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Reactivity and Stability of C.I. Reactive Red 120 at High Temperature

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Abstract: Reactivity and stability of a bis(monochloro-s-triazine) reactive dye (C.I. Reactive Red 120) between 90 and 130 °C at various pH values were studied using HPLC. The obtained rate constants for the hydrolysis of the dye show that the reactivity in the range of 100 °C to 130 °C and at pH values lower than 10.0 is close to the reactivity at 90 °C and pH 11.0, indicating that severe hydrolysis of the active groups of the dye could be avoided at high temperatures by lowering the pH. Meanwhile, the concentrations of the degradation products of the dye at high temperatures, as determined from its chromatographic analysis, were found to be far higher than that at low temperatures, while those of the hydrolysis products did not significantly vary with temperature. These results show that most of the losses of the dye at high temperatures and low pH are caused by the degradation, rather than hydrolysis, of the dye.

Keywords: Reactive dye, Reactivity, Stability, High temperature, HPLC

Introduction

Longer dyeing times and higher energy costs involved in the two-bath dyeing process have triggered a search for alternative processes for the manufacture of polyester/cotton blends using one-bath one-step dyeing process [1-10]. After it was found that some dispersive dyes can be used in alkali dyebath or nearly neutral dyebath, increasing attention has been focused on the one-bath one-step dyeing process using disperse/reactive dyes at high temperature and low pH. This process, however, was industrially successful only when applied to a few commercial reactive dyes with double active groups (e.g., bis-3-carboxypyridinium-s-triazine reactive dye) [4,5]; most of general commercial reactive dyes did not yield satisfactory dyeing results by this process. Especially perplexing is the bis(monochloro-s-triazine) reactive dye, which does not work well at high temperatures and at low pH, although it has some similar advantages in dyeing to bis-3-carboxypyridinium-s-triazine reactive dye at high temperature (e.g., two alkaline resisting s-triazine active groups, larger molecular structure, and higher substantivity than other reactive dyes with single active group).

To determine the cause for poor results for dyeing using bis(monochloro-s-triazine) reactive dye at high temperature and low pH, a detailed study of the dyeing behavior of the bis(monochloro-s-triazine) reactive dyes at high temperatures is necessary. The present work attempts to discuss the dyeing behavior of bis(monochloro-s-triazine) reactive dye from following two aspects.

Reactivity of the Bis(monochloro-s-triazine) Active Group at High Temperatures

Use of reactive dyes at high temperatures is difficult. An important reason is their high reactivity at high reaction temperatures under basic conditions (10-15 g/*l* Na_2CO_3). High reactivity of the dye causes a rapid reaction between the dye and fibers resulting in uneven dyeing; more importantly, the hydrolysis reaction of the reactive groups is generally considered to be so severe that most of the dye gets hydrolyzed before reacting with the fibers [11]. However, at low pH, as the hydroxyl ion concentration decreases, in theory, the hydrolysis reactivity of the dye should also decrease, which may to some extent compensate for the increased reactivity caused by the rising temperature. Although this theory seems to have been applied towards high-temperature dyeing of the bis-3-carboxypyridinium-s-triazine reactive dye [12], it is not known if it may be also applied to the bis(monochloro-s-triazine) reactive dyes. Therefore, the reactivity of bis(monochloro-s-triazine) reactive dyes was determined at high temperatures under close to conventional dyeing conditions by lowering the pH of the dyeing bath, as previous reports have suggested temperature as a more important factor than pH affecting reactivity of the dye at high temperatures [12].

Stability of the Parent Dye at High Temperatures

Most of the bis-diazo reactive dyes having two reactive groups may undergo repeated condensation reactions forming imine linking groups and bridge groups and coupled reactions that may form azo groups in the synthetic process of the dye, thus displaying ample high-temperature anti-resistance and alkali susceptible groups such as azo groups, imine linking groups, and bridge groups in the parent dye. It is not known whether there are some differences in the stability of the dye at high and at low temperatures, which may influence the dyeing effects at high temperatures. Therefore, the present work also explores the difference in stability of the parent dye at high and low temperatures based on the hydrolysis reactions of the bis(monochloro-s-triazine) reactive dye.

The reactivity of a reactive dye is usually represented by

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its hydrolysis rate [13,14]. The amounts of the dye and its reaction products in solution are usually measured by high-performance liquid chromatography (HPLC), particularly anti-phase ion-pair HPLC [15-17]. As the hydrolysis and degradation products of the dye have different structural features (i.e., hydrophobic structure, molecular polarity, van der Waals force and hydrogen bond), different reaction products of the dye are retained at different times on the surface of the non-polar stationary phase of the chromatographic column when driven by the mobile phase containing an ion-pairing agent [18]. Consequently, the different reaction products can be separated simultaneously and rapidly and analyzed qualitatively and quantitatively. Compared with other methods, HPLC is simpler, faster, and more accurate [19]. Thus, the technique is widely applied to study the behavior and mechanism of reactive dyes [20-23].

In this paper, C.I. Reactive Red 120 (Reactive Red KE-3B), a reactive dye, sensitive to alkali [24-26], was selected for this study. The reactivity of C.I. Reactive Red 120 is characterized by rate constants of the hydrolysis reaction between the dye and hydroxyl ion. The hydrolysis products and degradation products of the dye were analyzed by reversed-phase ion-pair HPLC.

Experimental

Agents and Materials

All solvents used for HPLC analysis were of HPLC grade (Merck Co., Ltd., Germany). The ion-pairing agent tetrabutylammonium bromide (TBA), $NH_4H_2PO_4$, NaH_2PO_4, Na_2HPO_4, NaOH, Na_2CO_3, $NaHCO_3$, HCl, H_3BO_3, and Na_2HBO_3 were of analytical grade. Deionized water (18.3 MΩ·cm) was freshly prepared before every use.

