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Kinetic Study of the Synthesis of Some Model Bifunctional Reactive Dyes

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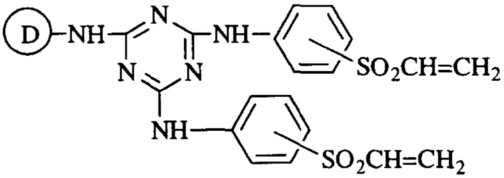
ABSTRACT

Two model reactive dyes containing two vinyl sulfonyl groups were synthesized. The reactions between two vinylsulfonylanilines and a model dye have been studied in DMF at 90 ± 1°C respectively and the rate constants of the reactions were determined by the Thin Layer Chromatograph scanning method. It was found that the rate constant of the reaction of 3-vinylsulfonylaniline and the model dye was 25 times faster than that of 4-vinylsulfonylaniline. © 1997 Elsevier Science Ltd

Keywords: Kinetics study, synthesis, model dyes, bifunctional reactive dyes.

INTRODUCTION

Bifunctional reactive dyes containing a vinylsulfonyl group and a monochlorotriazine group are widely used, and it is known that the two reactive groups have different reactivity [1]. The rate constant of hydrolysis of the vinylsulfonyl group is 2.5 to 3.0 times greater than that of the chloro substituent in the monochorotriazine residue [2]. It is thus difficult to obtain a high fixation yield, because in the dyebath at a given temperature the two different reactive groups cannot react with cellulose at the same time. We have now synthesized some new reactive dyes, (1) containing two vinyl sulfonyl groups in order to evaluate their potential for increased fixation yield.



The synthetic route to dyes containing a monochlorotriazine and a vinyl sulfonyl group is well known. In this paper, we measure the rate constant of the reaction of vinylsulfonylanilines and the chloro substituent on the triazine ring in order to ascertain a method for preparing this kind of dye. We used 4-aminoazobenzene as the chromophore group (D in formula I) and an insoluble vinyl sulfonyl compound as a model dye. The absence of a sulfonic acid group enables the isolation, purification and characterisation of the vinylsulfonyl dye and its reaction products to be effected more easily.

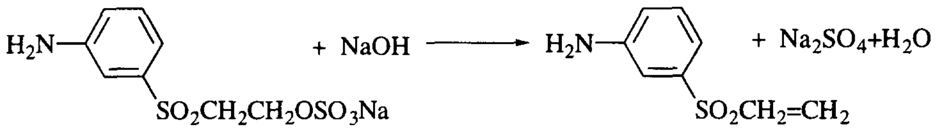
EXPERIMENTAL

Preparation of intermediates and of model bifunctional reactive dyes

Synthesis and purification of 3-vinylsulfonylaniline and 4-vinylsulfonylaniline
3-vinylsulfonylaniline was prepared according to Scheme 1.

3–(β-sulfatoethylsulfonyl) aniline(commercial product) was dissolved in water by 20% aq. sodium carbonate, and then 10% aq. NaOH was added at 0°C–5°C. The resulting white deposit was filtered off and was recrystallized from ether to give 3-vinylsulfonylaniline. 4-vinylsulfonylaniline was obtained by similar way.

Relevant analytical data are given in Table 1.



Scheme 1

TABLE 1
Analysis Data of Model Compounds

Compound	*m.p.* (°C)*	*Element Analysis (%)*						*MS*
		Calcd			*Found*			
		C	*H*	*N*	*C*	*H*	*N*	*m/e*
3-vinylsulfonylaniline	51–52	52.44	4.96	7.65	52.30	4.96	7.59	183
4-vinylsulfonylaniline	74–75	52.44	4.96	7.65	52.43	4.94	7.63	183
model dye 1	104–106	56.15	3.66	19.93	56.17	3.72	19.54	492

* m.p. is not uncorrected.

Synthesis and purification of Model Dye 1

Model dye 1 was prepared according to Scheme 2.

3-vinylsulfonylaniline was dissolved in acetone at 0–5°C and reacted with cyanuric chloride for 1 h at pH 3–4 [2]. The reaction temperature was then raised to 30–35°C and the initial condensation product further reacted with 4-aminoazobenzene. The model dye 1 thus obtained was purified by volume chromatography and recrystallized to give the pure dye 1, analytical data of which are also shown in Table 1.

