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Reactivity, chemical selectivity and exhaust dyeing properties of dyes possessing a 2-chloro-4-methylthio-*s*-triazinyl reactive group

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Abstract

Several 2-chloro-*s*-triazinyl reactive dyes, each possessing a different substituent in the 4-position of the triazine ring, were synthesised, and their rates of hydrolysis and methanolysis were determined over a range of temperatures. The order of reactivity was 4-alkylthio > 4-methoxy > 4-dimethylamino. Unlike the 4-methylthio- and 4-dimethylamino-derivatives, in which the chlorine atom was replaced cleanly, both on hydrolysis and methanolysis, the 2-chloro-4-methoxy-*s*-triazine underwent concurrent displacement of both chlorine and methoxy substituents. The 2-chloro-4-methylthio-derivative displayed a high propensity to undergo methanolysis, rather than hydrolysis, in homogeneous solution and this preference for undergoing alcoholysis was mirrored in excellent fixation to cotton on exhaust dyeing.

Keywords: Reactive dye; Monochloro-*s*-triazine; Alcoholysis; Hydrolysis; Methylthio

1. Introduction

High wet fastness in dyeing of cellulosic textiles is best gained by the use of reactive dyes; these are the only colourants which link covalently to cellulose. Fixation is invariably achieved in the presence of aqueous alkali. Under these conditions, nucleophilic cellulosate ion, Cell-O^-, is in competition with hydroxide ion, OH^-, for reaction with the electrophilic reactive group(s) of the dye. In order to gain greater insight into the competitive fixation–hydrolysis reactions, an investigation into the rates of methanolysis (as a homogeneous model for the fixation process) and hydrolysis of a series of 2-chlorotriazinyl derivatives was undertaken. The effects of temperature and pH on the hydrolysis of dichlorotriazinyl reactive dyes had been reported [1–4], as had been the hydrolysis and alcoholysis behaviour of some halo-*s*-triazinyl [5–9] and vinylsulphonyl reactive dyes [10]. Also, methanol had been reported as a suitable model for cellulose with which to investigate the chemical selectivity of various reactive dyes [11]; that is their preference to undergo alcoholysis rather than hydrolysis.

Much of the earlier work had concentrated on the effects of temperature and pH changes on the hydrolysis and alcoholysis of various reactive systems, but 2-chloro-4-alkylthio-*s*-triazines had not been studied. This present investigation compares the reactivity and chemical selectivity of a series of 2-chloro-*s*-triazines, in homogeneous methanol/water solution, and correlates these results with fixation efficiencies on exhaust dyeing of cotton.

2. Experimental

2.1. Analytical methods

HPLC analyses were performed with a Hewlett Packard 1100 series instrument fitted with a quaternary pump.

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Table 1
HPLC analysis conditions

Reaction	Column cartridge size (mm)	Mobile phase	Method	Temperature (°C)
Synthesis of Dyes **1**, **2**, and **3**	125-4	Acetonitrile–dicyclohexyl ammonium phosphate	Gradient	40
Synthesis of Dyes **1b**, **2a**, **2b**, **3a**, **3b** and **4**	125-4	Acetonitrile–dicyclohexyl ammonium phosphate	Gradient	40
Hydrolysis of Dyes **2** and **3**	125-4	Acetonitrile–dicyclohexyl ammonium phosphate	Gradient	40
Synthesis of Dye **4a**	250–4	70% Acetonitrile–30% cetavlon	Isocratic	30
Hydrolysis of Dye **1**	250-4	70% Acetonitrile–30% cetavlon	Isocratic	30
Methanolysis of Dye **2**	250-4	70% Acetonitrile–30% cetavlon	Isocratic	30
Methanolysis of Dye **3**	250-4	65% Acetonitrile–35% cetavlon	Isocratic	30

The following gradient programme was used:

Min	% Acetonitrile	% Dicyclohexyl ammonium phosphate
0	30	70
5	50	50
6	40	60
7	30	70

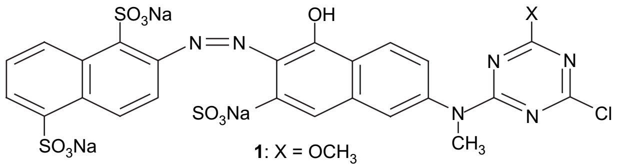
The column was a Purospher RP-18 (5 μm) packing with a LiChrocart HPLC column cartridge. The mobile phase flow rate was 2 ml/min and the injection volume was 5 μl. Dicyclohexyl ammonium phosphate (0.25%) or cetavlon (0.5%) was used as ion-pair agent. Samples were analysed using a diode array detector. Other details are listed in Table 1.

