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The Hydrolysis Kinetics and Dyeing Properties of 3′-Carboxypyridino-triazine Reactive Dyes

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ABSTRACT

*The kinetics of the hydrolysis of 3′-carboxypyridino-*s*-triazine reactive dyes were studied at 60–130°C in a neutral medium using HPLC. A series of hydrolysis rate constants were obtained and the effects of pH and temperature on the reaction were evaluated. It was found that pH is a key factor at low temperature, but that when the temperature was raised, temperature becomes the more important influence on the hydrolysis. The reactivities of the monochloro- and 3′-carboxypyridino-*s*-triazine dyes were compared and the results showed that the hydrolysis rate constants of the latter were two grades higher than those of the former. The dyeing properties were also examined and it was demonstrated that the most favourable pH value for dyeing at high temperature is 8; the neutral medium employed in commercial processes is thus not necessarily the optimum condition.*

Keywords: Reactive dye, hydrolysis, kinetics, dyeing properties, nicotinic acid, quaternisation.

INTRODUCTION

3′-Carboxypyridino-*s*-triazine reactive dyes were commercially introduced in 1984, the dyes containing two quaternised nicotinic acid residues. These dyes are designed to react with cellulose at high temperature in a neutral dyebath, thus making a one bath/one step dyeing of blended polyester/cotton possible.[1]

Reactive dyes and auxillaries containing a quaternary ammonium moiety as the leaving group have been widely studied and the use of tertiary amines as a reaction acceleration catalyst in the application of monochlorotriazine dyes in cold batch dyeing has been reported.[2,3] We have previously reported on the catalytic effect of tertiary amines such as nicotinic acid and 1,4-diazabicyclo-(2,2,2)-octane (DABCO) on the dyeing of monochlorotriazine dyes at high temperatures in a neutral medium.[4] This present work is concerned with the hydrolysis kinetics and application properties of 3′-carboxypyridino-*s*-triazine dyes, such dyes being typified by the Kayacelon React dyes (KYK).

RESULTS AND DISCUSSION

Hydrolysis of quaternised dyes

The Kayacelon React dyes are designed to have a high affinity, this being achieved by introduction of multiple reactive groups in order to achieve good exhaustion during high temperature dyeing, i.e. the so-called 'twin-chromophore' type. Their synthesis and the inherent hydrolysis reaction of such dyes is shown in Scheme 1.

The commercial dyes usually contain three main components, i.e. **1**, **2** and **3**, as shown in Scheme 1. In order to simplify the investigation, the dyes D-I and D-II containing only one reactive group were synthesised; the hydrolysis of D-I and D-II is shown in Scheme 2.

Using the quaternised D-I, hydrolysis was first carried out at various temperatures and under different pH values. The relative concentrations of the two species, i.e. the original D-I and hydrolysed dye, were determined by HPLC at various stages of the reaction. Some typical results are shown in Fig. 1.

It was found that the hydrolysis of D-I increased with increase in temperature at a constant pH value. The hydrolysis was complete after about 20 min when the pH of buffer medium used was 9. The rate of disappearance of D-I ($-\mathrm{d}[\mathrm{D}]/\mathrm{d}t$) can be expressed by Equation (1), in which $[\mathrm{D}]_t$ and $[\mathrm{OH}^-]$ are the concentrations of D-I and hydroxyl ion at any specific time t.