The reactive dye used (Figure 1) was a purified commercial sample of bis(monochloro-s-triazine) dye C.I. Reactive Red 120 (Reactive Red KE-3B) purchased from ZhejiangYide Chemical Co., Ltd., China.

Chromatographic Conditions

HPLC analyses of hydrolyzed dye samples were carried out on a U-3000 liquid chromatograph (Thermo Fisher Scientific, Shanghai, China) using an Acclaim C18 Hypersil ODS-2, 150×4.6 mm, 5 μm column (Thermo Fisher) as the stationary phase and a mixture of solvents 1 and 2 as the mobile phase. Solvent 1 was 100 % acetonitrile containing 0.025 mol/*l* tetrabutylammonium bromide and solvent 2 was a 30/70 (v/v) mixture of solvent 1 and deionized water buffered with 0.05 mol/*l* ammonium dihydrogen phosphate. The aqueous part of the mobile phase was filtered before use, through 0.22 μm membrane filters, using a glass vacuum solvent-filtration apparatus and degassed using an ultrasonic generator at a frequency of 53 kHz. The dye solutions were filtered through 0.22 μm water-based disposable needles and 20 μl of the dye solution was analyzed at 536 nm with a Spectra Focus Forward Optical Scanning detector at 30 °C using a gradient of solvents 1 and 2 (Table 1) at a flow rate of 1.0 m*l*/min.

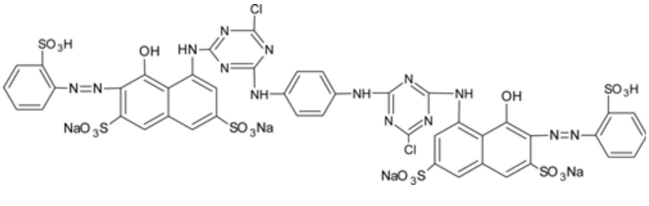

Figure 1. Structure of C.I. Reactive Red 120.

Table 1. Linear gradient system for bis(monochloro-s-triazine) reactive dye C.I. Reactive Red 120

Time (min)	Solvent 1 (%)	Solvent 2 (%)
0	20	80
5	50	50
11	50	50

Hydrolysis Experiment of the Dye at 90 °C

A 0.6 g sample of the dye was hydrolyzed by adding to a 150 m*l* pre-heated (90 °C) buffer solution ($pH_{20^\circ C}$=11.0) after which 2 m*l* of the hydrolyzed dye solution was withdrawn at specified time intervals (5, 10, 20, 30, 40, 60, 80, 100, 120, 140, 160, 180, 200, and 220 min). The hydrolytic reaction of each withdrawn aliquot was arrested by adding it to 20 m*l* of a pH 6.0 buffer solution (20 °C). The aliquot was then diluted to a constant volume in a 25 m*l* volumetric flask and cooled to room temperature. The samples were subjected to chromatographic analysis performed after filtration using 0.22 μm syringe needle filters.

Hydrolysis Experiments of the Dye at Varying Temperatures (100, 110, 120, and 130 °C)

As it was difficult to withdraw samples from a sealed dye cups at temperatures higher than 100 °C, the hydrolysis experiments at high temperatures (100-130 °C) were performed in a special device. The procedure is exemplified with a hydrolysis experiment at 130 °C. A 20 m*l* (from a 1 *l* stock) sample of pH 8.0 buffer (20 °C) was placed in special stainless steel dye cups (purchased from XIAMEN Rapid precision machinery Co., Ltd., China, Figure 2(a)). The specially designed dye cup has a feeding hole on the top part of the lid that can be closed at high temperatures due to higher inside pressure of the dye cup than outside. Upon exerting pressure from a self-refilling syringe (purchased from Socorex, Switzerland, Figure 2(b)), the hole opens to allow injecting the dye solution from the inner chamber of the self-refilling syringe into the dye cup. Upon removing the pressure from the self-refilling syringe, the cup can be sealed again due to the pressure inside.

Further, depending on the number of samples in the experiment, 20 m*l* of pH 8.0 buffer solution (prepared

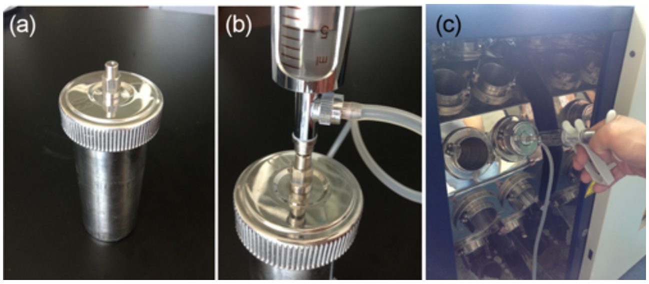

Figure 2. Illustration of the device for the high temperature (100-130 °C) hydrolysis experiment.

earlier) were put into each of the 12 dye cups, after which they were placed in a thermostatically controlled silicon carbide dyeing machine (ECO DYER, XIAMEN Rapid precision machinery Co. Ltd., China, Figure 2(c)). On pre-heating to a pre-determined temperature (for instance 130 °C), 5 m*l* of the dye solution (5 g/*l*) was injected into the dye cups from the feeding hole by using the self-refilling syringe for the hydrolytic reaction at 130 °C. At certain time intervals (10, 20, 30, 40, 50, 60, 80, 100, 120, 140, 160, and 180 min, respectively, a total of 12 samples), 25 m*l* of pH 6.0 (20 °C) buffer solution was injected into the dye cups to stop the reaction. Of this, 20 m*l* solution was withdrawn and diluted to 25 m*l* to obtain a 400 mg/*l* solution followed by their chromatographic analysis after being filtered by 0.22 μm syringe needle filters.

The hydrolysis temperature and pH of the buffer solution were varied to study the effect of various conditions.

