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The influence of temperature on the kinetics of concurrent hydrolysis and methanolysis reactions of a monochlorotriazine reactive dye

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Abstract

The competitive methanolysis and alkaline hydrolysis reactions of a monochlorotriazine reactive dye were studied at 50–80°C, and the rate constants for these reactions were determined. It was found that each 10°C temperature increase led to more than a two-fold increase in the overall reactivity of the dye. In the temperature range employed, the rate constant for the methanolysis process was 6–13 times higher than the rate constant for hydrolysis. Further, the preference for the methanolysis reaction decreased with increasing temperature. For each 10°C temperature rise, the rate constant for hydrolysis increased approximately three-fold and the rate constant for methanolysis increased more than two-fold. Rate constants for both reactions were found to be pseudo-first-order. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Monochlorotriazine reactive dye; Hydrolysis; Methanolysis; Kinetics; Temperature; HPLC

1. Introduction

In the application of reactive dyes to cellulosic fibers under alkaline conditions, hydrolysis of the reactive dyes always competes with the fixation step. For practical usefulness a high ratio of fixation to hydrolysis is needed. Since dye–fiber fixation takes place after the dye has been adsorbed on the fibre, the efficiency of the fixation process is strongly influenced by the affinity of the dye for cellulose.

Owing to the complexity of the cellulose–aqueous dyebath heterogeneous system, where the adsorption and diffusion of reactive dyes have to be taken into consideration, the homogenous alcohol–water system has often been used to study the kinetics of competitive fixation and hydrolysis reactions [1–23]. Such studies have focused on the influence of pH, temperature, and alcohol concentration on the competing reactions, as well as on the suitability of different hydroxylated compounds as models for cellulose. With regard to the latter aspect of these studies, methanol has been proposed as a suitable model [23].

The aim of the present work was to study the influence of temperature, in the range of 50–80°C, on the fixation and hydrolysis of a monochlorotriazine reactive dye (C.I. Reactive Red 43). In these studies, a mixture of methanol and alkaline

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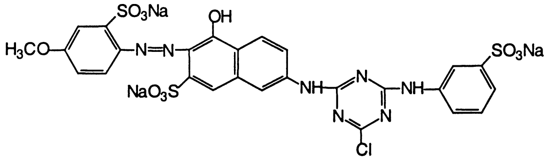
buffer solution, corresponding to a 10:1 liquor ratio, was used. Time-dependent changes in the amounts of active and solvolysed forms of the dye were monitored simultaneously by high-performance liquid chromatography (HPLC).



2. Experimental

2.1. Materials

C.I. Reactive Red 43 was obtained from BASF. The pH 11 buffer was obtained from Riedel-de Haën AG, pH 7 buffer was obtained from Carlo Erba, methanol was obtained from Carlo Erba, and HCl was obtained from KT Podnart, Slovenia. The chemicals used as the mobile phase in HPLC analyses were MeCN (from Riedel-de Haën AG), $Bu_4N^+Br^-$ (from Fluka Chemie AG), $NH_4H_2PO_4$ (from Kemika), and deionized water.

2.2. Hydrolysis and methanolysis reactions

A solution of dye (0.025 g) in pH 7 buffer (5 ml) and deionised water (25 ml) was heated to a predetermined temperature (50, 60, 70 or 80°C), and then added to a mixture of pH 11 buffer (220 ml) and methanol (25 g) that was preheated to the same temperature. The resultant dye solution (pH 10.92) was stirred at constant temperature, and 10 ml aliquots were withdrawn at various time intervals, cooled, and neutralised by the addition of dilute HCl.

Table 1
Gradient system employed in HPLC analyses

Time (min)	Solvent A[a] (%)	Solvent B[b] (%)
0	20	80
5	30	70
10	40	60

[a] A, 100% MeCN containing 0.025 M $Bu_4N^+Br^-$.

[b] B, 30/70 mixture of MeCN containing 0.025 M $Bu_4N^+Br^-$ and deionised water containing 0.05 M $NH_4H_2PO_4$.

2.3. HPLC analysis

Neutralised dye solutions were analysed by a HPLC using a 250×4 mm C-18 ion-pair reversed-phase column (Hypersil ODS 3 μm, from Säulentechnik Knauer) and a mixture of solvents A (100% MeCN containing 0.025 M $Bu_4N^+Br^-$) and B (30/70 mixture of MeCN containing 0.025 M $Bu_4N^+Br^-$ and deionised water containing 0.05 M $NH_4H_2PO_4$) [24] as the mobile phase. The gradient system (Table 1) was used at a flow rate of 1.3 ml/min, and the injected volume of dye solution was 20 μl. Dye solutions were detected at 500 nm, using a Spectra Focus Forward Optical Scanning detector (Thermo Separation Products).

