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Studies on New Reactive Dyes Having Two Vinyl Sulfone Groups. Part II: Kinetic Studies of the Condensation Reaction between C.I. Reactive Red 120 and *m*- and *p*-(β-Sulfatoethyl-Sulfonyl)Aniline

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ABSTRACT

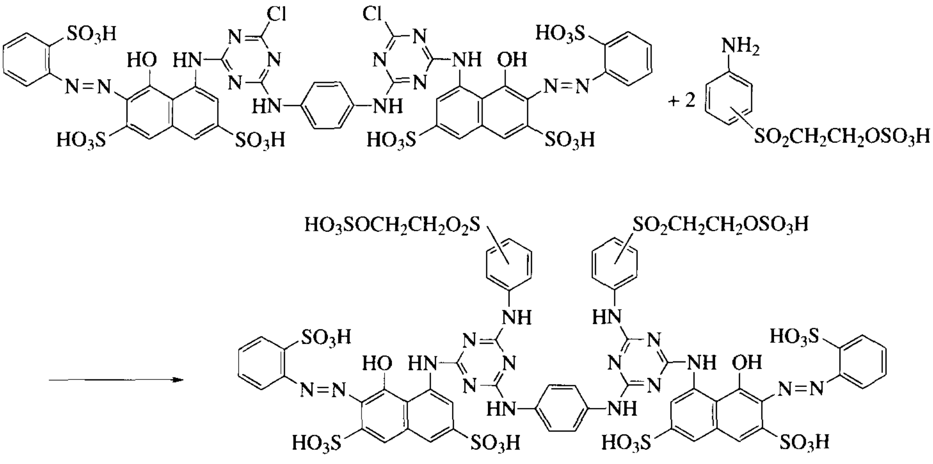
The condensation reaction between C.I. Reactive Red 120 and m- *and* p-*(*β*-sulfatoethyl-sulfonyl)aniline has been studied using the TLC-double scanning method. The condensation reaction follows a consecutive reaction route, and the rates of the first-step reaction (*k_1*) are about twice as fast as those of the second-step reaction (*k_2*). The rate constants of the two step reaction (*k_1 *and* k_2*) vary with reaction temperature and pH. The rate constants of the condensation reaction between* m-*(*β*-sulfatoethyl-sulfonyl) aniline and C.I. Reactive Red 120 are about 10 times greater than for* p-*(*β*-sulfatoethyl-sulfonyl)aniline. © 1998 Elsevier Science Ltd*

Keywords: reactive dye, kinetic study, condensation reaction, vinyl sulfone, C.I. Reactive Red 120, rate constant, TLC-double scanning, consecutive reaction.

INTRODUCTION

Reactive dyes having two vinylsulfone-type fiber-reactive groups possess outstanding dyeing properties. They can be synthesized by condensing C.I. Reactive Red 120 with β-sulfatoethyl-sulfonyl-aniline. Kinetic studies of the synthesis process involving condensation of vinylsulfonyl-aniline with the residue chlorine of the triazine ring have shown that the rate constant of the reaction between *m*-vinylsulfonyl-aniline and the third chlorine of the triazine ring is about 25 times greater than that of *p*-vinylsulfonyl-aniline [1]. This result was obtained by using model dyes and a model vinylsulfonyl-aniline without a sulfonic acid group. However, introduction of a sulfonic acid group also greatly changes the reaction parameters. In this present paper, kinetic studies of the condensation reaction of C.I. Reactive Red 120 and *m*- and *p*-(*β*-sulftoethyl-sulfonyl)aniline were carried out using the TLC-double scanning method in order to illustrate details of the reaction pathway.

The condensation reaction of C.I. Reactive Red 120 and *m*- and *p*-(*β*-sulfatoethyl-sulfonyl)aniline may be represented in Scheme 1:



Scheme 1

In general, the condensation reaction may be expressed as follows:

$$A + 2B \rightarrow D$$

This is a ter-molecular reaction, usually taking place by two consecutive bimolecular reactions following one another, i.e.

$$A + B \rightarrow C \tag{1}$$

$$C + B \rightarrow D \tag{2}$$

where C denotes the intermediate formed from A and B. Once C is formed, C reacts further with another molecule B to yield the final product D.

