

Hydrolysis and Methanolysis Reactions of a Homobifunctional Reactive Dye

M. Klančnik

Department of Textiles, Faculty of Natural Sciences and Engineering,
University of Ljubljana, Snežniška 5, SI – 1000 Ljubljana, Slovenia

Original scientific paper

Received:

Accepted:

The reaction kinetics of a homobifunctional bis(monofluoro-*s*-triazine) reactive dye was studied in a mixture of alkaline solution and methanol at 70 °C by ion-pair reversed-phase high performance liquid chromatography. From the measured pseudo-first order reaction rate constants, the chemical reactivity and the selectivity of the particular reactive dye forms, were evaluated.

Keywords:

Reactive dye, Cibacron LS, hydrolysis, methanolysis, rate constants, HPLC.

Introduction

Homobifunctional reactive dyes containing two monofluoro-*s*-triazine reactive groups, were introduced as Cibacron LS dyes about five years ago by Ciba-Geigy. These dyes represent an economical and ecologically-friendly progressive range of reactive dyes. The dyes are characterised by a very high substantivity towards cellulose fibres and therefore they achieve good exhaustion levels in the presence of very low electrolyte concentrations, these being only about 25 % of the amount of salt normally required for reactive dyes in exhaust dyeing of cellulose¹.

Because of their two reactive groups, bifunctional dyes have an increased probability of chemical reaction with cellulose fibres compared to monofunctional dyes with one reactive group. As with other bifunctional dyes, the dyes of Cibacron LS type also achieve very high fixation values of about 80 %. It is expected that after the replacement of the fluorine atom on one triazine reactive group in the homobifunctional Cibacron LS dye by a cellulose substituent in the fixation reaction, or by a hydroxyl group in an unfavourable hydrolysis reaction, the reactivity of the remaining monofluorotriazine group is greatly decreased.

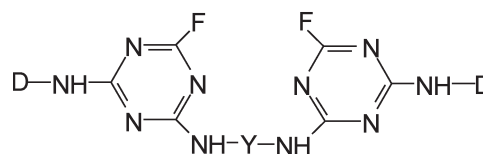
In basic research on fixation reactions and the chemical selectivity of reactive dyes, alcohols are often used as models for the hydroxyl groups of cellulose^{2–23}. Previous work in this area comprises studies of only simple monofunctional reactive dyes. The aim of the present research was to determine the reactivity and the selectivity of the initial bis(monofluoro-*s*-triazine) form, as well as the still reactive, partly hydrolysed, and methanolysed forms of the scarlet homobifunctional Cibacron LS dye in a homogeneous mixture of methanol and alkaline buffer solution, corresponding to a model 10:1 liquor ratio at the recommended fixation temperature of 70 °C. The concentrations of all dye forms in the reacting mixture and their changes during the course of the reaction were

monitored simultaneously by high performance liquid chromatography.

Experimental

Reactive dye

The dye used was a commercial sample of the bis(monofluoro-*s*-triazine) dye Cibacron Scarlet LS-2G of the following general chemical structure, where D incorporates a monoazo-based chromogen moiety and Y an alkyl $-(CH_2)_n-$ unit²⁴.



Hydrolysis and methanolysis reactions

A solution of 0.025 g of the dye in 5 ml of buffer of pH_{20 °C} 7 (Carlo Erba) and 25 ml of deionised water was heated to 70 °C, and then added to a mixture of 220 ml of buffer of pH_{20 °C} 11 (Riedel-de Haën AG) and 25 g of methanol (p.a., Carlo Erba), preheated to the same temperature. After various times, 10 ml aliquots were withdrawn from the constantly stirred reaction mixture thermostatically controlled at 70 °C. The dye samples removed were quenched in ice-water mixture and neutralised by the addition of dilute HCl (p.a., KT Podnart) to stop further reactions.