3. Results and discussion

Monochlorotriazine reactive dyes react with nucleophiles by the nucleophilic addition–elimination substitution mechanism [25]. In the present reaction medium, hydroxide ions and methoxide ions are the important nucleophiles [3,7,16,26]. The reactions can be represented in simplified form shown in Fig. 1, where D denotes the dye chromogen.

The HPLC chromatograms recorded at different times and temperatures showed the expected decrease in monochlorotriazine dye concentration and an increase in the concentration of methanolysed and

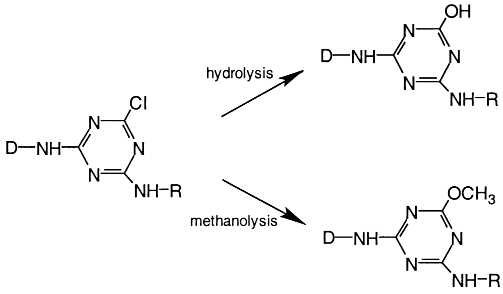


Fig. 1. Competitive hydrolysis and methanolysis reactions of a monochlorotriazine dye.

hydrolysed forms. Also, significant time-dependent changes in the proportions of the various dye forms were observed. Fig. 2 shows an example of the chromatograms produced at 70°C.

By assuming that nucleophilic attack on the reactive triazine group is the rate-determining step of the hydrolysis and methanolysis reactions and that the concentrations of nucleophilic species are constant when using a large excess of the alcohol and alkaline buffer solution, the reaction rates at constant temperature can be determined with the aid of Eqs. (1) and (2) [27,28]:

$$\text{rate of hydrolysis} = \frac{\mathrm{d}[H]}{\mathrm{d}t} = k_{\mathrm{H}} \cdot [A] \qquad (1)$$

$$\text{rate of methanolysis} = \frac{\mathrm{d}[M]}{\mathrm{d}t} = k_{\mathrm{M}} \cdot [A] \qquad (2)$$

where $[A]$, $[H]$, and $[M]$ are the concentrations of monochlorotriazine, hydrolysed and methanolysed forms of the dye at reaction time t, and k_{H} and k_{M} are the rate constants for hydrolysis and methanolysis.

The overall rate of decrease in the concentration of the monochlorotriazine dye form at constant temperature was determined by Eq. (3):

$$\frac{-\mathrm{d}[A]}{\mathrm{d}t} = k \cdot [A] \qquad (3)$$

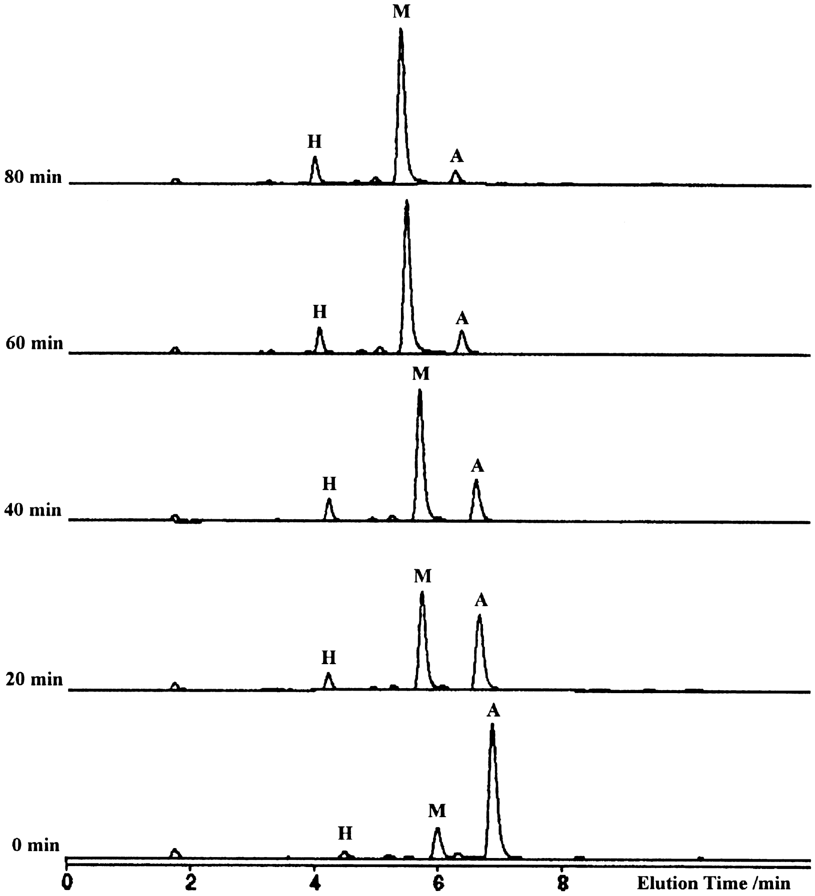


Fig. 2. HPLC chromatograms of C.I. Reactive Red 43 following treatment with alkaline methanol solution at 70°C, where A, M and H are the active monochlorotriazine, the methanolysed and the hydrolysed dye, respectively.

