}$$

L_0 and L_t represent the peak areas of A obtained by TLC scanning at reactive time 0 min and t min, respectively.

Determination of the quantitative change of model dye by TLC scanning
First 0.06904 g (0.2 mmol) of model dye in 1.0 ml of DMF was heated to a specific temperature, then 0.03665 g (0.2 mmol) of vinylsulfonyl aniline was added. Samples were removed at intervals and diluted with acetone. The volume of samples and acetone are showed in Table 3. Then 2 μl of samples were spotted onto a plate and separated. Two spots were present; the devoloping solvent used was dichloroethane-acetone (20:1 v/v). The R_f value of the components are also given in Table 3.

Reaction of m-vinylsulfonyl aniline with model dye. The data of the reaction rate at various temperatures are shown below (Tables 4, 5, 6).

On plotting 1/L of model dye against time (in min) at 40 ± 1°C, a straight line was obtained (Fig. 2).

The regression equation is $1/L = 0.0152\ t + 5.906$ and the correlation coefficient was 0.994 at 40 ± 1°C.

On plotting 1/L of model dye against time (in min) at 50 ± 1°C, a straight line was obtained (Fig. 3).

TABLE 3
R_f Value of Spot and Volume of Sample and Acetone

Model dye reacted with	*R_f of Spot 1*	*R_f of Spot 2*	*Sample volume (μl)*			*Acetone volume (ml)*		
			40°C	50°C	60°C	40°C	50°C	60°C
m-vinyl sulfonyl aniline	0.47	0.76	40	30	30	0.2	0.6	0.6
p-vinyl sulfonyl aniline	0.37	0.73	—*	40	40	—	0.3	0.4

*The reaction rate of *p*-vinylsulfonyul aniline with model dye at 40°C was too slow to determine the quantitative change of model dye by this method.

TABLE 4
Data of the Reaction Rate of *m*-Vinylsulfonyl Aniline with Model Dye at 40°C

Time (min)	*2*	*10*	*30*	*40*	*55*	*70*	*85*
Peak area (L)	168918.9	164552.1	157626.3	151736.1	149412.3	144743.5	137991.9
1/L ($\times 10^6$)	5.920	6.077	6.344	6.590	6.693	6.909	7.247

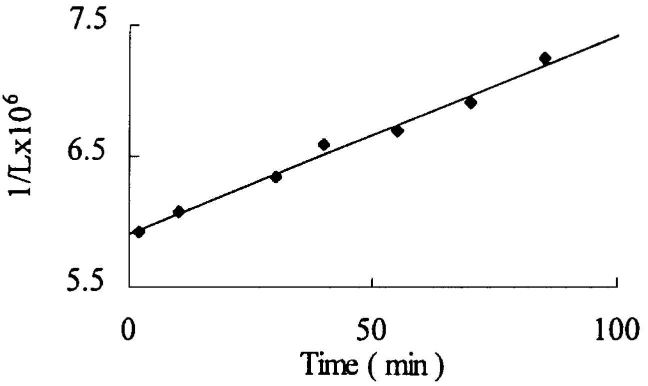


Fig. 2. Reaction rate curve of *m*-vinyl sulfonyl aniline and model dye at 40°C.

TABLE 5
Data of the Reaction Rate of *m*-Vinylsulfonyl Aniline and Model Dye at 50°C

Time (min)	*6*	*16*	*26*	*46*	*66*	*76*
Peak area (L)	109105.9	103505.7	96265.3	79845.8	74204.5	70404.3
$1/L(\times 10^6)$	9.165	9.661	10.388	12.5 24	13.476	14.200

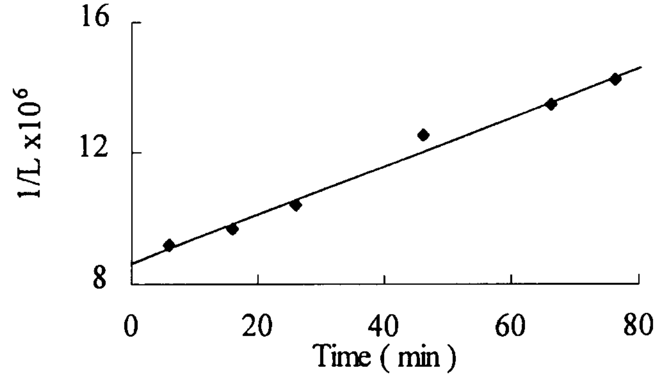


Fig. 3. Reaction rate curve of *m*-vinyl sulfonyl aniline and model dye at 50°C.