Mass spectra were recorded with a Micromass Instruments LCT orthogonal time-of-light mass spectrometer fitted with a Z-Spray electrospray ion source operating in negative mode at 3 kV needle potential. Nitrogen was used as a drying and sheath gas. Infusion was at a rate of 20 ml/min with a Harvard Instruments syringe pump for sample introduction.

Measurement of the effective dyestuff content of the model dyes was determined by titration against titanium (III) chloride [12]. The effective agent content (strength) of each dye was expressed as ‘‘Mole In’’, that is, the number of grams containing 1 mol of dye. UV–vis spectra were recorded using a Camspec M350 double-beam spectrophotometer.

2.2. Kinetic experiments

Hydrolyses of model dyes (Fig. 1) were performed with a 10^{-4} mol solution of dye in 10^{-2} mol sodium carbonate.



1: X = OCH_3
2: X = SCH_3
3: X = $N(CH_3)_2$
4: X = Cl

Fig. 1. 2-Chloro-4-substituted-*s*-triazinyl (orange) dyes investigated in this study.

Samples (5 ml) were taken at suitable time intervals, quenched with a pre-cooled mixture of 5 N HCl (2–3 drops) and pH 7 buffer solution (2 drops) was added to give a pH between 6.5 and 7.0. Each 5 ml sample was then kept in an ice bath before being subjected to HPLC analysis. Table 2 shows the temperatures at which hydrolysis of each model dye was performed.

Selectivities were determined, at a temperature corresponding to a pseudo first order hydrolysis rate of 0.0006 min^{-1}, in a homogeneous mixture of water (180 ml, 10 mol), methanol (8 ml, 0.2 mol) and sodium carbonate (1.06 g, 0.01 mol).

2.3. Exhaust dyeing of cotton

Bleached and mercerised cotton woven fabrics were dyed with 1, 2, 4, 6, and 9% omf (at a liquor ratio, LR, of 10:1) at three different temperatures to determine the optimum dyeing temperature of Dyes **1**, **2**, **3** and **4** (Fig. 2 and Table 3).

Colour strengths of dyed fabrics were measured using a Datacolor International Spectroflash 600 spectrophotometer. The average of four reflectance measurements, taken at different positions on the fabric, was recorded and the *K*/*S* value at the maximum wavelength absorption was determined.

ISO 105:CO6 was used for the estimation of colour wash fastness of the dyed fabrics.

Table 2
Hydrolysis temperatures used in kinetic studies

Dye	Temperature (°C)		
1	40	45	50
2	40	45	50
3	65	70	75
4	35	40	45

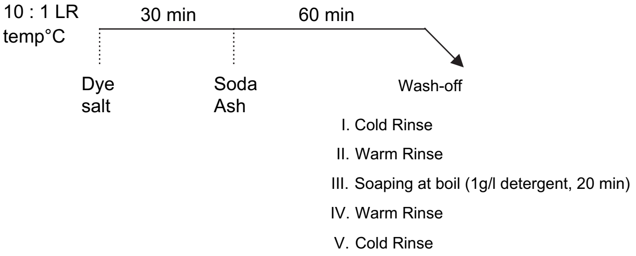


Fig. 2. Dyeing method employed.

The *colour fastness to acid treatment* (“*acid hydrolysis*”) was estimated by the following modified acid perspiration test, ISO 105-E04.

Specimens of dyed textile, in contact with cotton and nylon adjacents, of similar dimensions, were wet out in dilute acetic acid (9.3 ml/l) using a liquor ratio of 20:1 for 30 min at room temperature (mass of composite samples were between 0.60 and 0.75 g). The composite sample was then placed between two glass plates (each of mass ca. 55 g) and excess solution was squeezed off without removing the plates. The composite sample was then allowed to remain between the plates for 6 h at 37 ± 2 °C. After 6 h the composite sample was rinsed with cold water, the specimen was separated from the adjacent pieces of fabric and dried at room temperature. The staining of the adjacents was assessed using the grey scale.