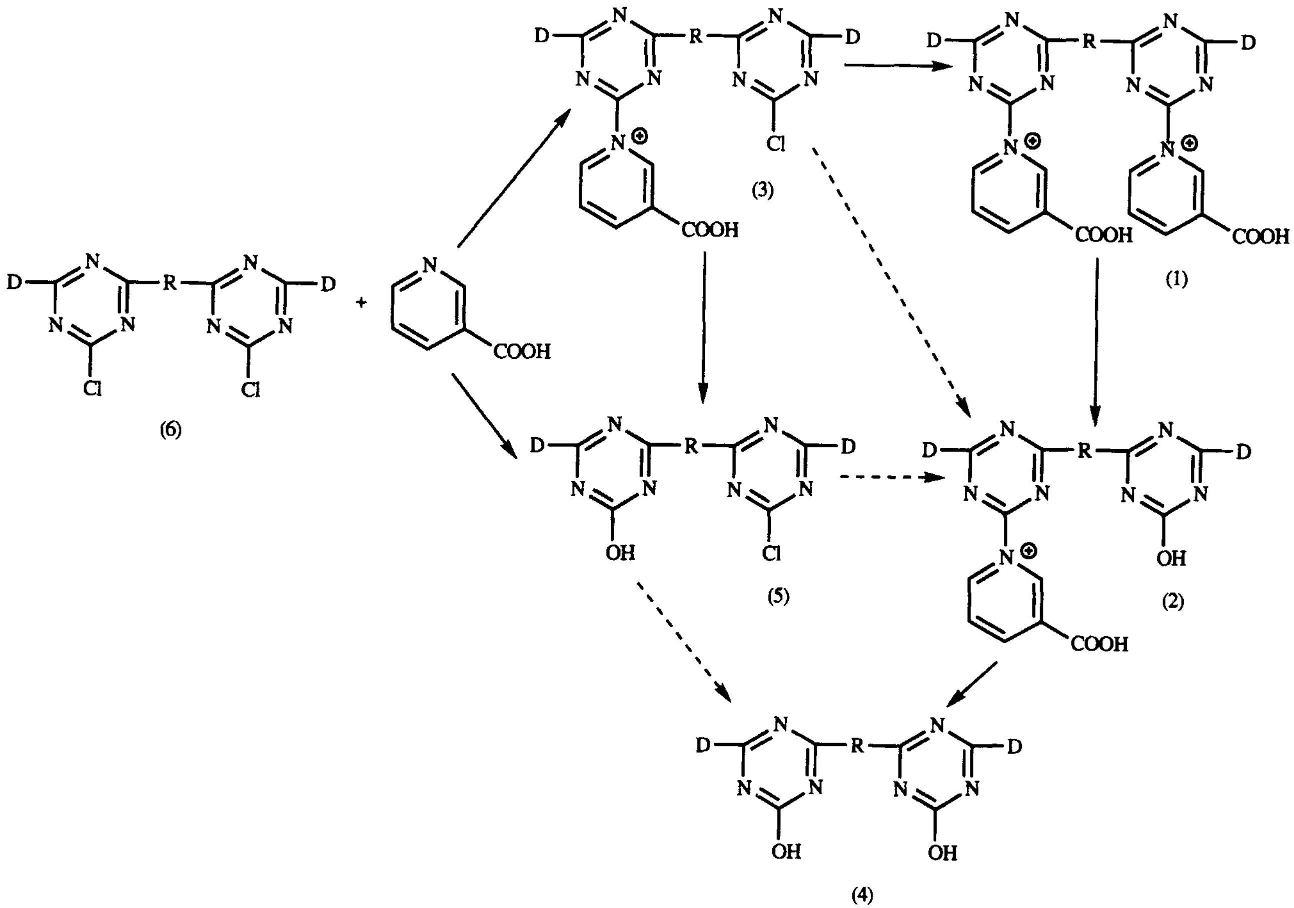
$$-\mathrm{d}[\mathrm{D}]/\mathrm{d}t = k[\mathrm{OH}]^{\alpha}[\mathrm{D}]_t. \qquad (1)$$

It is clear from Equation (1) that in a buffer medium the reaction is pseudo-first-order with respect to the dye concentration, and hence Equation (2) and (3) can then be derived