HPLC analysis

High performance liquid chromatographic analysis of the dye samples was performed by a Thermo Separation Products instrument using octadecylsilan (Hypersil ODS 3 μm) in a column of 250 mm × 4 mm i.d. as the stationary phase, and a mixture of solvents A and B as the mobile phase²⁵. Solvent A was 100 % acetonitrile (CHROMA-

SOLV[®] for HPLC, Riedel-de Haën AG) containing 0.025 mol l⁻¹ tetrabutylammonium bromide (p.a., Fluka Chemie AG). Solvent B was a 30/70 mixture of acetonitrile containing 0.025 mol l⁻¹ tetrabutylammonium bromide and deionised water containing 0.05 mol l⁻¹ ammonium dihydrogen phosphate (p.a., Kemika). The gradient system shown in Table 1 was used at a flow rate of 1.3 ml min⁻¹. The injected volume of the samples analysed was 20 μ l. Solutions of the homobifunctional reactive dye were detected at a wavelength of 501 nm by a Spectra Focus Forward Optical Scanning detector.

Table 1 – Linear gradient system

Time <i>t</i> /min	Solvent A	Solvent B
0	20	80
6	30	70
12	40	60
13	20	80

Results and discussion

Reactive dyes containing fluoro-*s*-triazine groups react with nucleophilic reagents by the nucleophilic bimolecular (heteroaromatic) substitution mechanism²⁶.

The reactions of a homobifunctional dye of symmetrical chemical structure in a mixture of alkaline buffer solution and methanol represent a complex system of parallel and consecutive hydrolysis and methanolysis reactions, which can be illustrated by a simplified scheme such as Fig. 1, where D denotes a dye chromogen.

The expected time-dependent changes in the amounts of the six dye forms in the reaction mixture according to Fig. 1 were confirmed by HPLC analysis (Fig. 2). The value of the sum of the integrated areas of all six peaks, each corresponding to particular dye forms, was constant during the course of reaction.

The dye forms in the HPLC chromatograms were qualitatively identified by comparison of their peak retention times with those obtained in chromatograms of only hydrolysed and methanolysed samples of the same Cibacron Scarlet