The regression equation is $1/L = 0.0748\ t + 8.628$ and the correlation coefficient was 0.993 at 50 ± 1°C (Table 6).

On plotting 1/L of model dye against time (in min), a straight line was obtained (Fig. 4).

The regression equation is $1/L = 0.0815\ t + 4.967$ and the correlation coefficient was 0.997 at 60 ± 1°C.

Reaction of p-vinylsulfonyl aniline with model dye. The data of the reaction rate at various temperatures are shown below (Table 7, 8).

TABLE 6
Data of the Reaction Rate of *m*-Vinylsulfonyl Aniline and Model Dye at 60°C

Time (min)	*5*	*10*	*20*	*30*	*50*	*60*	*70*
Peak area (L)	178559.2	173130.8	154222.1	137467.9	112988.9	100730.4	92354.9
1/L ($\times 10^6$)	5.600	5.776	6.484	7.274	8.850	9.927	10.827

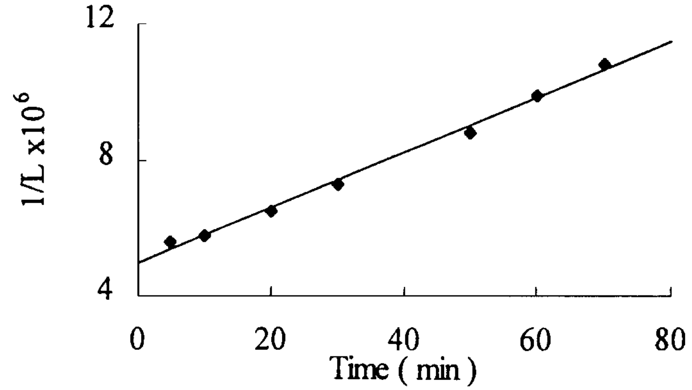


Fig. 4. Reaction rate curve of *m*-vinyl sulfonyl aniline and model dye at 60°C.

TABLE 7
Data of the Reaction Rate of *p*-Vinylsulfonyl Aniline and Model Dye at 50°C

Time (min)	*1*	*10*	*20*	*30*	*45*	*60*	*90*
Peak area (L)	464549.1	460735.7	446477.4	422003.1	407118.4	390043.0	3540 52.8
1/L($\times 10^6$)	2.153	2.170	2.240	2.369	2.456	2.564	2.824

On plotting 1/L of model dye against time (in min), a straight line was obtained (Fig. 5).

The regression equation is $1/L = 0.0077\ t + 2.113$ and the correlation coefficient was 0.997 at 50 ± 1°C.

On plotting 1/L of model dye against time (in min), a straight line was obtained (Fig. 6).

The regression equation is $1/L = 0.0096\ t + 1.749$ and the correlation coefficient was 0.993 at 60 ± 1°C.

RESULTS AND DISCUSSION

From the regression equation and (2), the final results for the rate constants of the reaction between vinyl sulfonyl anilines and the model dye are listed in Table 9.

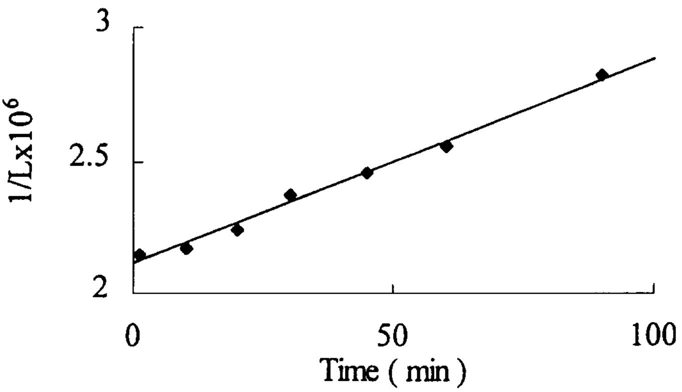


Fig. 5. Reaction rate curve of *p*-vinyl sulfonyl aniline and model dye at 50°C.

TABLE 8
Data of the Reaction Rate of *p*-Vinylsulfonyl Aniline and Model Dye at 60°C

Time (min)	*2*	*20*	*30*	*40*	*50*	*65*	*80*
Peak area (L)	559931.7	506268.4	501594.5	469917.6	455504.3	420405.8	392562.3
1/L ($\times 10^6$)	1.786	1.975	1.994	2.128	2.195	2.379	2.547