The buffer solutions used for the experiments were

1. pH_{20^oC}=11.0:0.05 mol/*l* $NaHCO_3$ (500 m*l*)+0.1 mol/*l* NaOH (227 m*l*), diluted to 1000 m*l* with water
2. pH_{20^oC}=10.0:0.2 mol/*l* boric acid-potassium chloride (250 m*l*)+0.1 mol/*l* NaOH (439 m*l*), diluted to 1000 m*l* with water
3. pH_{20^oC}=9.5:0.025 mol/*l* sodium borate (500 m*l*)+0.1 mol/*l* NaOH (88 m*l*), diluted to 1000 m*l* with water
4. pH_{20^oC}=9.0:0.05 mol/*l* sodium borate (800 m*l*)+0.2 mol/*l* Boric Acid-Potassium Chloride (200 m*l*)
5. pH_{20^oC}=8.0:0.025 mol/*l* sodium borate (500 m*l*)+0.1 mol/*l* HCl (205 m*l*), diluted to 1000 m*l* with water
6. pH_{20^oC}=6.0:0.2 mol/*l* Na_2HPO_4 (123 m*l*)+0.2 mol/*l* NaH_2PO_4 (877 m*l*).

Results and Discussion

Reactive Mechanism of Alkaline Hydrolysis of C.I. Reactive Red 120 and Qualitative Analysis of Chromatographic Peaks

The reactivity of the reactive dyes has often been determined by its hydrolytic reaction in excessive alkaline buffer solution and has been expressed in terms of the hydrolysis rate constants of the dyes and hydrolysates. In general, HPLC has been used for such determinations.

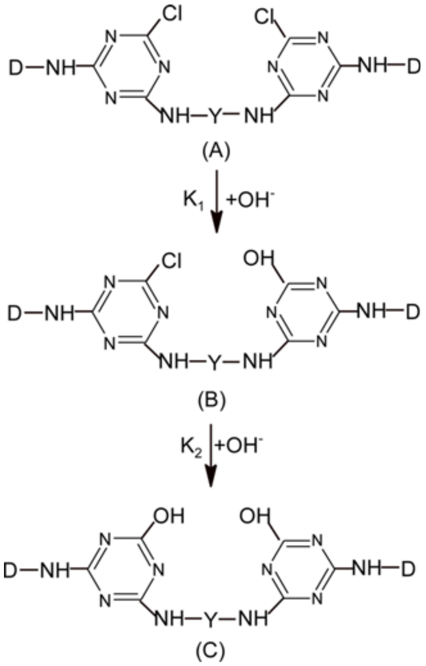

Figure 3. Reaction mechanism of alkaline hydrolysis of C.I. Reactive Red 120, where D in the chemical structure denotes a dye chromogen and Y denotes a benzene ring.

For a dye such as bis(monochloro-s-triazine) reactive dye C.I. Reactive Red 120 that contains a symmetrical chemical structure, the underlying reaction mechanism for nucleophilic substitution with an alkaline buffer solution can be represented in a simplified form as shown in Figure 3.

The hydrolytic reaction, on extending the reaction time, proceeded until the bis(monochloro-s-triazine) dye A was hydrolyzed to monochloromonohydroxybis-s-triazine dye B. Further, B was hydrolyzed to bis(monohydroxy-s-triazine) dye C.

Figure 4 shows the chromatograms of C.I. Reactive Red 120 (concentration=400 mg/*l*) obtained upon being hydrolyzed for 0, 30, 60, and 120 min at 90 °C, pH=11.0. Structurally, as the various hydrolytic products differed only by an atom or a group, the peaks of the three forms appeared one after the other and the retention times of peaks were very close (Figure 4). In reversed phase liquid chromatography, each dye form represented by a different peak could be determined from the polarity of the substituent groups of the dye, with the more polar molecule appearing first followed by the less polar molecule [18,27]. As the polarity of -OH is higher than that of -Cl, the sequence of appearance of the three dye forms in the chromatogram would be the bis(monohydroxy-s-triazine) dye form C (retention time 6.1 min) followed by the monochloromonohydroxybis-s-triazine dye form B (retention time 6.5 min) and then the bis(monochloro-s-triazine) dye form A (retention time 7.0 min).