The kinetic equations are:

$$\frac{dC_A}{dt} = -k_1' C_A C_B \tag{3}$$

$$\frac{dC_C}{dt} = k'_1 C_A C_B - k'_2 C_C C_B \tag{4}$$

If we allow the reactant B to be more excessive than reactant A, the kinetic equation then becomes:

$$\frac{dC_A}{dt} = -k_1 C_A \tag{5}$$

$$\frac{dC_C}{dt} = k_1 C_A - k_2 C_C \tag{6}$$

Equation (5) gives:

$$\ln \frac{C_{A0}}{C_A} = k_1 t \tag{7a}$$

$$C_A = C_{A0e-k_1 t} \tag{7b}$$

where C_A is the concentration of A at time t, C_{A0} is the initial concentration of A, and k_1 is the rate constant of reaction (1), and therefore

$$C_C = \frac{k_1 C_{A0}}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \tag{8}$$

where C_C is the concentration of intermediate C at time t, C_{A0} is the initial concentration of A, and k_1 and k_2 are the rate constants of first-step reaction (1) and second-step reaction (2), respectively.

For consecutive reaction, the concentration of intermediate C will reach a maximum value during the period of the reaction. When the concentration of intermediate C reaches the maximum value,

$$\frac{dC_C}{dt} = 0 \tag{9}$$

and therefore

$$t_{\max} = \frac{\ln k_1 - \ln k_2}{k_1 - k_2} \tag{10}$$

where t_{max} is the time at which the concentration of intermediate C reaches the maximum value.

When C_A, C_{A0} and t_{max} are experimentally determined, the rate constant k_1 and k_2 may then be calculated.

KINETIC STUDIES OF THE CONDENSATION REACTION BETWEEN C.I. REACTIVE RED 120 AND *m*- AND *p*(β-SULFATOETHYLSULFONYL)ANILINE

Preliminary study

The dyes were prepared according to Scheme 1.

A sample (1.727 g) of C.I. Reactive Red 120 (1.0×10^{-3} mol) was added to 40 ml water and the mixture heated to 95°C. 0.562 g *m*-(β-sulfatoethyl-sulfonyl)aniline (2.0×10^{-3} mol) in 10 ml water was then added, maintaining a temperature of 95°C throughout. Aliquot portions (0.1 ml) were taken every 5 min, and added to 1 ml cold water to stop the reaction. A sample, 0.005 ml of solution, was applied to a chromatographic plate (silica GelG + 0.2% CMC), which was dried, developed and the peak areas of the spots measured (CS-930). On plotting the changes in areas against time of reaction in minutes, the curves shown in Fig. 1 were obtained.

From Fig. 1, it can be seen that the condensation reaction of C.I. Reactive Red 120 and *m*-(β-sulfatoethyl-sulfonyl)aniline is a complicated reaction; three spots appeared during the process of the reaction; the concentration of the intermediate C gradually increases initially, and then decreases as the