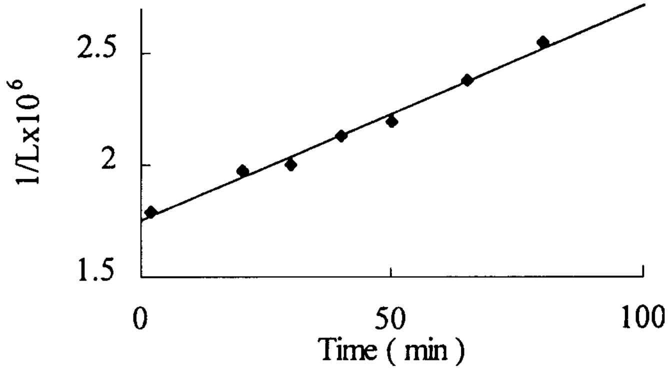


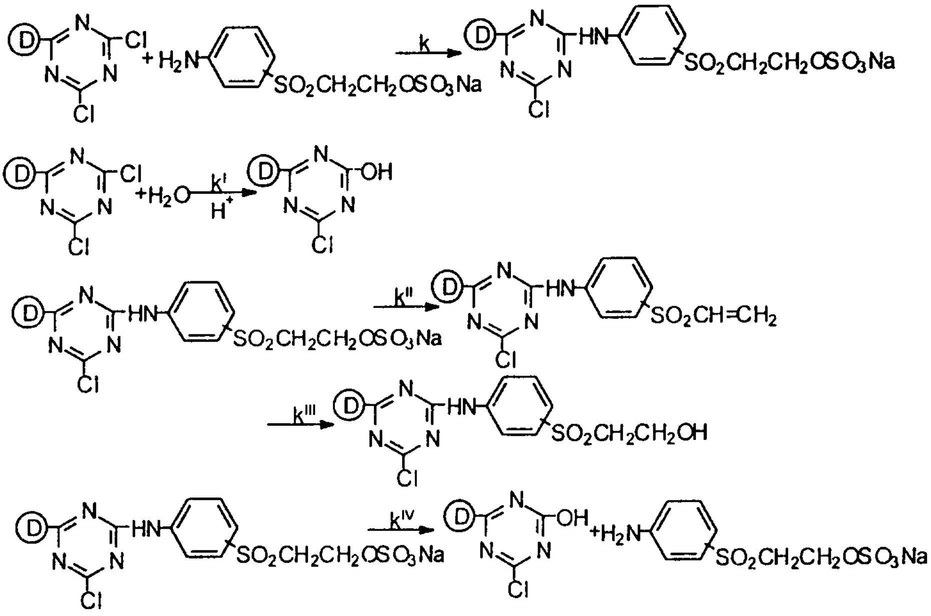
Fig. 6. Reaction rate curve of *p*-vinyl sulfonyl aniline and model dye at 60°C.

From Table 9, it is evident that rate constant of the reaction of *m*-vinyl sulfonyl aniline with the model dye is about 6 times faster than that of *p*-vinyl sulfonyl aniline with the model dye at 50°C and about 3 times faster at 60°C. The reason for this is the same as outlined in our previous report [6]. Owing to the practical procedure of syntheses of such dyes is in aqueous solution, there are several competitive reactions (as shown in Scheme 3). The k and $k^{\mathrm{I-IV}}$ values represent the rate constants of formation and hydrolysis of dye, respectively. Whether *m*- or *p*-vinylsulfonyl aniline is used, $k^{\mathrm{I-IV}}$ values

TABLE 9
Rate Constant of Reaction of Vinylsulfonyl Anilines with Model Dye

Rate constant of reaction	k_1*	k_2*
40°C	0.077 L mol^{-1} min^{-1}	—
50°C	0.910 L mol^{-1} min^{-1}	0.155 L mol^{-1} min^{-1}
60°C	1.723 L mol^{-1} min^{-1}	0.588 L mol^{-1} min^{-1}

* k_1 and k_2 represent the rate constants of reaction between model dye and *m*- and *p*-vinylsulfonyl aniline, respectively.



Scheme 3

are almost the same [2]. Thus the larger the value of *k* the greater is the quantity of product obtained.

This shows that in the condensation reaction, when *m*-vinylsulfonyl aniline is employed, a low temperature is needed, and less hydrolyzed dye is formed and the yield of dye can thus be higher.

CONCLUSIONS

The homogeneous reactions between a vinylsulfonyl aniline and the chloro subsistuent of the dichlorotriazinyl group of a model dye have been studied kinetically by the TLC scanning method. The standard curve of the reaction was determined. Changes of concentrations of reactants could then be determined, and the rate of the above reactions were measured at various temperatures. The results show that the rate constant of the reaction of *m*-vinyl sulfonyl aniline with the model dye was about 6 times faster than that of *p*-vinylsulfonyl aniline with model dye at 50°C, and about 3 times faster at 60°C.

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