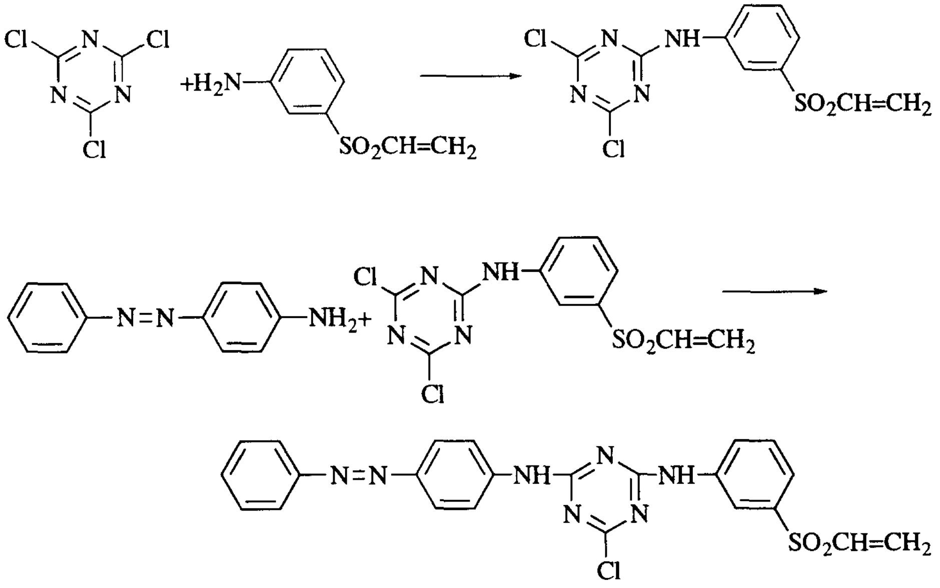
^{1}H NMR(TMS,$CDCl_3$) of above are as follows: 3-vinylsulofonylaniline δ7.33–7.15(m,3H), δ6.88(m,1H), δ6.63(m,1H), δ6.42(d,1H,J = 16.54Hz), δ6.01(d,1H,9.71Hz) δ2.97(m,2H).

4-vinylsulfonylaniline δ7.65–7.62(m,2H), δ6.71–6.68(m,2H), δ6.62(m,1H), δ6.32(d,1H,J = 16.64Hz), δ5.90(d,1H,9.8Hz), δ3.27(m,2H). Model dye 1 δ7.98–7.49(m,13H), δ6.65(m,1H), δ6.49(m,1H), δ6.07(m,1H), δ2.70(s,2H).

Synthesis and purification of model products

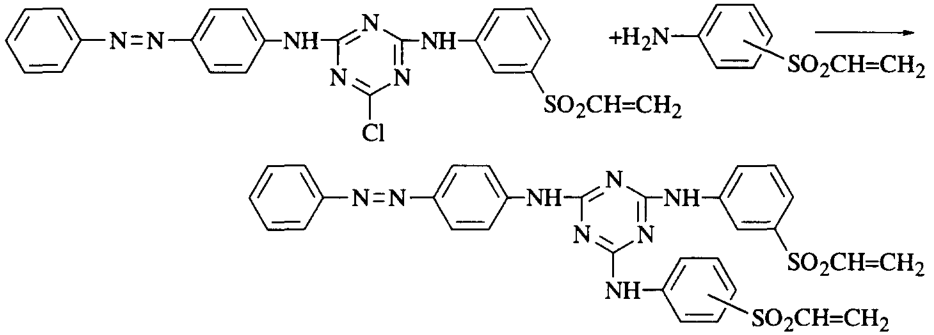
Model products were prepared according to Scheme 3.

Model dye 1 and 3-vinylsulfonylaniline were dissolved in 1,4-dioxane and refluxed for 1 hour to give the crude model product 1(MP–1). The product was purified by volume chromatography.



Model dye 1

Scheme 2



Scheme 3

Model product 2 (MP–2)was obtained by a similar way.

Analytical data for these products are shown in Table 2.