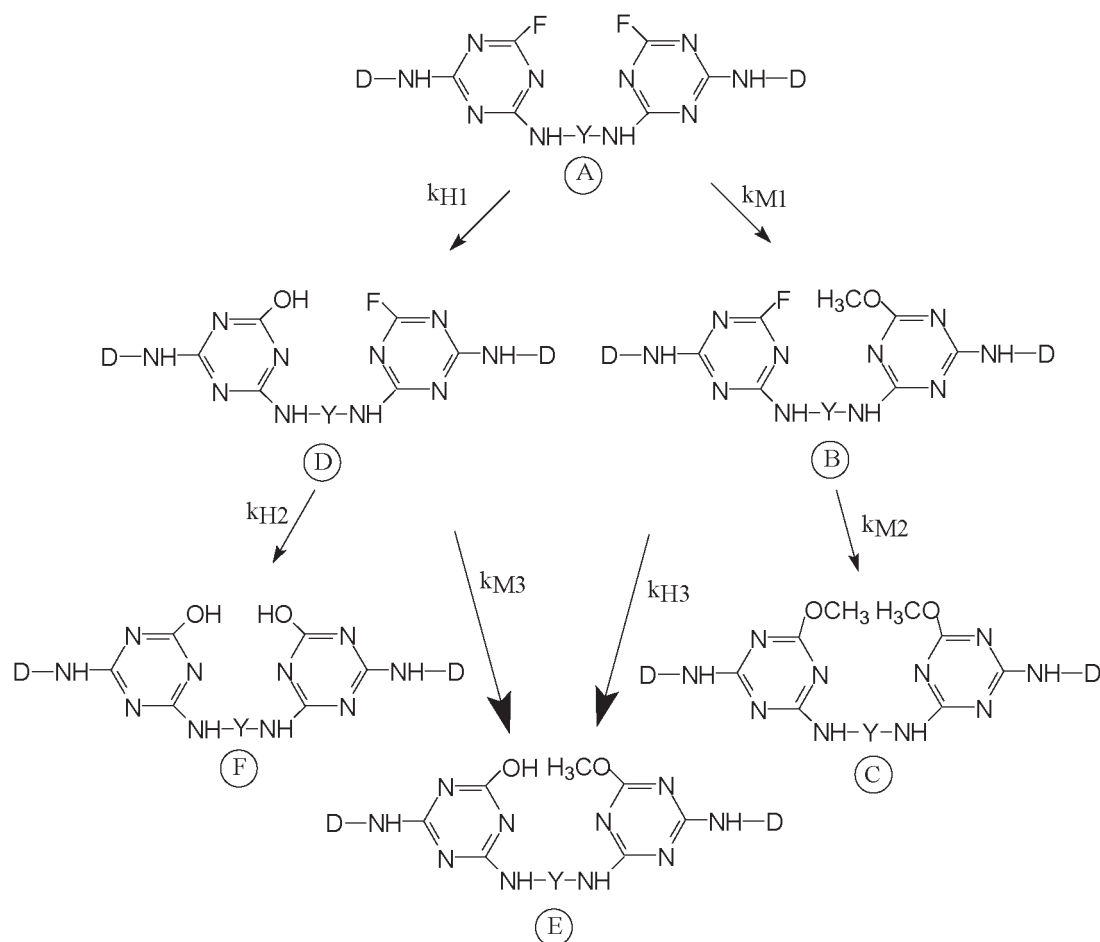


Fig. 1 – Parallel and consecutive hydrolysis and methanolysis reactions of the dye forms of a symmetrical homobifunctional bis(monofluoro-*s*-triazine) dye.

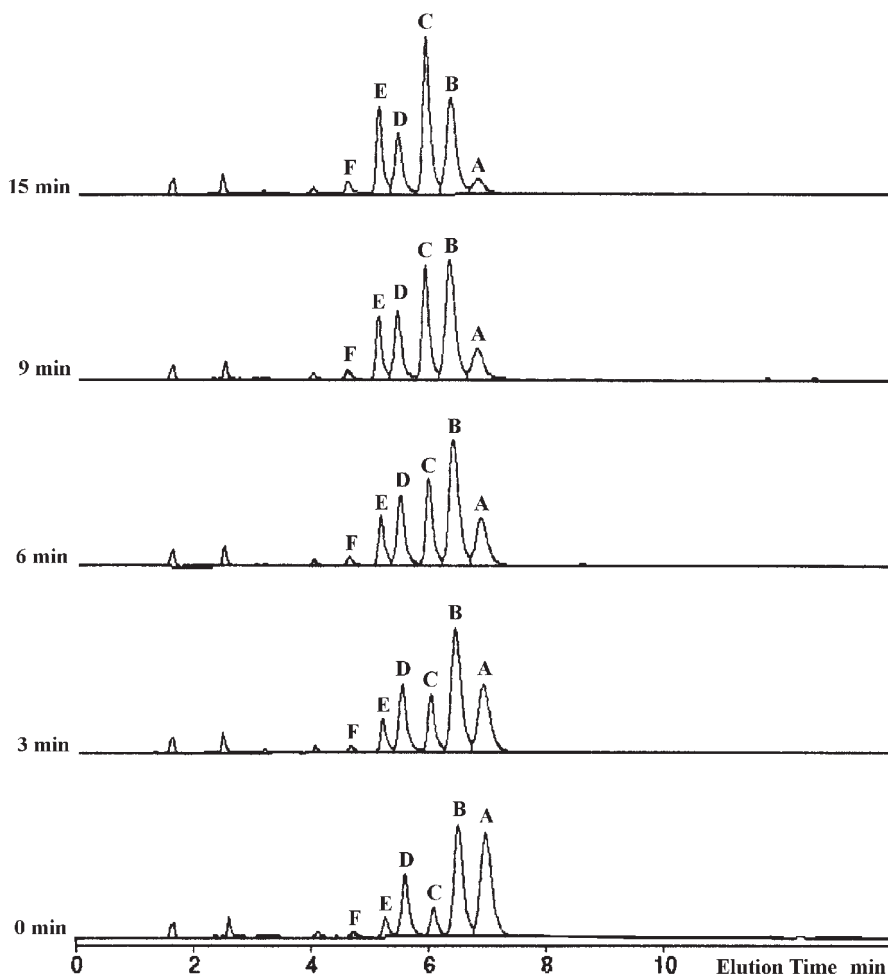


Fig. 2 – Chromatograms of Cibacron Scarlet LS-2G dye in the mixture of methanol and alkaline solution recorded after various reaction times, where A represents bis(monofluoro-*s*-triazine), B monofluoromonomethoxybis-*s*-triazine, C bis(monomethoxy-*s*-triazine), D monofluoromonohydroxybis-*s*-triazine, E monohydroxymonomethoxybis-*s*-triazine and F bis(monohydroxy-*s*-triazine) dye forms.