2.4. Chemicals

Methanol was of HPLC grade (water content < 0.02%); sodium carbonate was of analytical reagent grade. 2-Methylthio-4,6-dichloro-*s*-triazine was from Degussa and the orange dyebase was provided by Everlight Chemical Industrial Corp of Taiwan. Alcopol 070 (CIBA) was used as detergent in the washing off process.

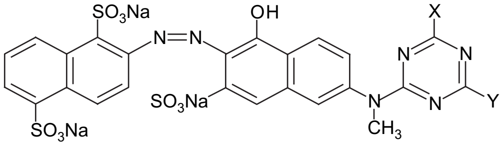
2.5. Synthesis of dyes (see Figs. 2 and 3)

2.5.1. Preparation of monochloro-s-triazinyl dyes

*2.5.1.1. 2-(1,5-Disulphonaphthyl-2-azo)-6-N-(4-methoxy-6-chloro-s-triazin-2-yl)-methylamino-1-naphthol-3-sulphonic acid (Dye **1**). 2-Methoxy-4,6-dichloro-s-triazine*. Sodium hydrogen carbonate (5.04 g) was added over 5 min to a solution of methanol (30 ml), water (3.7 ml) and cyanuric chloride (5.52 g) at 0–5 °C. The reaction mixture was warmed slowly to 30 °C and held at 30–35 °C for 30 min. It was then drowned into ice/water (70 ml), filtered off and dried in a desiccator over calcium chloride. Yield 5.08 g.

Table 3
Concentrations of salt and alkali employed

Dye (% omf)	Common salt (g/l)	Soda ash (g/l)
1	45	15
2	60	15
4	70	20
6	90	20
9	90	20



1a : X = OCH_3 Y = OH
1b : X = OCH_3 Y = OCH_3
2a : X = SCH_3 Y = OH
2b : X = SCH_3 Y = OCH_3
3a : X = $N(CH_3)_2$ Y = OH
3b : X = $N(CH_3)_2$ Y = OCH_3
4a : X = Cl Y = OH

Fig. 3. Additional dyes prepared to aid analysis.

*Dye **1***. Dyebase (strength 76%, Mole In 750, 0.0104 mol, 7.8 g) was dissolved in 50 ml of water at pH 6. To this solution, was added methoxydichloro-*s*-triazine solution (0.0195 mol/20 ml acetone) at pH 6 ± 0.2 and at 30 °C. After 45 min, the mixture was cooled to 20 °C and the product was precipitated by adding methylated spirit. The resulting orange solid was collected and dried under reduced pressure over calcium chloride. Yield 6.44 g; strength 89%; Mole In 869; *m/z* 708 $[M-H]^-$; *m/z* 626 $[M-H\text{-}SO_3H]^-$; λ_{max} (water) 489 nm; ε_{max} 35 817 $dm^3\ mol^{-1}\ cm^{-1}$.

*2.5.1.2. 2-(1,5-Disulphonaphthyl-2-azo)-6-N-(4-methylthio-6-chloro-s-triazin-2-yl)-methylamino-1-naphthol-3-sulphonic acid (Dye **2**).* Dyebase (0.015 mol, 11.25 g) was dissolved in water (80 ml). To this solution was added 2-methylthio-4-6-dichloro triazine solution (0.016 mol/20 ml acetone), at 30 °C, while the pH was kept at 6 ± 0.2. HPLC showed the reaction to be complete after 1.5 h, the product was precipitated by adding methylated spirit (150 ml) to the cold reaction mixture. Solid was collected and dried under reduced pressure, over calcium chloride. Yield 10.78 g; strength 91%; Mole In 872; *m/z* 725 $[M-H]^-$; *m/z* 643 $[M-H\text{-}SO_3H]^-$ λ_{max} (water) 489 nm; ε_{max} 34 975 $dm^3\ mol^{-1}\ cm^{-1}$.

*2.5.1.3. 2-(1,5-Disulphonaphthyl-2-azo)-6-N-(4-dimethylamino-6-chloro-s-triazin-2-yl)-methylamino-1-naphthol-3-sulphonic acid (Dye **3**).* Cyanuric chloride (0.027 mol, 4.98 g) was dissolved in acetone (30 ml) and the solution was added immediately to ice/water (60 ml), with a good stirring, at pH 6 ± 0.2.