in which k is the sum of the rate constants for the parallel methanolysis and hydrolysis reactions ($k_M + k_H$). Integrating Eq. (3) and replacing the concentrations of the monochlorotriazine dye form with the peak areas obtained from chromatograms gives Eq. (4):

$$\ln\left(\frac{A_0}{A}\right) = k \cdot t \tag{4}$$

where A_0 and A are the peak areas of the active monochlorotriazine form at time $t = 0$ and at a later reaction time t.

By plotting $\ln(A_0/A)$ against reaction time at constant temperature, a straight line passing through the origin was obtained for all temperatures (Fig. 3). Using Eq. (4), pseudo-first-order kinetics was observed at 80°C within 45 min, at 70°C within 70 min, and at 60 and 50°C within 80 min. The slope of the straight line corresponded to the overall reaction rate constant (k). The overall rate constants, as well as the squares of the correlation coefficients in the linear region of the plots in Fig. 3 are given in Table 2.

Dividing Eq. (2) by Eq. (1) gives Eq. (5), and integrating Eq. (5) between the limits of concentrations of the products at the initial time of measurement and at a later reaction time, gives Eq. (6):

$$\frac{d[M]}{d[H]} = \frac{k_M}{k_H} \tag{5}$$

$$\frac{k_M}{k_H} = \frac{M - M_0}{H - H_0} \tag{6}$$

in which M and M_0 are the concentrations of the methanolysed forms, and H and H_0 are the concentrations of the hydrolysed forms of the dye at times t and 0.

Since the methanolysed and hydrolysed forms have about the same extinction coefficient, their concentrations in Eq. (6) can be replaced by the values of their peak areas. Based on Eq. (6), it can be seen that the ratio of the concentrations of the hydrolysis and methanolysis products is equal to the ratio of the rate constants for the reactions. In addition, the ratio of the methanolysis to hydrolysis rate constants at a specified temperature can be determined from Eq. (6), as the slope of the plot of the concentration of the methanolysed form ($M - M_0$) versus the concentration of hydrolysed form ($H - H_0$) within the time interval for pseudo-first-order kinetics.

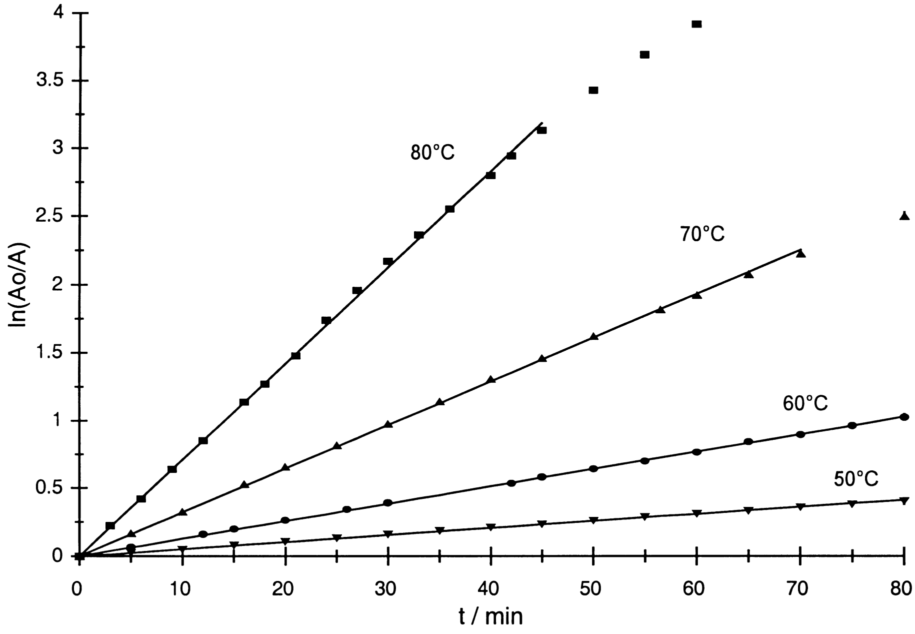


Fig. 3. Plot of $\ln(A_0/A)$ versus time (t) at various temperatures.

