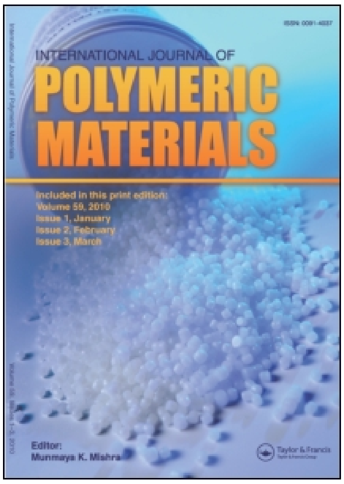


**International Journal of Polymeric Materials**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

# Influence of Temperature on Kinetics of Hydrolysis of Monochlorotriazine Reactive Dye

M. Klancnik[a]
[a] Department of Textiles, University of Ljubljana, Ljubljana, Slovenia

**To cite this Article** Klancnik, M.(2000) 'Influence of Temperature on Kinetics of Hydrolysis of Monochlorotriazine Reactive Dye', International Journal of Polymeric Materials, 47: 4, 735 — 739
**To link to this Article: DOI:** 10.1080/00914030008031329
**URL:** http://dx.doi.org/10.1080/00914030008031329

*Intern. J. Polymeric Mater.*, 2000, Vol. 47, pp. 735–739
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

# Influence of Temperature on Kinetics of Hydrolysis of Monochlorotriazine Reactive Dye

M. KLANČNIK

*University of Ljubljana, Department of Textiles, Snežniška 5,*
*SI-1000, Ljubljana, Slovenia*

*(Received 15 December 1998)*

The kinetics of hydrolysis of a commercial sample of the monochlorotriazine reactive dye was studied in an alkaline solution pH 10.9 at two temperatures, 80 and 50°C comparatively. The time dependent changes of the amounts of the active and hydrolysed forms of the dye were monitored by high-performance liquid chromatography.

The results indicate that within a defined time the pseudo-first-order kinetics can be considered. The rate constant of hydrolysis of the monochlorotriazine reactive dye at 80°C is about 33 times higher than at 50°C.

*Keywords:* Hydrolysis of reactive dye; monochlorotriazine reactive dye; HPLC

## INTRODUCTION

Reactive dyes are not stable in alkaline solutions because of their tendency to hydrolysis. Hydrolysis of reactive dyes is an unfavourable reaction and one of the fundamental problems in the dyeing process of cellulosic fibers. Investigations of the alkaline hydrolysis of reactive dyes are also important for elucidating the kinetics and mechanism of the fixation of reactive dyes to hydroxyl groups of cellulose.

One of the factors influencing the hydrolysis reaction of the reactive dyes is temperature. The kinetics of alkaline hydrolysis of a monochloro-*s*-triazine reactive dye was investigated at conditions of fixation to cellulose, 80°C and also at the lower temperature of 50°C.

## EXPERIMENTAL

The dye used was a commercial sample of the monofunctional monochloro-*s*-triazine reactive dye C.I. Reactive Red 43.

A solution of 0.025 g of the dye in 5 ml of buffer $pH_{20°C}$ 7 (by Carlo Erba) and 25 ml of deionised water was heated to 80°C (or 50 °C) and then added to mixture of 220 ml of buffer $pH_{20°C}$ 11 (by Riedel-de-Haën AG) preheated to 80°C (or 50°C). The dye solution of pH 10.9 was constantly stirred as it was heated at defined temperature. Once the temperature was reached, the measurements started: 10 ml aliquots were withdrawn from the dye solution at various times and immediately cooled and neutralised by the additional of dilute HCl to prevent further reactions.

The neutralised samples were analysed by a high performance liquid chromatograph HPLC (by Thermo Separation Products) using the same ion-pair reversed-phase system described previously (1). The solutions of the monofunctional dye, C.I. Reactive Red 43, were detected at a wavelength of 500 nm.

## RESULTS AND DISCUSSION

Monochloro-*s*-triazine reactive dyes react with hydroxide ions by the nuchleophilic addition-elimination (heteroaromatic) substitution mechanism shown in Figure 1, where *D* denotes a dye chromogen.