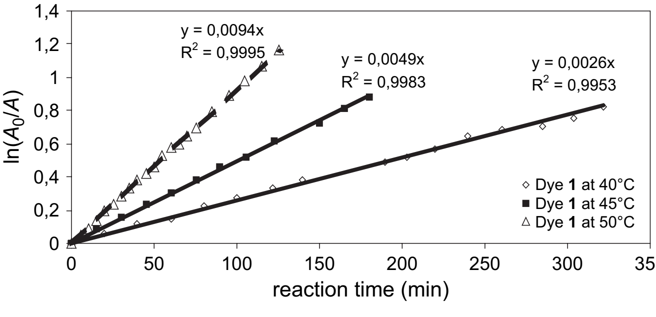


Fig. 4. Plot of $\ln(A_0/A)$ against time for Dye **1** (–OMe/Cl).

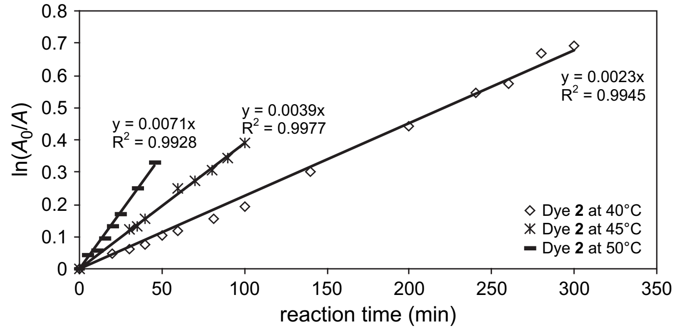


Fig. 5. Plot of $\ln(A_0/A)$ against time for Dye **1** (–SMe/Cl).

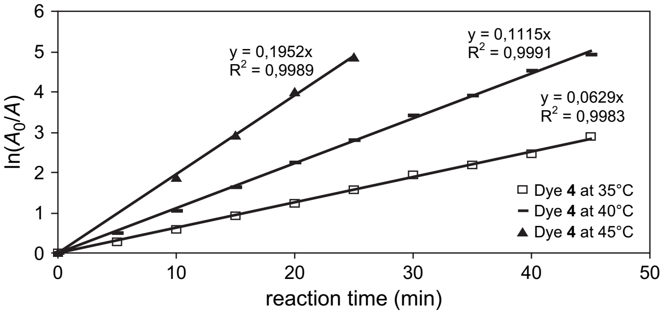


Fig. 7. Plot of $\ln(A_0/A)$ against time for Dye **4** (–Cl/Cl).

To this suspension was added dyebase solution (0.025 mol, 18.75 g in 80 ml water) at pH 6 ± 0.2 and at 0–5 °C. After 60 min, when the formation of the dichloro-*s*-triazine derivative was complete, the reaction mixture was allowed to warm to 25 °C, keeping the pH at 6–7, and was stirred for 90 min at this temperature. The resulting dichlorotriazine dye solution was then filtered to remove any insoluble impurities and the resulting solution was used directly. To this, dimethylamine hydrochloride (0.027 mol) was added, with stirring, at pH 8.5 ± 0.2 and at 25–30 °C. Sodium carbonate was used to adjust the pH. After 2 h, the mixture was cooled to 20 °C and the pH adjusted to 6.5. Methylated spirit was added with stirring and the resulting solid was collected and dried over calcium chloride. Yield 18 g; strength 90%; Mole In 877; *m*/*z* 722 $[M-H]^-$; 640 $[M-H\text{-}SO_3H]^-$; λ_{max} (water) 489 nm; ε_{max} 39 843 $dm^3\,mol^{-1}\,cm^{-1}$.

*2.5.1.4. 2-(1,5-Disulphonaphthyl-2-azo)-6-N-(4,6-dichloro-s-triazin-2-yl)-methylamino-1-naphthol-3-sulphonic acid (Dye **4**).* Cyanuric chloride (0.027 mol, 4.98 g), dissolved in acetone (30 ml), was added to ice/water (50 ml) with stirring at pH 6 ± 0.2. To the resulting suspension a solution of dyebase (0.025 mol, 18.75 g. in water, 80 ml) was added, at pH 6 ± 0.2 and at 0–5 °C. After stirring for 60 min, at 0 to 5 °C, the mixture was allowed to warm to 25 °C, at pH 6–7, and was stirred for a further 90 min at 25 °C. After 90 min the mixture was cooled to 20 °C and the pH adjusted to 6.5. Methylated spirit was added to the stirred solution and the resulting orange solid was collected and dried over calcium chloride. Yield 10.14 g; strength 93%; Mole In 840; *m*/*z* 713 $[M-H]^-$; 632 $[M-H\text{-}SO_3H]^-$; λ_{max} (water) 489 nm; ε_{max} 38 577 $dm^3\,mol^{-1}\,cm^{-1}$.