$$-\mathrm{d}[\mathrm{D}]/\mathrm{d}t = k_s[\mathrm{D}]_t \qquad (2)$$

$$\ln\left([\mathrm{D}]_t/[\mathrm{D}]_o\right) = k_s t \qquad (3)$$

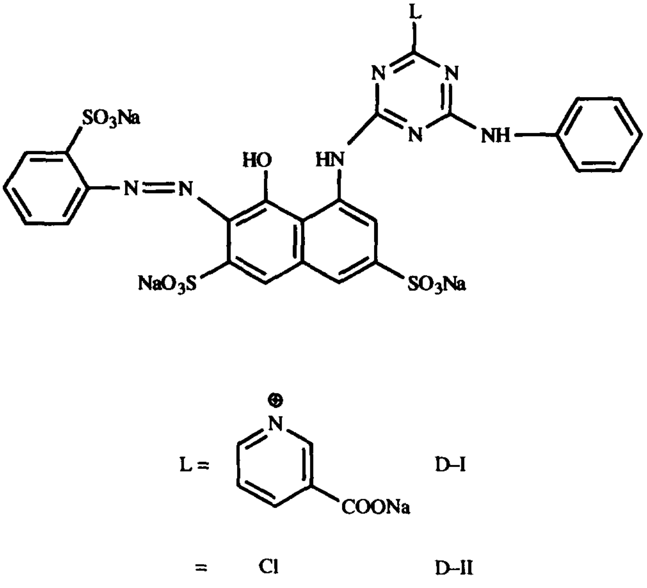
where $k_s = k[\mathrm{OH}^-]^{\alpha}$.



Scheme 1. Synthesis and hydrolysis of Kayacelon React (KYK) dyes.

The hydrolysis constant (k_s) of the quaternised D-I can be calculated from the concentration of the D-I as measured by HPLC, using Equation (3). Relevant data are shown in Table 1.

It was found that the hydrolysis rate of D-I was too fast to be measured under conditions of high temperature and high pH value. Table 1 shows that at a constant temperature in a weakly basic bath from pH 7 to 9, increasing the pH value by one unit results in an approximately one grade increase of the hydrolysis rate constants. These results demonstrate that the pH value is a key factor influencing the hydrolysis of the quaternised dyes. When the hydrolysis was carried out in a weakly acidic medium, the effect of pH became less, indicating that these dyes are more stable in a weakly acidic medium. With respect to the temperature, the effect of this on the hydrolysis is smaller compared with that of pH, each 10°C increase causing only a 2–6 times increase of the hydrolysis rate constants.



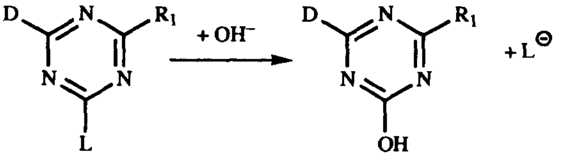
Comparison of the quaternised and monochloro-*s*-triazine dyes

The hydrolysis reactions are both pseudo-first-order with respect to the concentration of the quaternised dyes and monochlorotriazine dyes, but the reactivity differs greatly. Figure 2 shows the hydrolysis of the two dyes under identical conditions (i.e. pH 9 and 90°C). Under these experimental conditions, after approximately 20 min, the hydrolysis of D-I is complete, but only 3% of the monochlorotriazine dye D-II is hydrolysed.

The hydrolysis constants of the two dyes are compared in Table 2. The results indicate that the hydrolysis rate constants of the quaternised dyes are about two grades higher than those of the monochlorotriazine dyes, under equivalent conditions.

Application properties of the quaternised dyes

Six quaternised dyes, including Kayacelon React Red CN-3B and Yellow CN-RL, were used in the dyeing experiments. The other dyes, Reactive



Scheme 2. The hydrolysis of D-I and D-II.

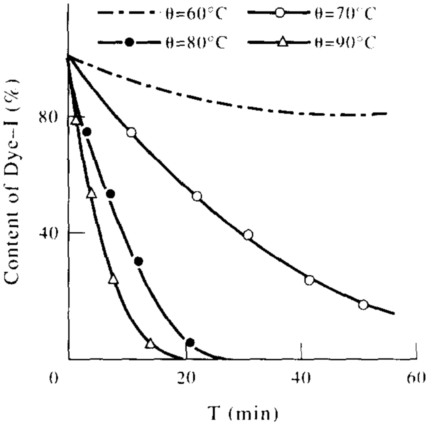


Fig. 1. Hydrolysis of the quaternised dye D-I.