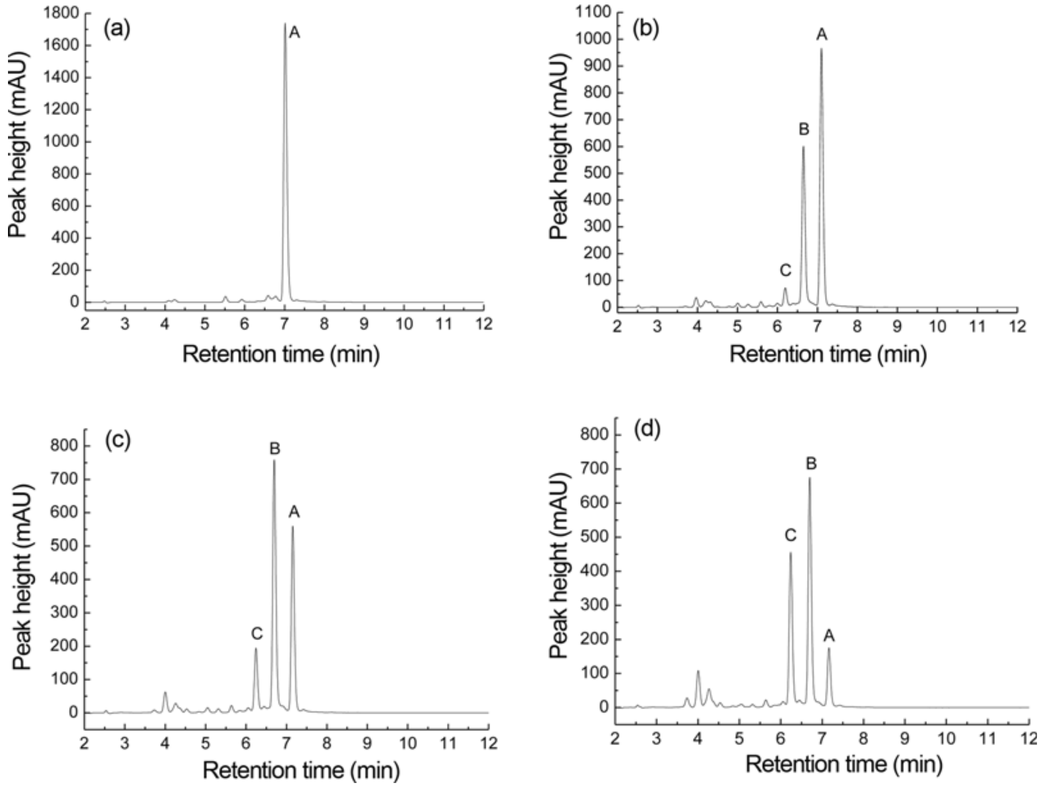

Figure 4. Chromatogram of C.I. Reactive Red 120 at various hydrolysis times at 90 °C, pH 11.0; (a) hydrolysis time: 0 min, (b) hydrolysis time: 30 min, (c) hydrolysis time: 60 min, and (d) hydrolysis time: 120 min.

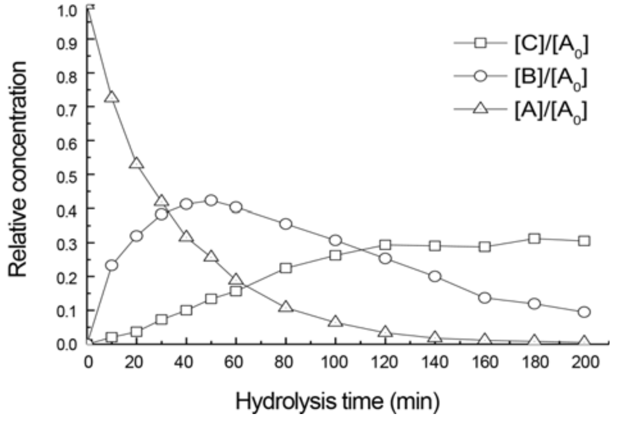

Figure 5. Plot of relative concentration of different products of hydrolysis of the dye against time at 130 °C, pH 8.0, where $[A]_0$ denotes the initial concentration of bis(monochloro-s-triazine) A at 0 min, $[C]/[A]_0$ denotes relative concentration of bis(monohydroxy-s-triazine) C against $[A]_0$, $[B]/[A]_0$ denotes relative concentration of monochloromonohydroxybis-s-triazine B against $[A]_0$, and $[A]/[A]_0$ denotes relative concentration of bis(monochloro-s-triazine) A against $[A]_0$.

The peak areas of the three forms of the dye were obtained by HPLC. All the forms display a similar response factor; thus, the concentration of each form would be proportional to its peak area in the chromatogram [13,14]. The ratio of the concentrations of the dye forms could be obtained from the ratio of the peak areas. A plot of the hydrolysis time on the *x*-axis and the relative concentrations (the concentration of each form of the dye against the initial concentration ($[A]_0$) of the dye form A) on the *y*-axis provided the hydrolysis curves under various conditions. Thus, for example, the curves of the hydrolysis indicating the results of the hydrolysis at 130 °C, pH 8.0 have been shown in Figure 5.

Increasing the hydrolysis time initially showed a constant decrease in the concentration of bis(monochloro-s-triazine) A (Figure 5) with a concomitant increase in monochloromonohydroxybis-s-triazine B whose concentration gradually declined upon attaining a maximum value. The concentration of bis(monohydroxy-s-triazine) C kept rising gradually. These results follow the dynamic mechanism of the first-order consecutive reaction [13,14]. The concentration dynamics of the different products of hydrolysis with time may also be observed from their changing peak heights in the chromatogram (Figure 4).

Reactivity of the Bis(monochloro-s-triazine) Dye at 90, 100, 110, 120, and 130 °C

Previous results have shown that the decreasing rate of hydrolysis of the bis(monochloro-s-triazine) dye at alkaline pH is in agreement with the equation for pseudo-first-order

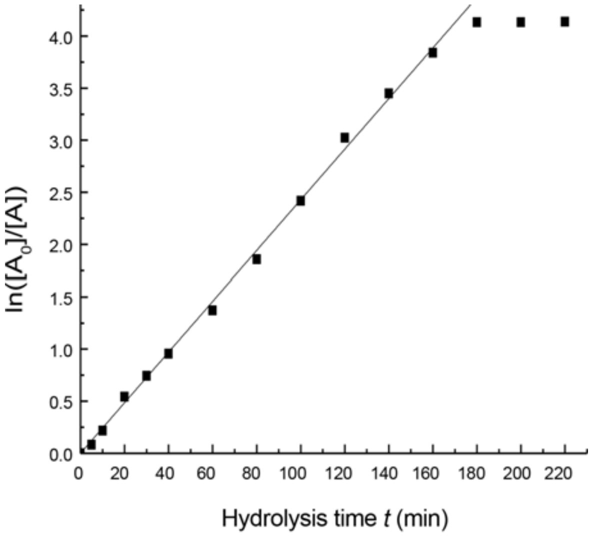

Figure 6. Plot of ln($[A]_0/[A]$) vs. hydrolysis time at 90 °C, pH 11.0.

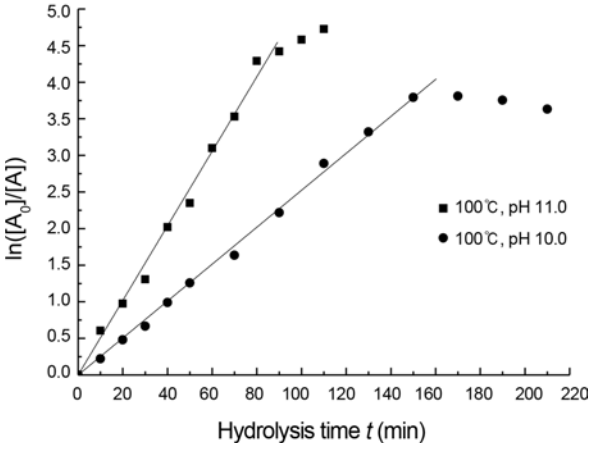

Figure 7. Plot of ln($[A]_0/[A]$) vs. hydrolysis time at 100 °C, various pH.