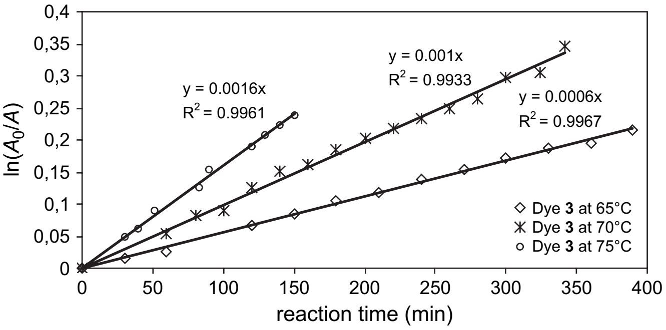


Fig. 6. Plot of $\ln(A_0/A)$ against time for Dye **3** ($-NMe_2/Cl$).

2.5.2. Preparation of "standards" to aid compound identification in HPLC studies

*2.5.2.1. 2-(1,5-Disulphonaphthyl-2-azo)-6-N-(4-methoxy-6-hydroxy-s-triazin-2-yl)-methylamino-1-naphthol-3-sulphonic acid (Dye **1a**).* Nicotinic acid (0.025 m, 3.08 g) was added to a solution of Dye **1** (0.005 mol, 4.35 g, Mole In 869, strength 89%) in water (100 ml). The solution was stirred at pH 5.0–5.5 and at 80–90 °C for 3 h, cooled to 20 °C and the pH raised to 6.5. The resulting quaternary salt was precipitated by the addition of methylated spirit, with stirring, collected and dried over calcium chloride. Yield 4.14 g; strength 87%; Mole In 997; *m*/*z* 796 $[M-H]^-$; λ_{max} (water) 492 nm; ε_{max} 35 903 $dm^3\,mol^{-1}\,cm^{-1}$.

This quaternary salt (1 g) was dissolved in 2 N sodium carbonate (50 ml) and the mixture was heated at 80 °C for 2 h. On cooling, the derived product was isolated by precipitation with methylated spirit, and dried over calcium chloride. Yield 0.8 g, *m*/*z* 691 $[M-H]^-$.

*2.5.2.2. Preparation of dyes **2a**, **3a**, **4a**, **1b**, **2b** and **3b**.* The dyes, **2a** and **3a** and **4a**, were prepared by dissolving 2–4 g of the appropriate monochloro-*s*-triazinyl analogue (Dyes **1**, **2**, **3**

Table 4
Pseudo first order hydrolysis rate constants (reactivity) of Dyes **1**, **2**, **3** and **4**

Model dye	Temperature (°C)	Overall reactivity (min^{-1})	R^2 value
Dye **1** (–OMe/Cl)	40	0.0026	0.9953
	45	0.0049	0.9983
	50	0.0094	0.9995
Dye **2** (–SMe/Cl)	40	0.0023	0.9945
	45	0.0039	0.9977
	50	0.0071	0.9928
Dye **3** ($-Nme_2/Cl$)	65	0.0006	0.9961
	70	0.0010	0.9933
	75	0.0016	0.9961
Dye **4** (–Cl/Cl)	35	0.0629	0.9983
	40	0.1115	0.9991
	45	0.1952	0.9989

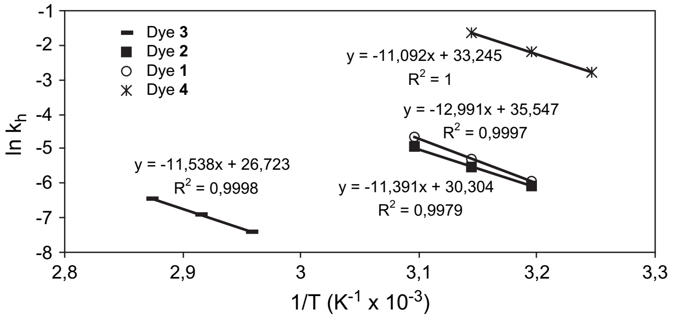


Fig. 8. Arrhenius plots of $\ln k_h$ against $1/T$ for hydrolysis of the model dye molecules in aqueous carbonate.