TABLE 1
Hydrolysis Constants of D-I ($k_s \times 10^3$)

pH *Temperature (°C)*	*9*	*8*	*7*	*6*	*5*
130			46.56	39.86	0.9030
115			8.520	6.280	0.8554
100		97.60	6.850	2.720	0.5763
90	235.7	37.44	6.625	0.9236	0.4658
80	160.3	18.91	2.851	0.2222	0.1600
70	35.88	3.137	0.3798	0.06518	0.06142
60	6.683	0.6246	0.1369	0.01869	0.02381
50	1.114	0.1094	0.01422		

Reds 1 and 2 (R-1, R-2) and Reactive Yellows 1 and 2 (Y-1, Y-2), were synthesised in our laboratory. They have the same chromophoric structures with respect to Kayacelon React Red CN-3B and Yellow CN-RL, but are different in the degree of total replacement of both chloro substituents by nicotinic acid, i.e. in their relative composition with respect to the components 1–3 shown in Scheme 1 (this is referred to in the following as the 'degree of quaternisation'). All the dyes have two triazine reactive groups. The effects of the dye composition, temperature and pH on the dyeing properties were examined. The dye fixation yield was calculated by measuring the extinction coefficients of the initial and residual dye liquors using a Model 751 spectrophotometer.

$$F = \left[1 - \frac{E_r}{E_o}\right] \times 100 \tag{4}$$

where F is fixation yield, E_r is the extinction coefficient of residual dye liquor and E_o is the extinction coefficient of the original dye solution.

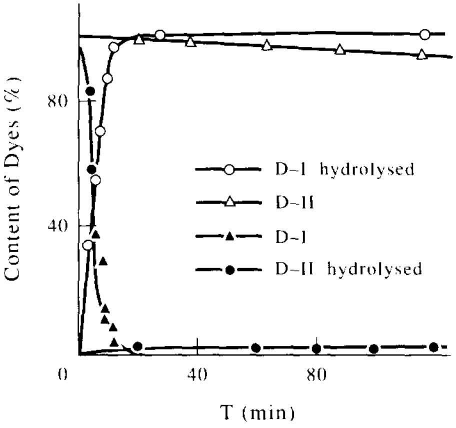


Fig. 2. Hydrolysis processes of the two dyes (90°C, pH = 9).

TABLE 2
Comparison of the Hydrolysis Rate Constants of D-I and D-II

pH	*7*		*8*	*9*	
Temperature (°C)	*130*	*115*	*100*	*90*	*80*
D-I $k_s \times 10^3$	46.6	8.52	97.6	235.7	160.3
D-II $k_s \times 10^3$	0.241	0.0849	0.449	0.996	0.158
$k_{D\text{-}I}/k_{D\text{-}II}$	200	100	217	236	1000