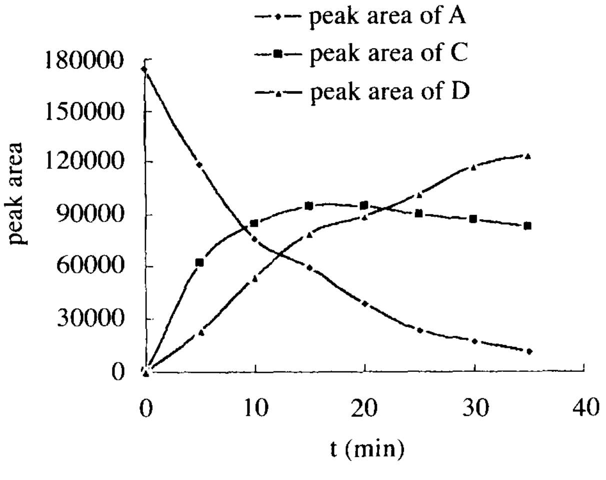
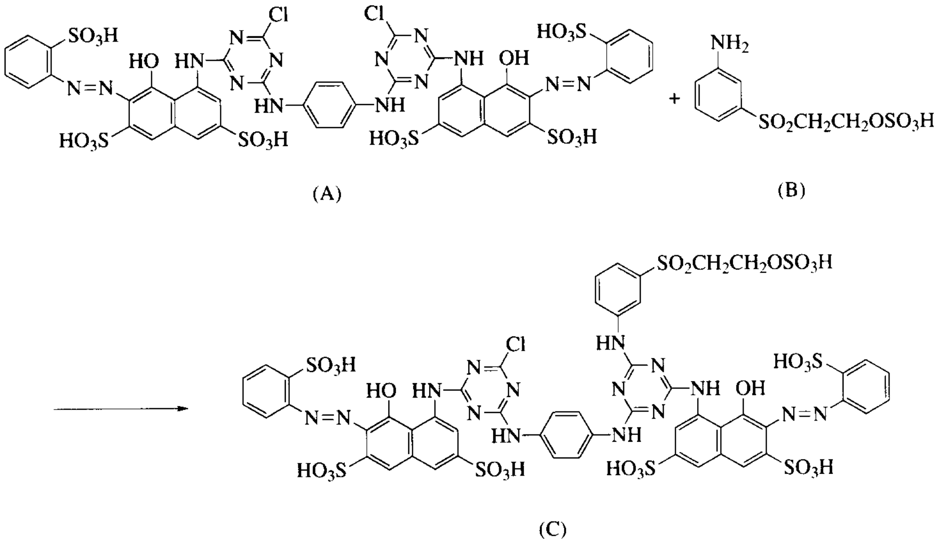
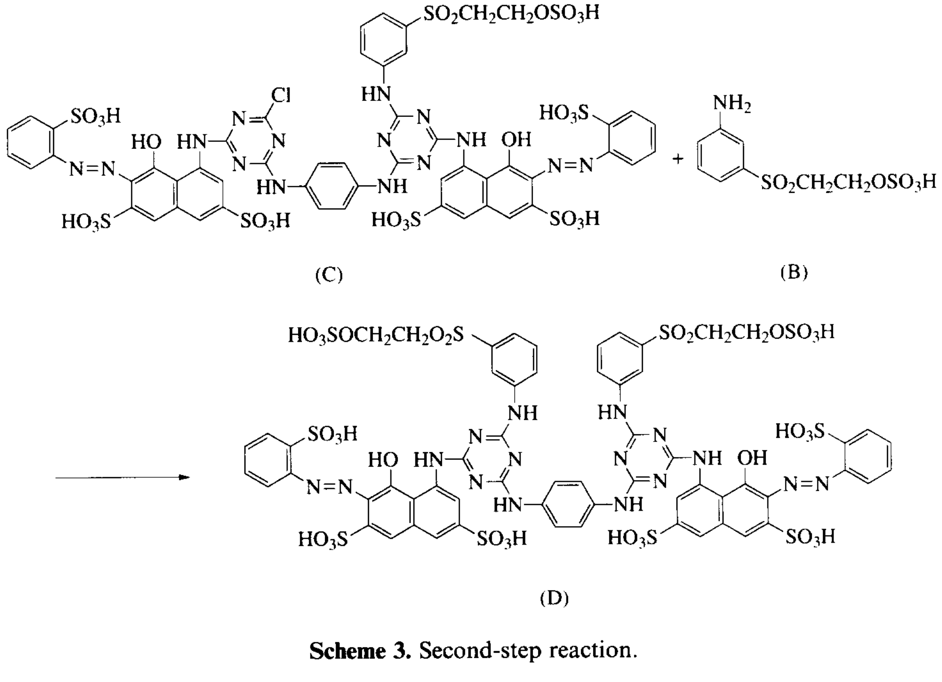


Fig. 1. Changes of area of A, C and D against time of reaction *t*.

reaction proceeds. This suggests that the overall reaction consists of the two consecutive steps shown in Schemes 2 and 3:



Scheme 2. First-step reaction.



Scheme 3. Second-step reaction.

In order to identify the three spots which appeared during the process of the reaction, the product mixture obtained above was separated by dry column chromatography, and the three chromatographic components were purified by precipitation with potassium acetate. Their purities were examined by thin layer chromatography; all of them gave single spots. The absorption wavelength and elemental analysis are given in Table 1.

First grade *m*-(*β*-sulfatoethyl-sulfonyl)aniline was recrystallized from distilled water, giving pure *m*-(*β*-sulfatoethyl-sulfonyl)aniline (calculated: C 34.16%, H 3.91%, N 4.98%; found: C 34.07% H 3.93%, N 4.93%).

Standard curve determination

Standard solutions of the dyes of concentration (1.5×10^{-3} mmol ml^{-1}) were obtained by dissolving 7.5×10^{-3} mmol of dyes A, C and D respectively in distilled water (50 ml). Taking aliquot portions of these solutions, further dilution gave a series of standard solutions of concentrations 0.15×10^{-3}, 0.30×10^{-3}, 0.45×10^{-3}..., 1.20×10^{-3} mmol ml^{-1}. 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 2 and Fig. 2).