LS-2G dye under identical chromatographic conditions, as well as by logical deduction according to the relative changes in their amounts in the reaction mixture with time and their orders of elution from the column. The amount of the bis(monofluoro-*s*-triazine) form exponentially decreases with reaction time, while the amounts of the monofluoromonohydroxybis-*s*-triazine and of the monofluoromonomethoxybis-*s*-triazine forms first increase and then decrease. The amounts of the bis(monomethoxy-*s*-triazine), of the monohydroxymonomethoxybis-*s*-triazine and of the bis(monohydroxy-*s*-triazine) dye forms increase with reaction time. The changes in amounts of the particular dye forms in the course of the reactions are clearly seen in Fig. 3. Methanolysis is always the preferred reaction with respect to hydrolysis, and therefore at any time the concentrations of the methanolysed dye forms are larger than the hydrolysed dye forms.

In the studied mixture, methoxide and hydroxide anions are the attacking nucleophiles in

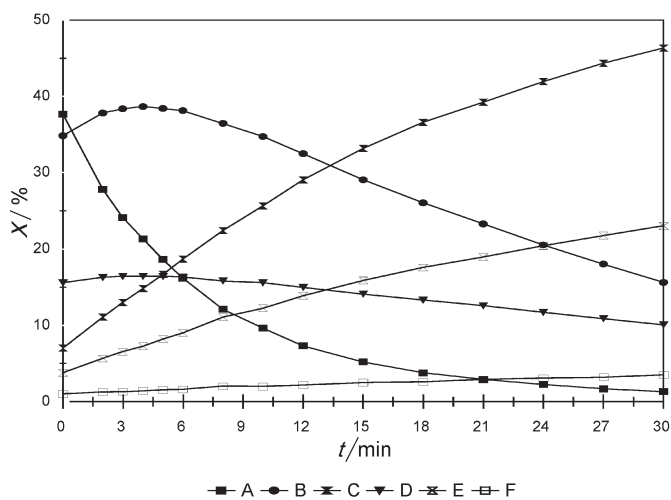


Fig. 3 – Plot of peak areas of bis(monofluoro-*s*-triazine) A, monofluoromonomethoxybis-*s*-triazine B, bis(monomethoxy-*s*-triazine) C, monofluoromonohydroxybis-*s*-triazine D, monohydroxymonomethoxybis-*s*-triazine E and bis(monohydroxy-*s*-triazine) form F of Cibacron Scarlet LS-2G dye against reaction time *t*.

reactions with the reactive dye forms. In the derivation of rate equations, we assumed that hydrolysis and methanolysis reactions proceed by the same nucleophilic bimolecular (heteroaromatic) substitution mechanism and that the attack of a nucleophilic (methoxide or hydroxide) anion on the electrophilic carbon of the reactive triazine group is the rate-determining step of the individual reactions, as well as that the nucleophilic anion concentrations are both constant during the course of reaction by the presence of a large excess of methanol and alkaline buffer solution, and that therefore pseudo-first order kinetics can be expected. The rate of decrease in the concentration of a bis(monofluoro-*s*-triazine) dye form at constant temperature may be written by the equation for a pseudo-first order reaction²⁷:

$$-\frac{d[A]}{dt} = (k_{H1} + k_{M1})[A] \quad (1)$$

in which [A] is the concentration of the bis(monofluoro-*s*-triazine) dye form at any reaction time t , and k_{H1} and k_{M1} are the pseudo-first order rate constants of parallel hydrolysis and methanolysis reactions of one monofluoro-*s*-triazine reactive group in the dye form A.

By integrating Eq. 1 and replacing the concentrations of the bis(monofluoro-*s*-triazine) dye form by its linearly related peak areas, Eq. 2 is obtained:

$$\ln\left(\frac{A_0}{A}\right) = (k_{H1} + k_{M1})t \quad (2)$$

where A_0 and A are the peak areas of the bis(monofluoro-*s*-triazine) form at time $t = 0$ and at a later reaction time t .