^{1}H NMR(TMS, $CDCl_3$) of model products:

MP-1

δ7.93–7.48(m, 17H), δ6.68(m, 2H), δ6.48(m,2H), δ6.08(d,2H, J = 9.67Hz), δ1.87(s, 3H).

MP-2

δ7.96–7.48(m, 17H), δ6.72–6.64(m, 2H), δ6.52–6.43(m, 2H), δ6.11–6.02(m, 2H), δ1.80(s, 3H).

Kinetic Study

Standard Curve of Model Dye 1 [3]

A standard solution of the dye in acetone at a concentration of 5.5×10^{-4} g/ml was prepared. Aliquot portions of this solution were further diluted to give a series of solutions. The samples were applied to chromatographic plates, developed and scanned. The peak areas of the spots were obtained

TABLE 2
Analysis Data of Model Products

Model product	*MW*	*m.p.* (°C)*	*Element Analysis*					
			Calcd			*Found*		
			C	*H*	*N*	*C*	*H*	*N*
MP-1	638.72	120–122	58.29	4.10	17.55	57.84	4.15	17.10
MP-2	638.72	135–137	58.29	4.10	17.55	57.80	4.19	17.21

*m.p. is uncorrected.

and plots were made for the peak areas *versus* corresponding moles. Standard curve data for model dye 1 is shown in Fig. 1 and Table 3.

The correlation coefficient $\gamma = 0.996$.

General derivation of rate equations

Because the reaction occurs in an anhydrous medium, the reaction equation is given by:

$$A + B \rightarrow C + D$$

in which A is the model dye 1; B is the vinylsulfonylaniline; C is the model product, and D is HCI.

The rate equation is:

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

This shows it is a second order reaction, so eqn (1). can be derived.

$$k = \frac{x}{tC_0(C_0 - x)} \tag{1}$$

From [4], because L and C show a linear relationship, eqn (2) can be obtained.

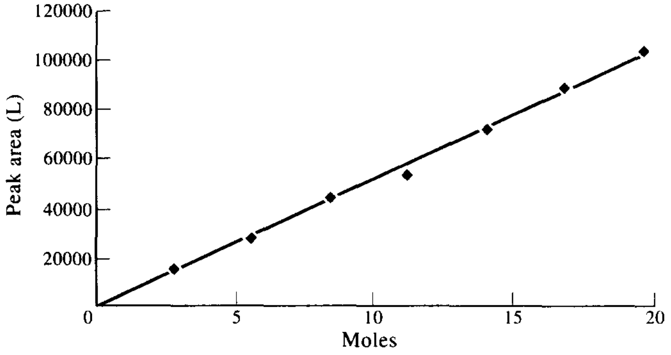


Fig. 1. Standard curve of model dye 1.

TABLE 3
Data of Standard Curve

moles×10^7	*2.80*	*5.60*	*8.39*	*11.20*	*14.00*	*16.80*	*19.60*
Peak Area	15592.3	28200.9	44790.3	53520.0	71751.9	89424.3	103413.9

$$\frac{C_0}{C_t} = \frac{L_\infty - L_0}{L_\infty - L_t} \tag{2}$$

in which L_0, L_t and L_∞ are the peak areas of A at time 0 min, t min and ∞. From eqn (2), eqn (3) can readily be derived.

$$\frac{x}{C_0 - x} = \frac{x}{C_0} - \frac{C_0}{C_0 - x} = \frac{L_0 - L_t}{L_t - L_\infty} \therefore k = \frac{1}{tC_0} \cdot \frac{L_0 - L_t}{L_t - L_\infty} \tag{3}$$

If L_∞ can be thought of as 0, so rate constant k is then given by eqn (4)

$$k = \frac{l}{tC_0} \cdot \frac{L_0 - L_t}{L_t} \tag{4}$$

Determination of the quantitative change of model dye 1 by TLC-double scanning

Reaction of 3-viylsulfonylaniline and model dye 1

0.07380 g (1.5×10^{-4}mol) of the dye in 2.0 ml DMF was heated at 90 ± 1°C and 0.02750 g (1.5×10^{-4}mol) 3-vinylsulfonylaniline was then added. Samples (0.06 ml) were removed at intervals and diluted with 0.5 ml acetone. The samples were then applied to chromatographic plates, developed and scanned.