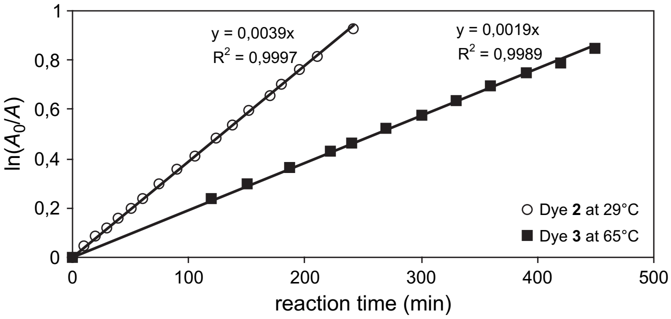


Fig. 9. Plot of $\ln(A_0/A)$ against time – selectivity experiments in a water/methanol mixture.

and **4**, respectively) in 2 N sodium carbonate (100 ml) at 80 °C. HPLC retention times of the prepared dyes were then noted and used in the identification of materials formed during the rate studies. The model compounds, **1b**, **2b** and **3b** were prepared by dissolving 2–4 g of Dyes **1**, **2** and **3** in a mixture of water (50 ml), methanol (200 ml) and Na_2CO_3 (5 g) at 70–75 °C. In each case HPLC showed a steady disappearance of the starting compound and formation of essentially homogeneous products.

3. Results and discussion

Reactive dyes containing chloro-*s*-triazinyl groups react with nucleophiles by an activated heteroaromatic nucleophilic substitution mechanism. For an aqeous solution of methanol in the presence of sodium carbonate, OH^- (hydroxide) and MeO^- (methoxide) compete to react with the triazinyl reactive system via parallel reactions. The success of each nucleophile can be expressed in terms of product ratios [13,14]

$$B_{hm} = \frac{[MeO - Dye][H_2O]}{[HO - Dye][MeOH]} \qquad (1)$$

where [MeO – dye] and [HO – dye] are the concentrations of the products of methoxide and hydroxide attack, respectively. B_{hm} is a product composition quantity and is a measure of selectivity of the reaction towards attack by methoxide rather than by hydroxide. Accordingly, introduction of a reactive dye into a homogeneous mixture of methanol/water medium under alkaline conditions furnishes MeO – dye and HO – dye, whose concentrations can be determined using HPLC. The hydrolysis and methanolysis reactions are second order. However, by using a large excess of methanol and water, pseudo first order reaction kinetics are observed. The pseudo first order rate equation for the hydrolysis of a monochloro-*s*-triazine dye at a constant temperature can be expressed as Eq. (2), in which [Dye – Cl] is the concentration of the model dye, t is the time and k_h is the pseudo first order rate constant that defines the reactivity of the chlorotriazine.

Table 5
Pseudo first order hydrolysis rate constants of Dye **1**

Model dye	Temperature (°C)	$k_{overall}$ (min^{-1})	k_{Cl} (min^{-1})	k_{OMe} (min^{-1})	Ratio (k_{OMe}/k_{Cl})
Dye **1**	40	0.0026	0.0009	0.0017	1.88
(–OMe/Cl)	45	0.0049	0.0017	0.0032	1.93
	50	0.0094	0.0033	0.0061	1.86

$$-\frac{\partial[Dye - Cl]}{[Dye - Cl]} = k_h \times \partial t \qquad (2)$$

The concentration change of the dye can be calculated from the peak area percentages of an HPLC chromotogram and a logarithmic plot of $\ln(A_0/A)$ gives a straight line passing through the origin. Pseudo first order kinetics were experimentally confirmed for Dyes **1**, **2**, **3** and **4** (Figs. 4–7, respectively) and the reactivities are given in Table 4, where A_0 is the initial concentration of the parent dye and A is the concentration at time t minutes.