Pseudo-first order kinetics were experimentally confirmed within an initial reaction time interval of 15 minutes, when the dependence of $\ln(A_0/A)$ on reaction time was still linear and the average square of the correlation coefficient in the linear plot for four experiments was 0.997. Rate measurements were also carried out with 10-fold greater and 10-fold smaller initial concentrations of the bis(monofluoro-*s*-triazine) dye at the same conditions. The obtained plots of $\ln(A_0/A)$ against time were linear with the unchanged slope confirming the pseudo-first order reaction character. The total pseudo-first order rate constant of the decrease in the amount of the bis(monofluoro-*s*-triazine) dye form, which according to Eq. 1 is equal to the sum of the rate constants of the two parallel reactions $k_{H1} + k_{M1}$, could be determined as the slope of the straight line passing through the origin in the graph of $\ln(A_0/A)$ vs. time (Fig. 4).

After 15 minutes of measurement the concentration of the bis(monofluoro-*s*-triazine) form in the mixture decreases relatively by an average of 86.1 %. The relative increase in the concentration

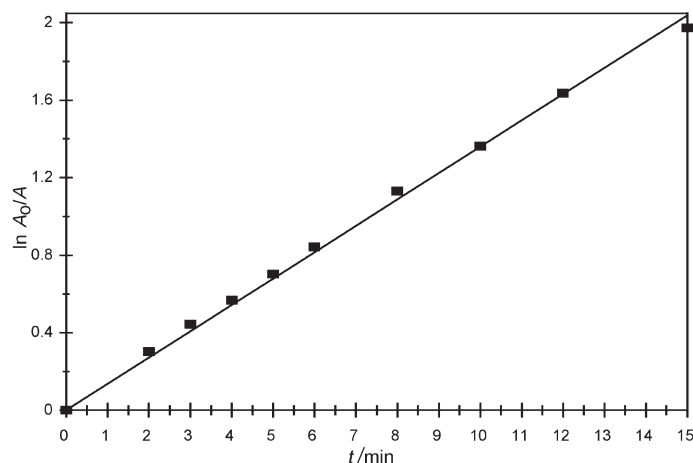


Fig. 4 – Plot of $\ln(A_0/A)$ against reaction time t .

of the monofluoromonomethoxybis-*s*-triazine dye form is on average 1.8 times higher than that of the monofluoromonohydroxybis-*s*-triazine form. After 15 minutes the relative increase in the concentration of the bis(monomethoxy-*s*-triazine) form is 2.4 times higher than that of the bis(monohydroxy-*s*-triazine) form, and also 1.2 times higher than that of the monohydroxymonomethoxybis-*s*-triazine form.

The rate of formation of the monofluoromonomethoxybis-*s*-triazine dye form B is:

$$\frac{d[B]}{dt} = k_{M1}[A] - (k_{H3} + k_{M2})[B] \quad (3)$$

where k_{H3} and k_{M2} are the pseudo-first order rate constants for competitive hydrolysis and methanolysis reactions of the remaining fluoro-*s*-triazine group in form B.

The rate of formation of the monofluoromonohydroxybis-*s*-triazine dye form D is:

$$\frac{d[D]}{dt} = k_{H1}[A] - (k_{H2} + k_{M3})[D] \quad (4)$$

where k_{H2} and k_{M3} are the pseudo-first order rate constants for parallel hydrolysis and methanolysis reactions of the remaining fluoro-*s*-triazine group in form D.

In Eqs. 3 and 4, [A], [B] and [D] are the concentrations of bis(monofluoro-*s*-triazine), of monofluoromonomethoxybis-*s*-triazine and of monofluoromonohydroxybis-*s*-triazine forms at any reaction time t .

From Fig. 3 it is evident that during the course of reaction the still reactive partly methanolysed form B and partly hydrolysed form D first increase to their maximum values and then decrease. The forms B and D reach their maximal concentrations at the same time, i.e. after 3 or 4 minutes of measurement depending on the particular experiment.

On dividing Eq. 3 by Eq. 4 we obtain:

$$\frac{d[B]}{d[D]} = \frac{k_{M1}[A] - (k_{H3} + k_{M2})[B]}{k_{H1}[A] - (k_{H2} + k_{M3})[D]} \quad (5)$$

When the concentrations of partly methanolysed B and partly hydrolysed D forms increase, their rates of formation are higher than their rates of consumption and therefore from Eqs. 3 and 4 it follows that $k_{M1}[A] > (k_{H3} + k_{M2})[B]$ and $k_{H1}[A] > (k_{H2} + k_{M3})[D]$.