Considering that the addition of hydroxide ion to the electrophilic carbon of the triazine group is the rate-determining step of hydrolysis reaction and the hydroxide ion concentration is kept constant, the rate of concentration decrease of monochlorotriazine dye form in an alkaline solution at a constant temperature can be expressed by the

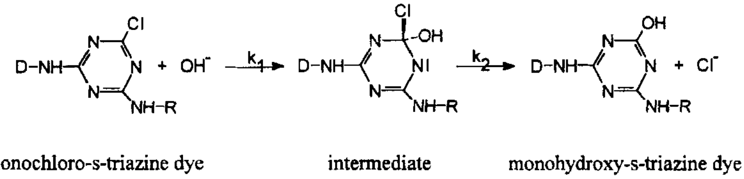


FIGURE 1 Alkaline hydrolysis of a monochloro-*s*-triazine dye.

Equation (1):

$$\frac{-d[A]}{dt} = k_{ps1} \cdot [A] \qquad (1)$$

in which $[A]$ is the concentration of the active, monochloro-*s*-triazine dye at hydrolysis time $t$ and $k_{ps1}$ is the pseudo-first-order rate constant of hydrolysis.

The HPLC chromatograms recorded after various times of hydrolysis at investigated temperatures: 80°C (Fig. 2) and 50°C (Fig. 3) show the expected decrease in the amount of the monochloro-*s*-triazine dye and the increase in the amount of the hydrolysed form of the dye and also a slower hydrolysis reaction of the reactive dye at 50°C.

The values of peak areas of components determined from the chromatograms are linearly related to their amounts. By integrating Eq. (1) and replacing the concentrations of the monochloro-*s*-triazine dye with its peak areas we obtain:

$$\ln\left(\frac{A_0}{A}\right) = k_{ps1} \cdot t \qquad (2)$$

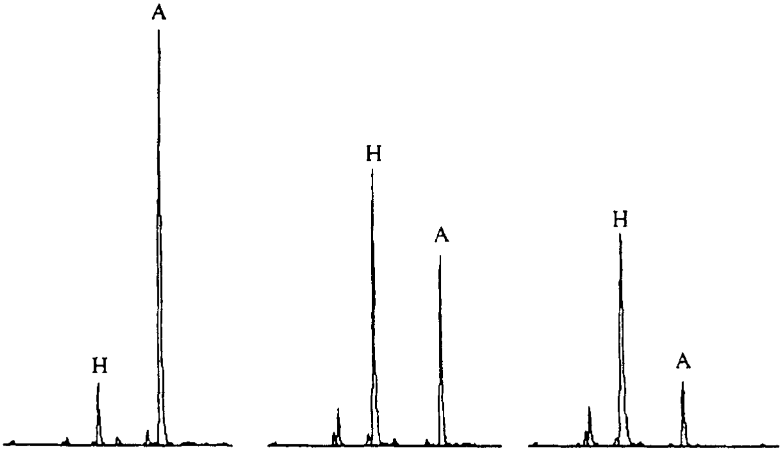
Where $A_0$ and $A$ are values of peak areas of the active, monochloro-*s*-triazine dye at the time $t = 0$ and at a later time $t$.

Data for $\ln(A_0/A)$ at 80°C and 50°C are plotted against hydrolysis time in Figure 4. For both temperatures the plots are straight lines passing through the origin. According to Eq. (2) the expected pseudo-first-order kinetics is confirmed. The slopes of lines are the corresponding pseudo-first-order rate constants $k_{ps1}$.

The average pseudo-first-order rate constant of the monochloro-*s*-triazine reactive dye at 80°C is $1.296 \cdot 10^{-2}\,\text{min}^{-1}$. It is calculated within a time of 110 minutes, when all hydrolysis measurements still show linear dependence of $\ln(A_0/A)$ on hydrolysis time and the average square of the correlation coefficient in the linear regression ($R^2$) is 0.9996.