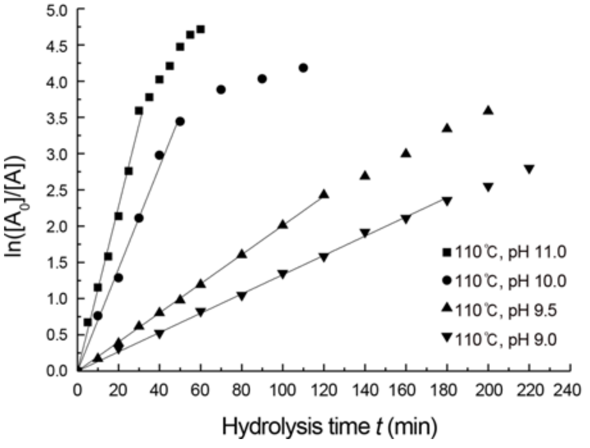

Figure 8. Plot of ln($[A]_0/[A]$) vs. hydrolysis time at 110 °C, various pH.

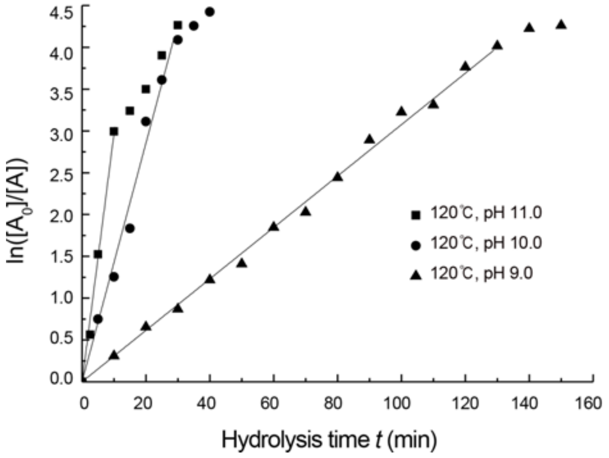

Figure 9. Plot of ln($[A]_0/[A]$) vs. hydrolysis time at 120 °C, various pH.

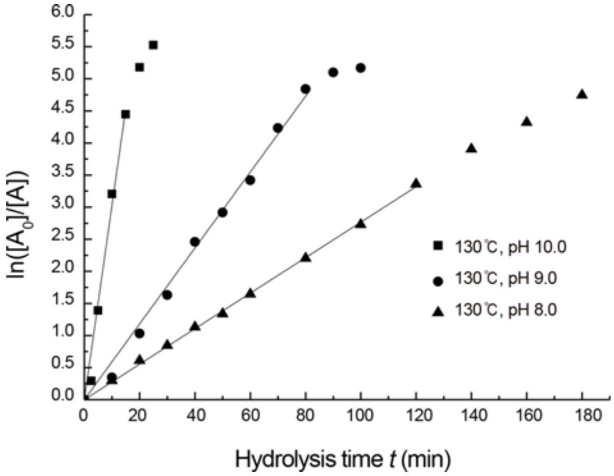

Figure 10. Plot of ln($[A]_0/[A]$) vs. hydrolysis time at 130 °C, various pH.

kinetics (equation (1)) [13,14]:

$$-d[A]/dt = k_1[A] \tag{1}$$

where $[A]$ is the concentration of bis(monochloro-s-triazine) dye at time t; k_1 is the pseudo-first-order rate constant of hydrolysis. By integrating equation (1) and replacing the concentration of the bis(monochloro-s-triazine) dye with its peak area, equation (2) could be obtained:

$$\ln([A]_0/[A]) = k_1 t \tag{2}$$

where $[A]_0$ and $[A]$ correspond to the bis(monochloro-s-triazine) dye at time $t=0$ and at a later time t, respectively.

The plots of ln($[A]_0/[A]$) against time t at varying temperatures yield a series of straight lines passing through the origin (Figures 6-10). The slope of the plot provides the rate constant k_1.

The values for the rate constants k_1 and linear correlation

Table 2. The hydrolysis rate constant k_1 of the bis(monochloro-s-triazine) dye and linear correlation coefficients R^2 at various temperatures and pH values

Temperature (°C)	pH	k_1 (min^{-1})	R^2	Range of linear regression (min)
90	11.0	0.0243	0.9991	0-160
100	10.0	0.0252	0.9990	0-150
	11.0	0.0509	0.9958	0-80
110	9.0	0.0133	0.9993	0-180
	9.5	0.0201	0.9999	0-120
	10.0	0.0705	0.9972	0-50
	11.0	0.1134	0.9954	0-30
120	9.0	0.0307	0.9972	0-110
	10.0	0.1428	0.9905	0-30
	11.0	0.2864	0.9856	0-10
130	8.0	0.0276	0.9994	0-120
	9.0	0.0591	0.9980	0-70
	10.0	0.2988	0.9933	0-15

coefficients R^2 obtained from fitting the plots in Figures 6-10 have been presented in Table 2. At a later stage in the hydrolysis, as the slope of the straight line deviates from a linear relationship, the graph is fitted at only the initial stage of the reaction. The fitting is carried out with as many fitting points as possible to obtain the maximum related coefficients and its range of linear regression has also been displayed in Table 2.

The hydrolysis rate constants k_1 at 100 °C, pH 9.0 and 130 °C, pH 11.0 could not be detected owing to the rather slow and excessively fast reactions respectively. Further, to obtain the rate constants close enough to the constant at 90 °C, pH 11.0, two more hydrolysis experiments (110 °C, pH 9.5 and 130 °C, pH 8.0) were carried out.