By supposing that at a time of measurement when the amounts of these dye forms are still increasing, long before they reach their maximas, the rates of consumption of these forms are negligible, compared to their rates of formation and hence Eq. 5 can be simplified to Eq. 6:

$$\frac{d[B]}{d[D]} = \frac{k_{M1}}{k_{H1}} \quad (6)$$

By integrating Eq. 6 Eq. 7 is obtained:

$$\frac{[B] - [B]_0}{[D] - [D]_0} = \frac{k_{M1}}{k_{H1}} \quad (7)$$

where $[B]_0$ and $[B]$ are the concentrations of the monofluoromonomethoxybis-*s*-triazine form, and $[D]_0$ and $[D]$ are the concentrations of the monofluoromonohydroxybis-*s*-triazine form at the beginning and at the particular time, when the amounts of these forms are still increasing and have not yet reached their maximal values.

The response of the absorption detector used is equal for all dye forms in the reaction mixture at the chosen wavelength²⁸, and hence instead of the ratio of the concentrations of the particular dye forms the ratio of their peak areas can be used in all the derived equations.

By considering the ratio of the rate constants of methanolysis to parallel hydrolysis of a monofluoro-*s*-triazine group in the bis(monofluoro-*s*-triazine) dye form, k_{M1}/k_{H1} , calculated from Eq. 7 and the sum of these rate constants determined as the slope of the line in the plot of $\ln(A_0/A)$ against time, the individual pseudo-first order rate constants k_{H1} and k_{M1} can be computed.

The rate constant of hydrolysis of the remaining monofluorotriazine group in the monofluoromonohydroxybis-*s*-triazine form D, k_{H2} , can be determined by considering the ratio of k_{H1}/k_{H2} obtained in the alkaline buffer solution alone²⁸ at the same temperature of 70 °C, having the value of 4.15.

From Eq. 4 at the time when the concentration of the partly hydrolysed dye form D reaches its maximum value and $\frac{d[D]}{dt} = 0$, the rate constant of methanolysis of the remaining monofluoro-*s*-triazine group in the monofluoromonohydroxybis-*s*-triazine form D, k_{M3} , can be calculated as follows:

$$k_{M3} = \frac{[A]}{[D]} k_{H1} - k_{H2} \quad (8)$$

where $[A]$ and $[D]$ represent the concentrations of the bis(monofluoro-*s*-triazine) and the monofluoromonohydroxybis-*s*-triazine dye forms at the time when the monofluoromonohydroxybis-*s*-triazine form reaches its maximum.

We assume that the ratio of the rate constants of competitive reactions of the partly hydrolysed form is equal to that of the partly methanolysed form: $k_{M3}/k_{H2} = k_{M2}/k_{H3}$.

At the time when the monofluoromonomethoxybis-*s*-triazine dye form is at its maximum concentration and $\frac{d[B]}{dt} = 0$, Eq. 3 can be rearranged as:

$$k_{H3} + k_{M2} = \frac{[A]}{[B]} k_{M1} \quad (9)$$

where $[A]$ and $[B]$ are the concentrations of the bis(monofluoro-*s*-triazine) and the monofluoromonomethoxybis-*s*-triazine dye forms at the time when the monofluoromonomethoxybis-*s*-triazine form reaches its maximum.

From Eq. 9, the particular rate constants for hydrolysis k_{H3} and methanolysis k_{M2} of the remaining monofluoro-*s*-triazine group in the monofluoromonomethoxybis-*s*-triazine form can be calculated by considering their rate constant ratio k_{M2}/k_{H3} and the rate constant of methanolysis k_{M1} .