As expected, in all cases, as the temperature was increased, the rate of hydrolysis increased. When the 4-dimethylamino substituent of a 2-chloro-*s*-triazine was replaced by a 4-methylthio substituent, a marked increase in reactivity was observed, as indicated by an increase in the rate of displacement of chloride by hydroxide or methoxide. However, the 2-chloro-4-methylthiotriazine was not as reactive as the precursor dichloro-*s*-triazine. From the Arrhenius plots, shown in Fig. 8, it can be deduced that, at equal temperature, the reactivity of a 2-chlorotriazinyl system possessing a 4-methylthio substituent (Dye **1**) is approximately 55 times higher than the 4-dimethylamino derivative (Dye **3**) which possesses a powerful electron donating dimethylamino group. As the electron donating power of the substituent increases, the electron deficiency of *s*-triazinyl ring carbon atoms

Table 6
Reaction rates of Dyes **2** and **3**, in a water/methanol mixture, at equal reactivity ($k_{hyd} = 0.0006$ min^{-1})

Dye	Temperature (°C)	Selectivity[a]	$(k_m + k_h)$[b] (× 10^{-2} min^{-1})	k_h[b] (× 10^{-2} min^{-1})	k_m[b] (× 10^{-2} min^{-1})	Ratio (k_m/k_h, average)
2	29	480[a]	0.39[b]	0.0365[b]	0.3535[b]	9.7
3	65	153[a]	0.19[b]	0.0487[b]	0.1413[b]	2.9

[a] Calculated according to Eq. (1).
[b] Measured in a homogenous methanol/water system.

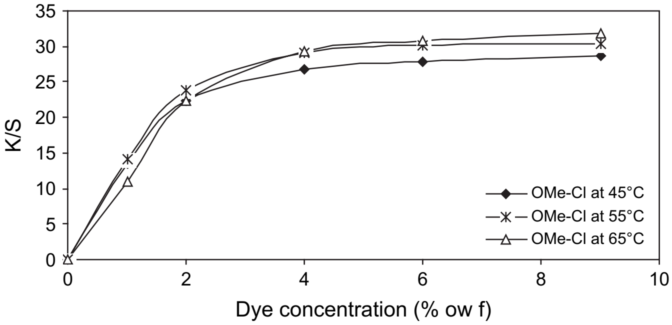


Fig. 10. Dye **1**: build up of Dye **1** at different temperatures.

reduces and this results in the slowing down of nucleophilic substitution.

In keeping with another study [15], hydrolysis of Dye **1** (methoxy-chloro-*s*-triazine) resulted in displacement of both methoxide and chloride and resulted in a mixture of two products. The carbon atom bearing the OMe substituent and the one bearing the Cl atom both undergo attack, by OH^-, at a comparable rate. This again depends primarily on the level of electron deficiency of these carbon atoms but perhaps also on steric accessibility. The ratio of chloride displaced to methoxide displaced was used to calculate the individual hydrolysis rate constants k_{Cl} (substitution of chloride) and k_{OCH_3} (substitution of methoxide), for the two competing reactions. As seen in Table 5, formation of 2-chloro-4-hydroxy-*s*-triazine was approximately 1.9 times faster than the formation of 2-methoxy-4-hydroxy derivative.

Temperatures corresponding to an equal reactivity, as assessed by an overall rate of hydrolysis of $k_{hyd} = 0.0006\ min^{-1}$, for Dyes **1**, **2**, **3** and **4** were calculated as 29 °C, 29 °C, 65 °C and 0 °C, respectively (Fig. 9). In order to gain insight into the relative propensities of the different reactive groups to undergo methanolysis in preference to hydrolysis, selectivity experiments were conducted in a homogeneous mixture of water/methanol at a temperature that corresponded to an equal rate of hydrolysis ($0.0006\ min^{-1}$) of the model dyes, Dye **2** and Dye **3**, in water (Fig. 5). Results are given in Table 5.

The overall rate constant of alcoholysis was dependant only on the concentration of the dye, as a large excess amount of both alkali and methanol was used (Eq. (3)). Results are given in Table 6.

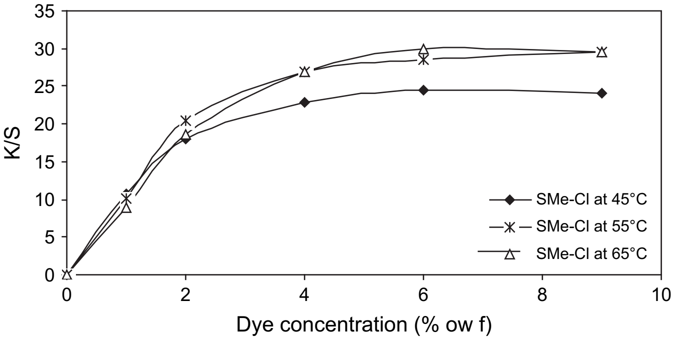


Fig. 11. Dye **2**: build up of Dye **2** at different temperatures.