The linear correlations of the curves from $\ln([A]_0/[A])$ against hydrolysis time t were found to be significant in the given range of linear regression (Table 2). A good linear correlation indicated that the hydrolysis of the bis(monochloro-s-triazine) reactive dye at various temperatures and pH values strictly follow the pseudo-first order reaction. Within a temperature range of 100-130 °C, with increase in pH, the hydrolysis rate constant of the bis(monochloro-s-triazine) dye increased. However, the rate constants were low at high temperatures and low pH. The hydrolysis rate constants k_1 obtained under these conditions (100 °C, pH 10.0; 110 °C, pH 9.5; 120 °C, pH 9.0; 130 °C, pH 8.0) were very close to those from 90 °C, pH 11.0, which suggested that a decrease in pH could reduce hydrolysis of the dye at higher temperatures. Although the rate constants k_1 under these conditions were not completely equal to those at 90 °C, pH 11.0, it is predicted that a low pH value should always be found to get similar reactivity at high temperature.

The equation for rate of formation of monochloromonohydroxybis-s-triazine at any point in time is as follows:

$$d[B]/dt = k_1\,[A] - k_2\,[B] \tag{3}$$

where $[A]$ and $[B]$ represent the concentrations of bis (monochloro-s-triazine) A and monochloromonohydroxybis-s-triazine B at any time t, respectively; k_1 and k_2 are the hydrolysis rate coefficients of A and B, respectively.

When the concentration of B reached a maximum, the rate was given by $d[B]/dt=0$ [13,14] and the hydrolysis rate coefficient k_2 could be calculated as follows:

$$k_2 = k_1[A]/[B] \tag{4}$$

where [A] and [B] represent the concentrations (or relative concentrations) of A and B, respectively, at the time that [B] reaches a maximum.

As the time interval for withdrawing the samples is not infinitesimally small, when k_2 was calculated, the values of [A] and [B] were obtained from the results of a fifth-order polynomial fitting of hydrolysis curves, to avoid error caused by random sampling. The polynomial fitting equations, correlation coefficients R^2, and the values of the rate constants k_2 in various conditions are presented in Table 3.

The hydrolysis of B was similar to that of A at various temperatures and pH values. As expected, with increase in pH, the hydrolysis rate constant k_2 of B increased at all temperatures. However, the hydrolysis rate constant was low at high temperatures and low pH. The rate constant k_2 under the tested hydrolytic conditions (100 °C, pH 10.0; 110 °C, pH 9.5; 120 °C, pH 9.0; 130 °C, pH 8.0) was close to that at 90 °C, pH 11; therefore, the bis(monochloro-s-triazine) dye under these conditions displays similar reactivity to that at 90 °C, in pH, to obtain similar reactivity to the conventional dyeing conditions. At the same time, the results showed that the hydrolysis of the dye was not main reason for the loss of the dye at high temperatures and low pH. Studies on the reactivity of the dye at various temperatures and pH values assist in determining the appropriate pH for applications and are useful for avoiding violent hydrolysis of the dye.

Stability of C.I. Reactive Red 120 at High Temperatures

The complex hydrolysis mechanism of the dye that contains imino bridge groups and linking groups also revealed that the sum of relative concentrations of the three forms ($[A]/[A]_0+[B]/[A]_0+[C]/[A]_0$) in the hydrolysis reaction of bis(monochloro-s-triazine) dye C.I. Reactive Red 120 was not equal to 1 at any time (except hydrolysis at 0 min), as represented in Figure 5. This suggests formation of some unknown side products in the process of the hydrolysis of the dye.

The chromatograms at various hydrolysis times at 130 °C, pH 8.0 are displayed in Figure 11. The peaks in the chromatograms (Figure 11) suggest existence of unknown materials from the start of the hydrolysis reaction. With increase in the hydrolysis time, the peak height and the peak area of the

Table 3. The polynomial fitting equations and correlation coefficients R^2 and the rate constants k_2 under various conditions