The average values for the ratios of rate constants for the methanolysis and hydrolysis reactions, and the squares of the correlation coefficients in the linear regression of $M - M_0$ with $H - H_0$ at different temperatures are shown in Table 3. The ratio of the rate constants for the competitive reactions (k_M/k_H) was relatively constant at constant temperature.

We found that the methanolysis reaction was faster at each temperature and that the preference for the methanolysis reaction decreased with increasing temperature. The latter results are consistent with the prior observation that which indicated the concentration of hydroxide ions in the homogeneous mixture increased faster than the concentration of methoxide ions as temperature increased [26]. A 10°C temperature increase produced a 1.3-fold decrease in k_M/k_H.

The rate constants for the methanolysis and hydrolysis reactions at constant temperature can be calculated by Eq. (7) and by considering the experimentally determined ratio of rate constants. The average values for the pseudo-first-order rate constants for methanolysis and hydrolysis are summarized in Table 4.

$$k = k_H\left(\frac{k_M}{k_H} + 1\right) \tag{7}$$

The results in Tables 2 and 4 indicate that each 10°C increase caused a 2.4-fold increase in the overall rate constant for the change in monochlorotriazine dye concentration, with a 2.3-fold increase in the methanolysis rate constant and a 3.1-fold increase in the hydrolysis rate constant.

It is well known that the reactivity of a reactive dye is determined by the type of reactive group, and that substituents present in the dye structure influence the reactivity of the reactive group. Reactivity also depends strongly on the temperature and pH of the medium. The dye used in this study contains two imino (–NH–) bridging groups, one linking the chromogen to the reactive group and the other connecting the sulfophenyl group to the triazine ring. It has been reported that an imino bridge [29,30] as well as the others groups (e.g. phenolics) [10,31] in the dye molecule can dissociate in an alkaline medium. As the temperature increases, a higher level of dissociation (deprotonation) of these groups is expected and, consequently, a reduction in the positive character of the carbon atom bearing the leaving group occurs, lowering the reactivity of the dye.

In the present work, the pH of the reaction mixture decreased by an average of 0.1 unit per 10°C increase in temperature. Lowering the pH lowered the concentration of the nucleophilic anions, although it did not change the ratio of methoxide ions to hydroxide ions. The concentration ratio of these species remained constant at each pH, at constant temperature, and decreased, according to thermodynamic hydroxide–methoxide equilibrium constants [26], with increasing temperature. The lower rate constant change when the

Table 2
Overall reaction rate constants (k) for the consumption of monochlorotriazine dye and the squares of the correlation coefficients in linear regression (R^2) at different temperatures

T (°C)	k (min^{-1})	R^2
50	5.09×10^{-3}	0.9984
60	1.28×10^{-2}	0.9995
70	3.18×10^{-2}	0.9996
80	7.08×10^{-2}	0.9996

Table 3
The ratios of the rate constants for methanolysis (M) to hydrolysis (H) and the squares of the correlation coefficients in the linear regression (R^2) at 50–80°C

T (°C)	k_M/k_H	R^2
50	13.0	0.9987
60	10.6	0.9997
70	7.8	0.9968
80	5.6	0.9967

Table 4
Rate constants for the increase in methanolysed (k_M) and hydrolysed (k_H) forms of C.I. Reactive Red 43 at 50–80°C

T (°C)	k_M (min^{-1})	k_H (min^{-1})
50	4.73×10^{-3}	3.6×10^{-4}
60	1.17×10^{-2}	1.1×10^{-3}
70	2.82×10^{-2}	3.6×10^{-3}
80	6.01×10^{-2}	1.07×10^{-2}

temperature was increased from 70 to 80°C, versus the change observed for 10°C increases at lower temperatures, could be due to the reduced increase in the concentrations of reacting anions, as well as the reduced chemical reactivity of the dye following deprotonation.

4. Conclusions

The decrease in monochlorotriazine reactive dye concentration in a homogeneous mixture of methanol and aqueous alkali has been shown to follow pseudo-first-order kinetics during the initial stages of the reaction conducted at 50–80°C. The methanolysis reaction is always faster than the concurrent hydrolysis reaction, due to the higher reactivity of meth-oxide ions. The ratio of the rate constants for methanolysis versus hydrolysis decreases with increasing temperature, suggesting that the reactive dye exhibits higher selectivity towards cellulose fibres at lower temperatures. As the reaction temperature increases, the rate of hydrolysis is greater than the methanolysis rate. It should be mentioned that temperature-induced variations in the ratio of reacting anions and/or structural changes in the dye can contribute to the observed reaction rate changes.

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