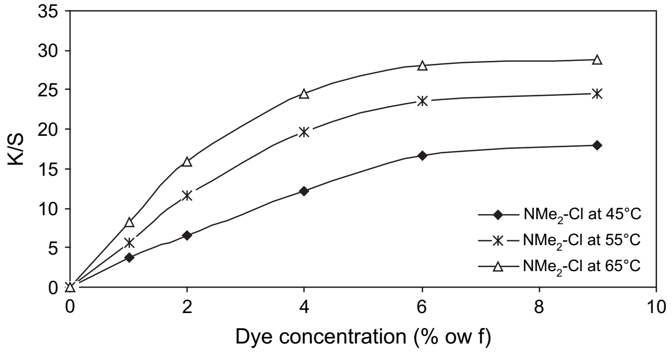


Fig. 12. Dye **3**: build up of Dye **3** at different temperatures.

$$-\frac{\partial[\text{Dye}-\text{Cl}]}{\partial t} = (k_h + k_m) \times [\text{Dye}-\text{Cl}] \tag{3}$$

Results showed that 2-chloro-*s*-triazinyl system possessing a 4-methylthio substituent was approximately three times more selective (towards methanolysis) than the monochloro-*s*-triazinyl system carrying a 4-dimethylamino substituent.

The technical properties of the dyes were also assessed. Initially the build-up profile of each of Dyes **1**, **2** and **3** was assessed over a range of temperatures, in order to determine the optimum application temperature of each. Results are displayed in Figs. 10–12.

The build up of each dye, at its optimum application temperature, is displayed in Fig. 13. The methoxy-chloro-*s*-triazine, Dye **1**, probably fixes via displacement of a combination of either methoxide or chloride.

Fixation by replacement of methoxide would result in a fixed chloro-*s*-triazinyl bound dye, a type of species associated with poor stability to acid (see below). No selectivity data were available on such displacements. However, it has been shown that the methylthio derivative, Dye **2**, reacts much more selectively with an alcohol (methanol), in a homogeneous aqueous solution, than does the corresponding dimethylamino derivative. This dye does also display good build up and fixation when applied to cotton by an exhaust dyeing process, as

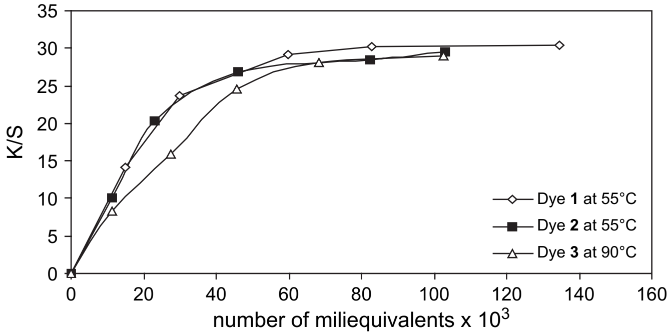


Fig. 13. Build-up curves of Dyes **1**, **2** and **3** at their optimum application temperature.

evidenced by a higher visual depth of shade than the dimethylamino analogue, Dye **3**.

Evaluation of colour fastness to acid treatment (“acid hydrolysis”, see Section 2.3) was consistent with the reaction mechanism proposed for the hydrolysis and alcoholysis of Dye 1. Cotton fabrics dyed with Dye **4** (used as a control) and Dye **1** both gave a grey scale cross-stain, on nylon, of 3. Conversely, Dyes **2** and **3** were less acid sensitive, giving a stain, on nylon, of 4.

4. Conclusions

The reactivity, selectivity and dyeing properties of three different 2-monochloro-*s*-triazinyl reactive dyes possessing different substituents in the 4-position, were evaluated. The 2-chloro-4-methylthio-*s*-triazine exhibited promising warm dyeing properties. Stabilities of dyed fabrics to acid conditions were consistent with fixation of the 2-chloro-4-methoxy-*s*-triazine taking place via displacement of both methoxide and chloride, the former leading to fixed chloro-*s*-triazine, which would be expected to hydrolyse to fixed hydroxytriazine, a species known to exhibit poor stability to acid.

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