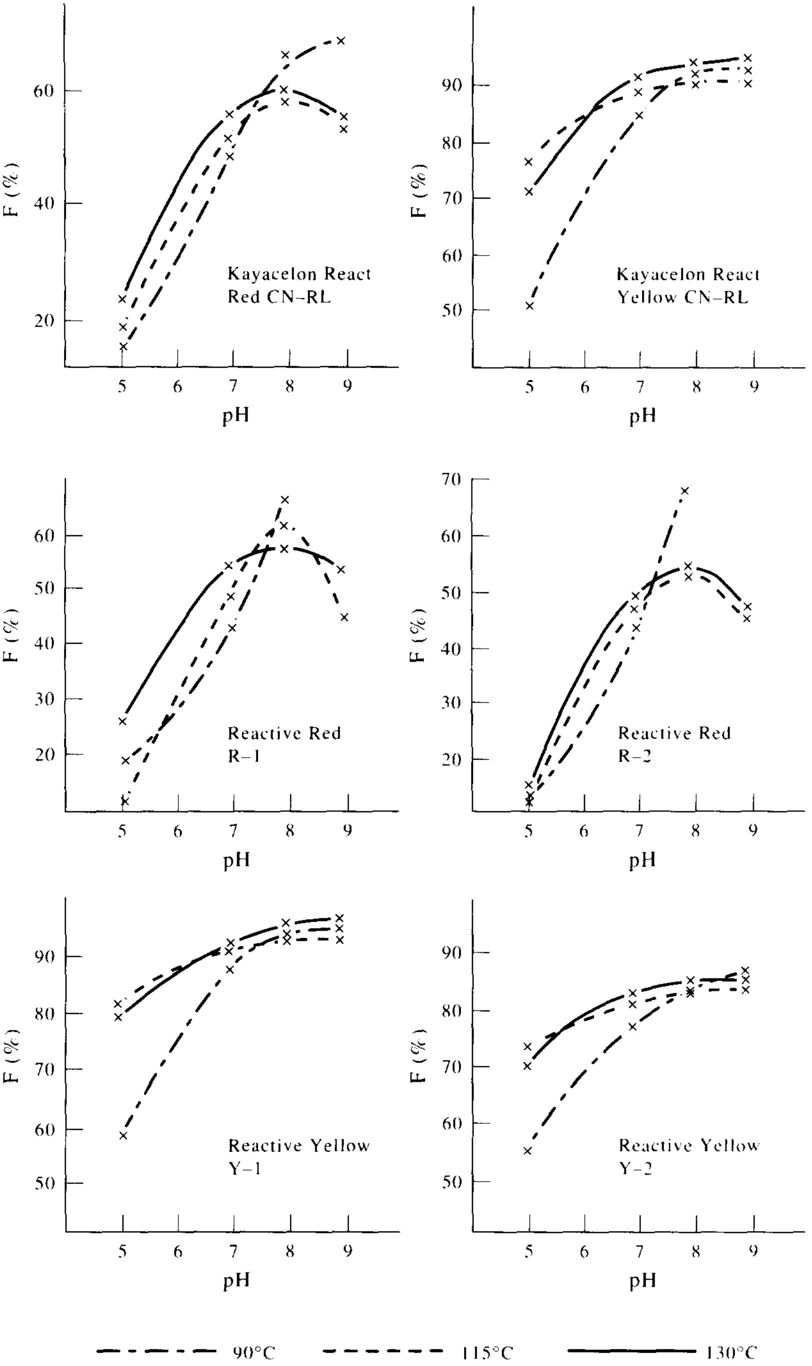


Fig. 3. Fixation of the quaternised dyes at various temperatures and pH values.

Figure 3 illustrates the results obtained and individual effects are noted in the following sections.

The effect of dye composition on the fixation yield

The quaternised dyes used were initially analysed by HPLC and their compositions are listed in Table 3. It was found that components **4** and **5** were formed in a negligible amount, the quaternisation degree of the yellow dyes is lower than that of the red dyes.

Comparing the dyeing results and the data in Table 3 indicates that the 'degree of quaternisation' is a major factor on the fixation yields at high temperature in a neutral bath. The yellow dyes Y-1 and Kayacelon React Yellow CN-RL have almost the same degree of quaternisation, and the maximum fixation yields, approaching 90%. However, Y-2 is only slightly quaternised and the fixation yield of this dyes only reaches 80%. The dyes R-2 and Kayacelon React Red KN-3B have only a 4% difference in quaternisation degree, and the fixation yield of the former is 10% higher than that of the latter. The results indicate that, in general, the greater the degree of quaternisation, the higher is the dye reactivity; higher fixation yields will then be obtained.

The effect of temperature and pH on the fixation yields

The dyeing results also showed that the fixation yields are strongly influenced by the pH of the dyebath when the temperature is low, but that when the temperature is raised, the effect of pH becomes less. However, all the quaternised dyes showed maximum fixation yields at pH 8. When the pH value was raised, the fixation yields decreased, due to the increase of the hydrolysis of the dyes at the higher pH value. With respect to the three quaternised yellow dyes, the pH of the dye bath had a slight influence on the fixation in neutral medium at high temperature.

HPLC analysis of the residual dye liquors showed that the residual dyes in the liquor were mainly the dyes containing chlorotriazine reactive groups and hydrolysed dyes. This result indicates that the presence of a highly reactive moiety in the dye is the main factor on the fixation of the dyes under high temperature conditions in a neutral medium.