When the values of all the calculated rate constants and of the peak areas of the dye forms A, B and D at a time before the forms B and D reach their maximum are inserted in Eq. 5, it is seen that values of the terms $(k_{H3} + k_{M2})[B]$ and $(k_{H2} + k_{M3})[D]$ are not negligibly small and that the ratio calculated in this way on the right side of Eq. 5 is higher than the primarily used ratio of $([B] - [B]_0)/([D] - [D]_0)$ by 8.6 %, 3.3 % or 2.3 %, depending on the particular experiment. On this account for an individual experiment the formally used ratio of the increase in the amount of the partly methanolysed form to that of the partly hydrolysed form $([B] - [B]_0)/([D] - [D]_0)$ is reduced by the appropriate percentage. The ratio reduced in this way is equal to the ratio of the rate constants of methanolysis to hydrolysis of the bis(monofluoro-*s*-triazine) form, k_{M1}/k_{H1} . Thus the calculations of all rate constants for methanolysis and hydrolysis of particular dye forms have now to be repeated by the already explained procedure. In these calculations five place decimal values of the rate constants were used in order to eliminate errors caused by their rounding off.

The particular rate constants of parallel and consecutive hydrolysis and methanolysis reactions of the reactive forms of the homobifunctional dye in the studied mixture of methanol and buffer solution are collected in Table 2, and their ratios in Table 3, the results being average values of three experiments.

The calculated values for the pseudo-first order rate constants were also confirmed by a com-

Table 2 – Rate constants of methanolysis and competitive hydrolysis of the monofluoro-*s*-triazine group in the bis(monofluoro-*s*-triazine) form (k_{M1} , k_{H1}), in the monofluoromonohydroxybis-*s*-triazine form (k_{M3} , k_{H2}), and in the monofluoromonomethoxybis-*s*-triazine form (k_{M2} , k_{H3}) of Cibacron Scarlet LS-2G dye

k_{M1}	k_{H1}	k_{M3}	k_{H2}	k_{M2}	k_{H3}
$10^{-1} \cdot \text{min}^{-1}$	$10^{-2} \cdot \text{min}^{-1}$	$10^{-2} \cdot \text{min}^{-1}$	$10^{-3} \cdot \text{min}^{-1}$	$10^{-2} \cdot \text{min}^{-1}$	$10^{-2} \cdot \text{min}^{-1}$
1.09	2.66	2.82	6.4	4.88	1.11
± 0.01	± 0.11	± 0.11	± 0.3	± 0.05	± 0.02

Table 3 – Ratio of rate constants of methanolysis to hydrolysis of the monofluoro-*s*-triazine group in the bis(monofluoro-*s*-triazine) form (k_{M1} , k_{H1}), in the monofluoromonohydroxybis-*s*-triazine form (k_{M3} , k_{H2}), and in the monofluoromonomethoxybis-*s*-triazine form (k_{M2} , k_{H3}) of Cibacron Scarlet LS-2G dye

k_{M1}/k_{H1}	$k_{M3}/k_{H2} = k_{M2}/k_{H3}$	k_{M1}/k_{M2}	k_{M2}/k_{M3}	k_{M1}/k_{M3}	k_{H1}/k_{H2}	k_{H3}/k_{H2}	k_{H1}/k_{H3}
4.1	4.4	2.2	1.8	3.9	4.1	1.8	2.4

puter program, the curves of peak areas of the dye forms against time corresponding to those in Fig. 3 were obtained.

From Table 3 it is seen that the rate constant of methanolysis of the monofluoro-*s*-triazine group in any reactive form of Cibacron Scarlet LS-2G dye, is on average more than 4 times higher than the rate constant of parallel hydrolysis of that group. The dominance of methanolysis is a result of the greater nucleophilic reactivity of methoxide ions compared to hydroxide ions, and probably the greater solvation of hydroxide ions in the reaction mixture.

The rate constant of methanolysis of the monofluoro-*s*-triazine group in the bis(monofluoro-*s*-triazine) form A, is about twice as high as that in the monofluoromonomethoxy form B, and about 4 times higher than that in the monofluoromonohydroxy form D. The ratio of the hydrolysis rate constants for these dye forms is also about the same.

The dissociated hydroxyl group on the triazine ring in the partly hydrolysed form D is more electron-donating than the methoxyl group in the partly methanolysed form B, leading to a stronger deactivation of the remaining reactive group to further reaction with nucleophiles. The results show that the reactivity of the remaining monofluoro-*s*-triazine group, in the partly hydrolysed form, is about twice as low as that in the partly methanolysed form.