The regression equations are:

$$A_A = 3.483 \times 10^{13} W_A, \qquad r = 0.9995$$

$$A_C = 3.922 \times 10^{13} W_C, \qquad r = 0.9993$$

$$A_D = 4.469 \times 10^{13} W_D, \qquad r = 0.9994$$

TABLE 1

Absorption Wavelengths and Elemental Analysis of Dye A, C and D

				Elemental analysis (%)		
Dye	*Molecular formula*	*λ_{max} (nm)*		*C*	*H*	*N*
A	$C_{44}H_{24}N_{14}S_6O_{20}Cl_2K_6$ $9H_2O$	535.2	Calcd:	30.57	2.43	11.35
			Found:	30.85	2.32	10.95
C	$C_{52}H_{33}N_{15}S_8O_{26}ClK_7$ $10.5H_2O$	535.8	Calcd:	30.64	2.65	10.31
			Found:	30.41	2.60	10.28
D	$C_{60}H_{42}N_{16}S_{10}O_{32}K_8$ $12H_2O$	536.5	Calcd:	30.69	2.61	9.55
			Found:	30.62	2.28	9.73

TABLE 2
Dosage Weights and the Peak Area Relationship of A, C and D

	$W_n \times 10^9$ (Mol)							
	0.30	*0.60*	*0.90*	*1.20*	*1.50*	*1.80*	*2.10*	*2.40*
A_A	10,091.0	21,436.4	30,529.7	41,966.1	53,765.1	62,787.0	72,910.8	82,905.6
A_C	12,236.4	23,261.2	35,461.5	47,146.6	58,549.7	72,941.0	81,302.0	93,357.4
A_D	13,854.9	25,785.3	42,166.7	52,910.7	68,178.0	79,956.7	94,572.1	106,124.6

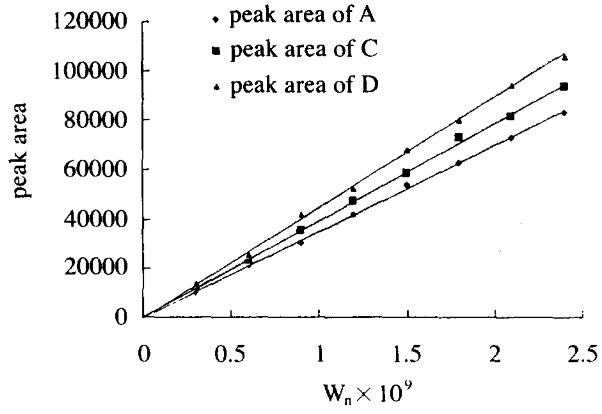


Fig. 2. Standard curve of A, C and D

Study of kinetics of C.I. Reactive Red 120 and *m*-(β-sulfatoethylsulfonyl)aniline

A buffer solution (5.0 ml) and 0.1727 g A (1.0×10^{-4} mol) were added to a 20 ml flask, placed in a thermostat, and the mixture stirred for 30 min to dissolve the dye completely. A solution, 5.0 ml of 0.562 g B (2.0×10^{-3} mol) (A:B = 1:20) was added to the reaction mixture and after addition of B, samples (0.05 ml) were removed at intervals, and added to 0.1 ml cold water to stop the reaction. A sample, 0.005 ml of solution, was applied to a chromatographic plate and the peak areas after development were measured by using the Shimadzu CS-930 double scanner.

For the reaction carried out at 95 ± 1°C and pH 4.0, the results are shown in Table 3 (see also Figs 3 and 4). Since $A_A = K'_A W_A = K_A C_A$. therefore

$$\ln(C_{A0}/C_A) = \ln(A_{A0}/A_A)$$

The regression equation was:

$$\ln(C_{A0}/C_A) = 0.1002t, \qquad r = 0.9980$$

and therefore, the rate of first-step reaction (k_1) is equal to 0.1002 min^{-1}.

TABLE 3

Experimental Data and Calculated Results of the Reaction between A and B at 95 ± 1°C and pH4.0

	Time (min)							
	0	*5*	*10*	*15*	*20*	*25*	*30*	*35*
A_A	200,853.5	124,850.3	80,396.2	46,093.2	30,001.2	17,365.9	9669.97	5833.75
A_B	0	62,150.8	77,638.8	82,561.9	76,533.4	65,426.9	61,732.5	56,836.9
A_D	0	23,092.9	55,237.5	80,500.6	92,280.5	104,504.1	113,153.3	126,817.9
$\ln\frac{C_{A0}}{C_A}$	0	0.4755	0.9156	1.4719	1.9013	2.4481	3.0336	3.5389