TABLE 3
Compositions of the Quaternised Dyes

Components	*1*	*2*	*3*	*4*	*5*	*6*
Kayacelon React Red CN-3B	73.6	3.43	15.9	—	0	7.17
R-1	69.9	8.8	21.3	—	0	—
R-2	74.0	7.2	18.7	—	0	—
Kayacelon React Yellow CN-RL	58.3	0	22.0	—	0	19.7
Y-1	59.0	0	27.8	—	0	13.2
Y-2	28.0	0	50.5	—	0	21.5

EXPERIMENTAL

Quaternisation of the chlorotriazine dyes

Kayacelon React Red CN-3B and Yellow CN-RL were commercial samples. The other dyes used were synthesised and purified as previously reported.[5] For example, the quaternisation of C.I. Reactive Red 120 was evaluated using the L_g (3^4) orthogonal experimental group under the following conditions:

No.	pH	temperature, °C	molar ratio*	time, h
1	5	85	1:6	4
2	6	85	1:3	5
3	7	85	1:8	6
4	7	90	1:3	5
5	6	90	1:6	6
6	5	90	1:8	4
7	7	80	1:6	6
8	5	80	1:3	4
9	6	80	1:8	5

In this section, the orthogonal experiments require only a minimum number of experiments to determine the optimum conditions for the quaternisation. Mathematical analysis of the results showed that the degree of quaternisation was mainly affected by the time and the pH of the reaction.

C.I. Reactive Red 120 [14.6 g (0.01 mol)] were dissolved in 60 ml water and the pH was adjusted to 5.5–6 with saturated NaH_2PO_4 solution; 50.2 g (0.041 mol) nicotinic acid were dissolved in 80 ml water with heating and the pH was also adjusted to 5.5–6. The two solutions were then mixed with 10 ml buffer solution of pH 5 and stirred at 85°C. The degree of reaction was controlled by the reaction time, which was usually 5–8 h.

When the reaction was complete, the solution was cooled to room temperature and 15% wt KCl of the volume was added, the product filtered, washed salt-free and dried.

The dye solution (0.1335 g in 50 ml water) and appropriate buffer solution were first prepared, then mixed in appropriate volumes and hydrolysed in a thermostatically controlled bath. After various intervals, samples were removed and the reaction was stopped by reducing the temperature and diluting the reaction solution from 1 to 10 ml with water. The rate of the hydrolysis could then be calculated from the concentrations of dyes present, which were determined by HPLC using a methanol and water flow phase (volume ratio 65:35, flow rate 0.8 ml/min).

The buffer solutions used in the experiments were

1. $pH = 5$: 0.1 N NaOH (24 ml) + 0.2 M potassium hydrogen phthalate solution (25 ml), made up to 100 ml with water
2. $pH = 6$: 0.1 NaOH (5.64 ml) + 0.2 M KH_2PO_4 (25 ml), diluted to 100 ml with water
3. $pH = 7$: 0.1 NaOH (29.54 ml) + 0.2 M KH_2PO_4 (25 ml), diluted to 100 ml with water
4. $pH = 8$: 0.1 N NaOH (4.0 ml) + 0.2 M boric acid–KCl (25 ml), diluted to 100 ml with water
5. $pH = 9$: 0.1 M sodium borate solution.

Dyeing and determination of dye fixation

An aqueous dyebath was first prepared by mixing dye and buffer solutions. Dyeing of cellulose (at 2% depth) was carried out at various temperatures at a liquor ratio of 30:1 in the presence of sodium chloride (30 g/l) in a high temperature dyeing machine. The dyeing process was designed to reflect the procedures used commercially for dyeing polyester/cotton blends. At the end of the dyeing process, the dyed fibres were soaped with OP solution (2 g/l, liquor ratio 30:1) for 20 min at 85°C, and the residual rinse liquor was then mixed with the spent dyebath liquor. The fixation of the dyes under the various conditions was then calculated. The OP used above is a surfactant of general formula $p\text{-R-C}_6\text{H}_4\text{-O(CH}_2\text{CH}_2\text{O)}_n\text{-H}$.

CONCLUSION

Investigations of the hydrolysis kinetics of 3′-carboxypyridino triazine reactive dyes showed that the reactivities of this type of dye were higher than those of monochlorotriazine dyes. Dyeing experiments indicated that the optimum pH value for maximum fixation during dyeing at high temperature was 8, implying that the normally recommended neutral medium is not necessarily the optimum condition.

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