Although, the studied dye contains imino groups as bridges between the reactive group and

the chromogen, as well as between the two reactive groups, the ionisation of these imino groups was neglected in the rate equations by assuming that even if the dissociation occurs it is only a minor effect, and that the rate constants of the possibly ionised dye forms are negligible compared with the relevant nonionised dye forms.

Conclusions

From the calculated pseudo-first order rate constants of the competitive methanolysis and hydrolysis reactions, the chemical reactivity and selectivity of the particular reactive dye forms of the scarlet homobifunctional Cibacron LS dye were evaluated. The rate constant of methanolysis of any reactive dye form is on average 4.2 (± 0.1) times higher than that of parallel hydrolysis. The chemical reactivity of the bis(monofluoro-*s*-triazine) dye form is 2.3 (± 0.1) times higher than that of the monofluoromonomethoxybis-*s*-triazine form and also 4 (± 0.1) times higher than that of the monofluoromonohydroxybis-*s*-triazine form; however, the chemical selectivity of all reactive forms of the homobifunctional dye studied is almost the same.

References:

1. Prospectus material of Cibacron LS dyes, Ciba
2. Dawson, T.L., Fern, A.S., Preston, C., *JSDC* **76** (1960) 210
3. Preston, C., Fern, A.S., *Chimia* **15** (1961) 177
4. Ackermann, H., Dussy, P., *Melliand Textilber.* **42** (1961) 1167
5. Baumgarte, U., *Melliand Textilber.* **43** (1962) 182
6. Ingamells, W., Sumner, H., Williams, G., *JSDC* **78** (1962) 274
7. Stamm, O.A., *Helv. Chim. Acta* **46** (1963) 3019
8. Hildebrand, D., *Bayer Farben Revue* No. 9 (1964) 29
9. Hildebrand, D., Beckmann, W., *Melliand Textilber.* **45** (1964) 1138
10. Rys, P., Zollinger, H., *Helv. Chim. Acta* **49** (1966) 761
11. Luttringer, J.P., Dussy, P., *Melliand Textilber.* **62** (1981) 84
12. Sivaraja Iyer, S. R., Ramaseshan, G., Chourishi, N. K., *JSDC* **97** (1981) 319
13. Zheng-Hua, Z., Kong-Chang, C., Jian-Xiong, L., Shu-Ling, C., Shou-Lan, W., *Dyes and Pigments* **11** (1989) 277
14. Xiao-Tu, L., Zheng-Hua, Z., Kong-Chang, C., *Dyes and Pigments* **11** (1989) 123
15. Renfrew, A. H. M., Taylor, J. A., *JSDC* **105** (1989) 441
16. Taylor, J. A., Renfrew, A. H. M., *JSDC* **106** (1990) 230
17. Zhenghua, Z., Kongchang, C., Ronggeng, Y., *Dyes and Pigments* **14** (1990) 129

18. Zheng-Hua, Z., Cheng-Zhong, J., *Dyes and Pigments* **19** (1992) 265
19. Zhenghua, Z., Xiaodong, Z., *Dyes and Pigments* **21** (1993) 243
20. Zhenghua, Z., Yiaodong, Z., *Dyes and Pigments* **21** (1993) 173
21. Zheng-Hua, Z., Wei-Ping, Z., *Dyes and Pigments* **24** (1994) 281
22. Bentley, T. W., Ratcliff, J., Renfrew, A. H. M., Taylor, J. A., *JSDC* **111** (1995) 288
23. Klančnik, M., *Dyes and Pigments* **46** (2000) 9
24. Phillips, D. A. S., *Advances in Colour Science & Technology* No. 1 (1998) 1
25. Smith, C. B., Thakore, K. A., *Text. Chem. Color.* **23** (1991) 23
26. Zollinger, H., *Color Chemistry*, 2nd edn., VCH, Weinheim, New York, Basel, Cambridge, 1991, 167–179.
27. Rys, P., Zollinger, H., Reactive dye-fibre systems, in Johnson, A. (Ed.), *The theory of coloration of textiles*, 2nd edn., Society of Dyers and Colourists, Bradford, 1989, 428–476.
28. Klančnik, M., Ph.D. Thesis, University of Ljubljana, 1999