TABLE 4
Data for the Reaction Rate

Time (min)	*2*	*21*	*40*	*50*	*60*	*80*
Peak Area(L)	262412.3	213177.1	161524.1	160581.6	136230.6	109328.9
$1/L \times 10^6$	3.81	4.69	6.19	6.22	7.34	9.15

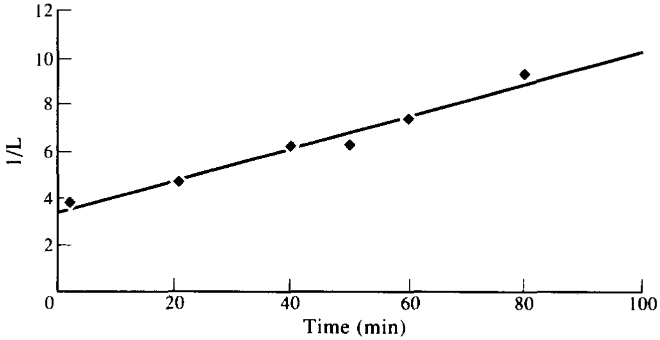


Fig. 2. A plot of 1/L versus time at 90 ± 1°C.

The experimental data thus obtained for the reaction rate are shown in Table 4.

On plotting 1/L of model dye 1 against time (in minutes) at 90 ± 1°C, a straight line was obtained. (Fig. 2).

The regression equation and correlation coefficient at 90 ± 1°C are $1/L = 0.0671t + 3.405$ and $\gamma = 0.985$ respectively.

Reaction of 4-vinylsulfonylaniline and model dye 1

Data for this reaction were obtained similarly and shown in Table 5.

On plotting 1/L against time t (in minutes) at 90 ± 1°C, a straight line was obtained. (Fig. 3).

The regression equation and correlation coefficient at 90 ± 1°C are $1/L = 0.003177t + 3.040467$ and $\gamma = 0.959$ respectively.

Results and discussion.

From the regression equation and eqn (4) the final results for the rate constants of the reaction between the vinylsulfonylanilines and the model dye are listed in Table 6.

From Table 6 the rate constant of the reaction of 3-vinylsulfonylaniline with the model dye is 25 times faster than that of 4-vinylsulfonylaniline. The reason for this is that when the vinylsulfonyl group is linked at the p-position

TABLE 5

Experiment Data of the Reaction Between 4-vinylsulphonylaniline and Model Dye 1

Time (min)	*2*	*10*	*40*	*60*	*80*	*120*
Peak Area (L)	325390.8	324782.6	321986.2	311646.8	298028.4	293109.2
$1/L \times 10^6$	3.073	3.079	3.106	3.209	3.355	3.412

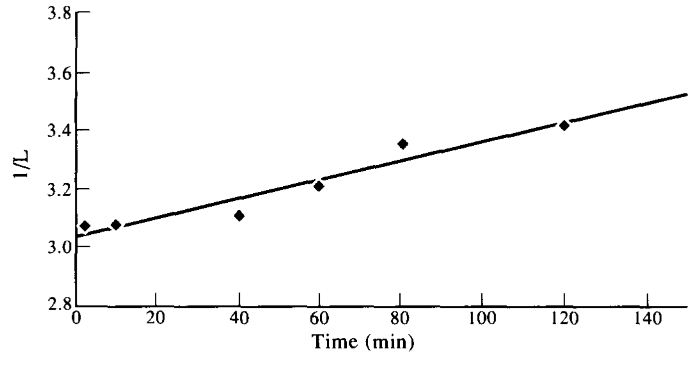


Fig. 3. A plot of 1/L versus time at 90 ± 1°C.

to the amino group the electrophilic character of the amino group is reduced because of the conjugation effect; in the case of 3-vinylsulfonylaniline this effect is very significantly decreased due to non-conjugation factors.

TABLE 6

Rate constant of Reaction of Model Dye 1 and Vinylsulfonylanilines

Rate constant of reaction	k_1	k_2
Value	2.4625 L mol^{-1} min^{-1}	0.09757 L mol^{-1} min^{-1}

k_1 and k_2 mean the rate constants of reaction between model dye 1 and 3- and 4- vinylsulfonylaniline at 90 ± 1°C respectively.

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