Temp. (^{o}C)	pH	Fitting equation	R^2	$[B]_{max}/[A]_0$	t_{Bmax} (min)	$[A]_t/[A]_0$	k_2 (min^{-1})
90	11.0	A: $Y=1.01631-0.02552X+3.14187E-4X^2-2.18039E-6X^3+7.82237E-9X^4-1.1034^5E-11X^5$	0.9917	0.4339	58.74	0.2448	0.0137
		B: $Y=-0.02306+0.02137X-3.58012E-4X^2+2.66599E-6X^3-9.46297E-9X^4+1.28135E-11X^5$	0.9984				
100	10.0	A: $Y=1.00429-0.02332X+2.49701E-4X^2-1.53907E-6X^3+5.25466E-9X^4-7.48377E-12X^5$	0.9991	0.4641	53.16	0.2778	0.0151
		B: $Y=0.0393+0.02277X-4.45858E-4X^2+3.98534E-6X^3-1.70671E-8X^4+2.76791E-11X^5$	0.9967				
	11.0	A: $Y=0.98674-0.05157X+0.00133X^2-1.90211E-5X^3+1.38927E-7\ X^4-3.95668E-10X^5$	0.9963	0.4848	27.64	0.2480	0.0260
		B: $Y=0.0091+0.04602X-0.00157X^2+2.32883E-5X^3-1.64932E-7\ X^4+4.48443E-10\ X^5$	0.9880				
110	9.0	A: $Y=0.9952-0.01477X+1.36878E-4X^2-9.18503E-7X^3+3.51379E-9X^4-5.35103E-12X^5$	0.9991	0.4373	114.95	0.2172	0.0066
		B: $Y=0.00469+0.01413X-1.90899E-4X^2+1.34063E-6X^3-4.81121E-9X^4+6.69218E-12X^5$	0.9941				
	9.5	A: $Y=1.00607-0.01934X+1.62119E-4X^2-6.68356E-7X^3+1.15029E-9X^4-2.7941E-13X^5$	0.9996	0.4448	65.05	0.2706	0.0122
		B: $Y=0.00947+0.01952X-3.22577E-4X^2+2.46214E-6X^3-9.03351E-9X^4+1.24634E-11X^5$	0.9949				
	10.0	A: $Y=0.9924-0.06668X+0.00199X^2-3.11872E-5X^3+2.44919E-7X^4-7.50286E-10X^5$	0.9973	0.4351	19.52	0.2510	0.0407
		B: $Y=0.00676+0.05777X-0.00271X^2+5.3681E-5X^3-4.84426E-7X^4+1.61303E-9X^5$	0.9852				
	11.0	A: $Y=0.99378-0.09777X+0.00444X^2-1.12014E-4X^3+1.51501E-6X^4-8.41144E-9X^5$	0.9985	0.4310	13.24	0.0260	0.0685
		B: $Y=0.00534+0.08329X-0.00564X^2+1.60984E-4X^3-2.18043E-6X^4+1.13417E-8X^5$	0.9944				
120	9.0	A: $Y=0.99939-0.03199X+5.54723E-4X^2-5.93344E-6X^3+3.38836E-8X^4-7.63794E-11X^5$	0.9991	0.4528	42.84	0.2838	0.0192
		B: $Y=0.03551+0.0276X-6.68562E-4X^2+7.49863E-6X^3-4.17598E-8X^4+9.0476E-11X^5$	0.9956				
	10.0	A: $Y=0.99558-0.15137X+0.01294X^2-6.27285E-4X^3+1.49302E-5X^4-1.33893E-7X^5$	0.9989	0.4351	11.33	0.2504	0.0822
		B: $Y=-7.06239E-4+0.10154X-0.0083X^2+2.93405E-4X^3-4.96659E-6X^4+3.21456E-8X^5$	0.9975				
	11.0	A: $Y=1.01284-0.12052X-0.00488X^2+0.00122X^3-5.52414E-5X^4+7.69598E-7X^5$	0.9949	0.3777	7.27	0.2103	0.1595
		B: $Y=0.00136+0.13467X-0.01681X^2+9.10378E-4X^3-2.49508E-5X^4+2.77982E-7X^5$	0.9911				
130	8.0	A: $Y=0.99185-0.03005X+4.56614E-4X^2-3.87368E-6X^3+1.66909E-8X^4-2.8E-11X^5$	0.9992	0.4212	45.59	0.2705	0.0177
		B: $Y=0.01253+0.02384X-4.88613E-4X^2+4.34632E-6X^3-1.86711E-8X^4+3.11448E-11X^5$	0.9938				
	9.0	A: $Y=1.00238-0.04149X+4.52895E-4X^2+3.198E-6X^3-8.66104E-8X^4+4.08888E-10X^5$	0.9993	0.4828	21.95	0.3256	0.0399
		B: $Y=8.74154E-4+0.05859X-0.00251X^2+4.6804E-5X^3-4.19719E-7X^4+1.44467E-9X^5$	0.9996				
	10.0	A: $Y=1-0.24131X+0.02292X^2-0.00105X^3+2.24073E-5X^4-1.75253E-7X^5$	1.0000	0.4303	5.64	0.2025	0.1617
		B: $Y=4.996E-16+0.17722X-0.02968X^2+0.00218X^3-7.74117E-5X^4+1.05977E-6X^5$	1.0000				

$[B]_{max}/[A]_0$ is the maximam value of curve $[B]/[A]_0$ obtained from the fitting results of the hydrolysis curve (Table 3), t_{Bmax} is the time when the value of $[B]/[A]_0$ is equal to $[B]_{max}/[A]_0$ and $[A]_t/[A]_0$ is the value of $[A]/[A]_0$ when t is equal to t_{Bmax}.