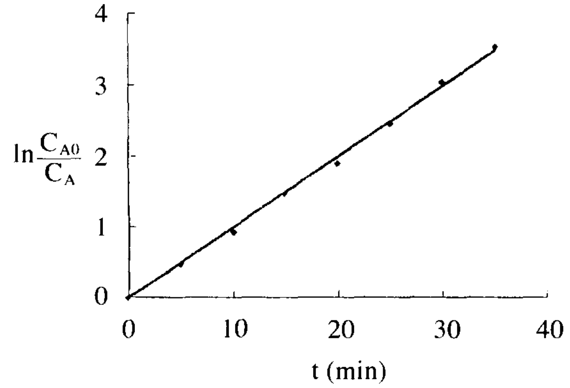


Fig. 3. Plots of ln (C_{A0}/C_A) versus reaction time t (min) of reaction 1 at 95 ± 1°C and pH 4.0.

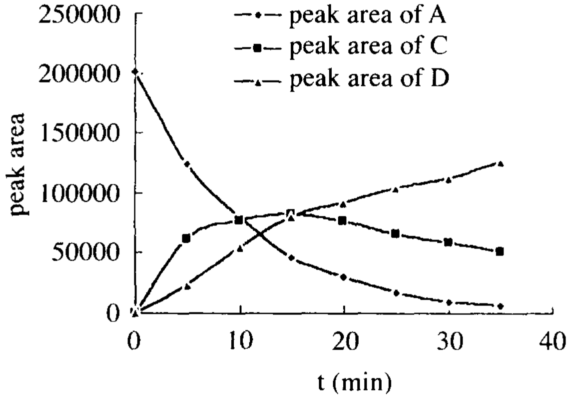


Fig. 4. Plots of peak areas versus reaction time t (min) of reaction 1 at 95 ± 1°C and pH 4.0.

From Fig. 4, $t_{\max} = 15$ min, the rate of second-step reaction (k_2) can thus be calculated. k_2 is equal to 0.0418 min^{-1}.

For the reaction carried out at different temperature and at different pH, similar results were obtained and these are summarized in Table 4.

TABLE 4
The Rate Constants of the Condensation Reaction between C.I. Reactive Red 120 and *m*-(β-Sulfatoethyl-Sulfonyl)Aniline

No.	*Reaction condition*	$k_1(min^{-1})$	$k_2(min^{-1})$
1	95 ± 1°C, pH 4.0	0.1002	0.0418
2	95 ± 1°C, pH 5.0	0.0783	0.0378
3	95 ± 1°C, pH 5.5	0.0557	0.0275
4	90 ± 1°C, pH 5.5	0.0399	0.0196
5	100 ± 1°C, pH 5.5	0.0769	0.0303

TABLE 5
The Rate Constants of the Condensation Reaction between C. I. Reactive Red 120 and *p*-(β-Sulfatoethyl-Sulfonyl)Aniline

No.	*Reaction condition*	$k_1(min^{-1})$	$k_2(min^{-1})$
1	95 ± 1°C, pH 4.0	0.0098	0.0050

The results of the kinetic studies of C.I. Reactive Red 120 and *p*-(β-sulfatoethyl-sulfonyl) aniline are shown in Table 5.

From these results, the rates of the first-step reaction (k_1) are about twice as fast as those of the second-step reaction (k_2), as is apparent from Tables 4 and 5. With increasing reaction temperature, the rates of the two steps reaction (k_1 and k_2) were increased. With decreasing reaction pH, the rates of the two steps reaction (k_1 and k_2) were also increased.

Under the same reaction conditions, the rate constants of the condensation reaction between *m*-(β-sulfatoethyl-sulfonyl)aniline and C.I. Reactive Red 120 were about 10 times greater than that of *p*-(β-sulfatoethyl-sulfonyl)aniline.

CONCLUSION

The condensation reactions between C.I. Reactive Red 120 and *m*- and *p*-(β-sulfatoethyl-sulfonyl)aniline have been studied kinetically. The condensation reactions consist of two consecutive steps, with different rate constants at different temperature and different pH. The rates of the first-step reaction (k_1) are about twice as fast as those of the second-step reaction (k_2). The rate constants of the condensation reaction between *m*-(β-sulfatoethyl-sulfonyl)aniline and C.I. Reactive Red 120 are about 10 times greater than that of *p*-(β-sulfatoethyl-sulfonyl)aniline.

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1. Yao Sheng, Doctorate Dissertation, ECUST, 1996 (Supervisor, Professor Zhu Zhenghua).