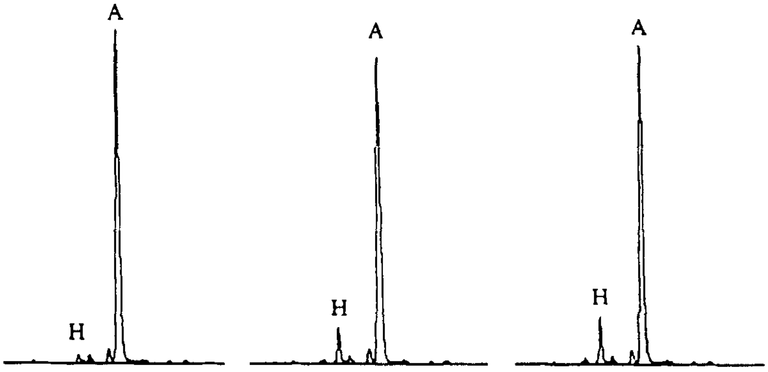
The average pseudo-first-order rate constant of hydrolysis of the monochloro-*s*-triazine dye at 50°C calculated within a time of 180 minutes is $3.9 \cdot 10^{-4}\,\text{min}^{-1}$ and the average square of the correlation coefficient ($R^2$) is 0.995.

The rate constant of hydrolysis of the red monochloro-*s*-triazine dye at 80°C is about 33 times higher than at 50°C.



(1) (2) (3)

FIGURE 2 Chromatograms of the commercial monochlorotriazine reactive dye recorded after various times of hydrolysis at 80°C: (1) 0 min, (2) 60 min and (3) 120 min; where components *A* and *H* represent monochlorotriazine and monohydroxytriazine forms.



(1) (2) (3)

FIGURE 3 Chromatograms of the commercial monochlorotriazine reactive dye recorded after various times of hydrolysis at 50°C: (1) 0 min, (2) 180 min and (3) 240 min; where components *A* and *H* represent monochlorotriazine and monohydroxytriazine forms.

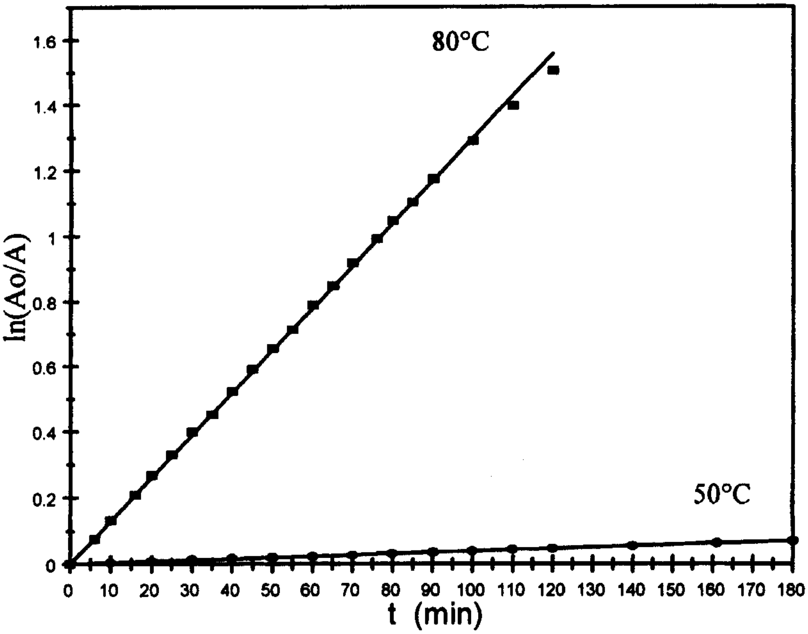


FIGURE 4 Plot of $\ln(A_0/A)$ *vs.* time of hydrolysis at 80 and 50°C.

## *References*

[1] Klančnik, M. (1997). *Zbornik predavanj in posterjev, 31. simpozij o novostih v tekstilstvu,* Ed. Gregor-Svetec, D., Faculty of Natural Sciences and Engineering, Department of Textiles, Ljubljana.

[2] Rys, P. and Zollinger, H. (1989). *The Theory of Coloration of Textiles,* 2nd edn., Ed. Johnson, A., Society of Dyers and Colourists, Bradford.