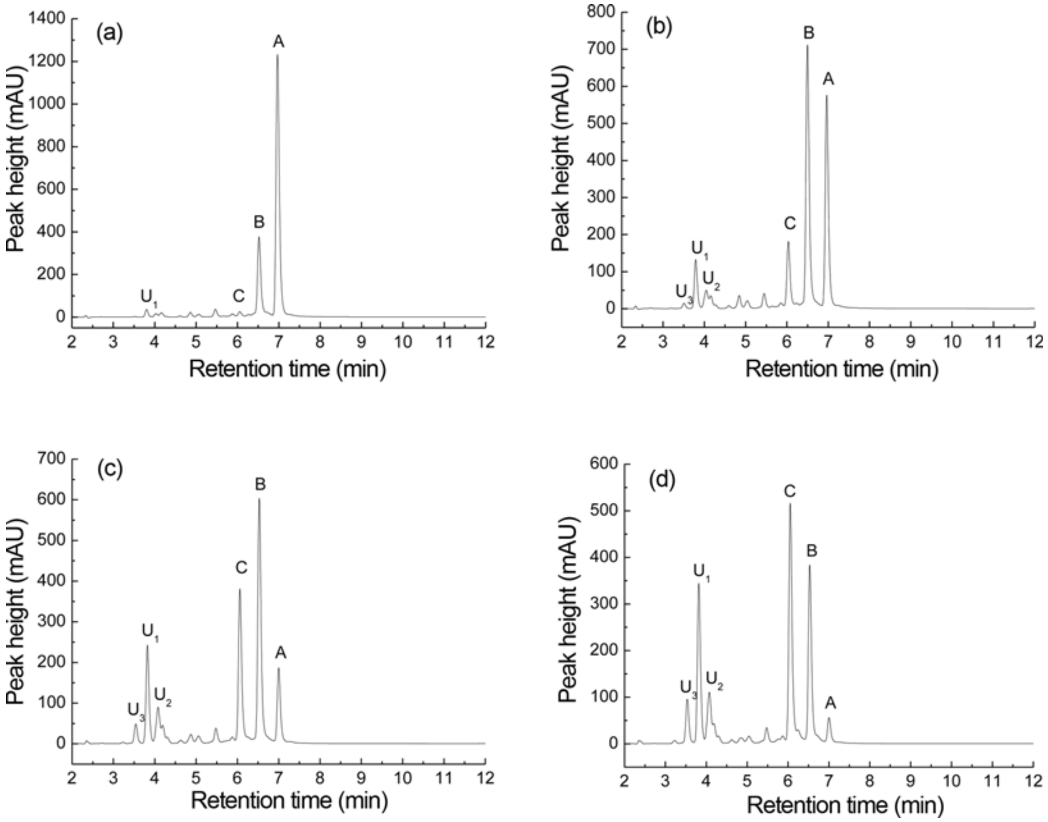

Figure 11. Chromatograms of C.I. Reactive Red 120 recorded after varying durations of hydrolysis in buffer of pH 8.0 at 130 °C, where A, B, and C represent bis(monochloro-s-triazine) form, monochloromonohydroxybis-s-triazine form, and bis(monohydroxy-s-triazine) form of the dye, respectively, and U_1, U_2, and U_3 represent unknown materials; (a) hydrolysis time: 10 min, (b) hydrolysis time: 40 min, (c) hydrolysis time: 80 min, and (d) hydrolysis time: 120 min.

Table 4. Relative concentrations of the dye, the hydrolyzed dye and the degraded dye in various hydrolysis times *t* at 90 °C, pH 11.0 and 130 °C, pH 8.0

t (min)	90 °C, pH 11.0			130 °C, pH 8.0		
	$([C]+[B]+[A])/[A]_0$	$1-([C]+[B]+[A])/[A]_0$	$[C]/[A]_0$	$([C]+[B]+[A])/[A]_0$	$1-([C]+[B]+[A])/[A]_0$	$[C]/[A]_0$
0	1	0	0	1	0	0
20	0.90397	0.09603	0.03238	0.88626	0.11374	0.03679
40	0.87847	0.12153	0.08407	0.82810	0.17190	0.1004
60	0.81427	0.18573	0.13424	0.74872	0.25128	0.15661
80	0.76451	0.23549	0.19671	0.68753	0.31247	0.22466
100	0.73860	0.26140	0.25896	0.63331	0.36669	0.26258
120	0.70686	0.29314	0.29909	0.58012	0.41988	0.29344
140	0.68860	0.31140	0.33471	0.50885	0.49115	0.29053
160	0.68009	0.31991	0.37111	0.44265	0.55735	0.28748
180	0.66722	0.33278	0.40111	0.43967	0.56034	0.31189

unknown materials increases rapidly. The retention time for these unknown materials lies between 2.5 min to 4.5 min, which is shorter than that of the dyes and hydrolyzed dyes, implying that most of them should be low molecular compounds that have probably arisen from the decomposition of the parent dye.

It should be noted that degradation products also appear at different levels under other conditions beside the above discussed condition (130 °C, pH 8.0). The total relative concentration of the dye hydrolysates $(([C]+[B]+[A])/[A]_0)$

and the total relative concentration of the degraded dye ($1-([C]+[B]+[A])/[A]_0$) at various hydrolysis times t at 130 °C, pH 8.0 and 90 °C, pH 11.0 may be seen in Table 4. Since the loss of the dye in the reaction process mainly comes from its degradation products and the C form that is unable to react with cellulose, the relative concentration of the bis (monohydroxy-s-triazine) dye ($[C]/[A]_0$) also was compared (Table 4). As the dye shows similar reactivity at 130 °C, pH 8.0 and at 90 °C, pH 11.0, the difference in the relative concentrations of C at the two conditions was small, while the total relative concentration of the degraded dye at higher temperature was much higher than that at lower temperature. Particularly, in the later stage of the reaction, the total relative concentration of the degraded dye at high temperature was almost twice that observed at low temperature which indicated that most of loss of dye at 130 °C, pH 8.0 was caused by the degradation of the dye instead of the hydrolysis of the dye.

It is possible that the stability of the azo group, bridge group, and linking group in the dye molecule was reduced in an alkaline solution at high temperature. However, the detection of degradation products at 536 nm indicates that these products feature absorption in the visible region. The absorption of C.I. Reactive Red 120 in the visible region is determined by long conjugated double bonds in the parent dye molecular. Given that conjugated double bond in the active group is short, the active group presents absorption only in UV region [18]. The imine bridge or liking group cuts off conjugation between the parent dye and the active group. Thus, the absorption of the degradation products of the dye in the visible region suggests that degradation products likely contain the chromogen of C.I. Reactive Red 120. The degradation observed may be mainly attributed to cleavage of the bridging and linking groups. Further study of the components and contents of the unknown materials would be meaningful to both the hydrolysis mechanism of the reactive dyes at high temperatures and an improvement for their applications. Definitely further investigations are required.

Conclusion

The study of reactivity and stability of the dye at high temperatures revealed a double-sided behavior of the bis(monochloro-s-triazine) reactive dye C.I. Reactive Red 120. First, the study of reactivity of the dye at high temperatures confirmed in theory that the pH value is the key factor influencing the reactivity of the dye at a constant temperature. The hydrolysis of the active group may be controlled by means of decreasing the pH of the dye bath at a high temperature to inhibit acute hydrolysis of the active group, suggesting that the hydrolysis of the bis(monochloro-s-triazine) active group is not main reason for loss of the dye at high temperature and low pH. Second, the study of the stability of the dye at high temperatures showed that the loss of the dye comes not just from the hydrolysis of the dye but to a large extent from the degradation of the dye, especially the degradation of the linking groups and the bridge groups. The double-sided behavior implies that the designing of molecular structures of types of reactive dyes used at high temperatures should focus more on the stability of the parent dyes at higher temperatures.

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