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The Kinetics of the Hydrolysis and Alcoholysis of some Model Monofluorotriazinyl Reactive Dyes

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ABSTRACT

Nine model halogenotriazinyl reactive dyes, including five monofluoro derivatives were synthesized. Fluoride- and chloride-ion-selective electrode methods were used to determine the rate constants of hydrolysis and alcoholysis both in alkaline solution and in water–sorbitol. The rate constants of the dichloro, monochloro and monofluorotriazinyl model dyes were compared and relationships between the chemical reactivity and the fixation rate established. ^1H *NMR was used to follow the reaction path of hydrolysis, and possible intermediates formed during the hydrolysis are discussed. The SCF-MO method was used to calculate the superdelocalizability* S_{rn}^{ppp} *on the reaction site and it was found that the natural logarithms of the rate constants of hydrolysis were linearly correlated to* S_{rn}^{ppp}*, the correlation equation being*

$$T \ln k_w(\times 10^{-3}) = 166{\cdot}65 S_{rn}^{ppp} - 24{\cdot}06$$

1 INTRODUCTION

Attention has been focused on fluoro-containing reactive dyes, which have excellent properties.[1] In order to study the higher fixation and reactivity of these dyes, the kinetics of hydrolysis and alcoholysis of some model reactive dyes was studied and the mechanism of hydrolysis investigated using ^1H NMR and MO theory.

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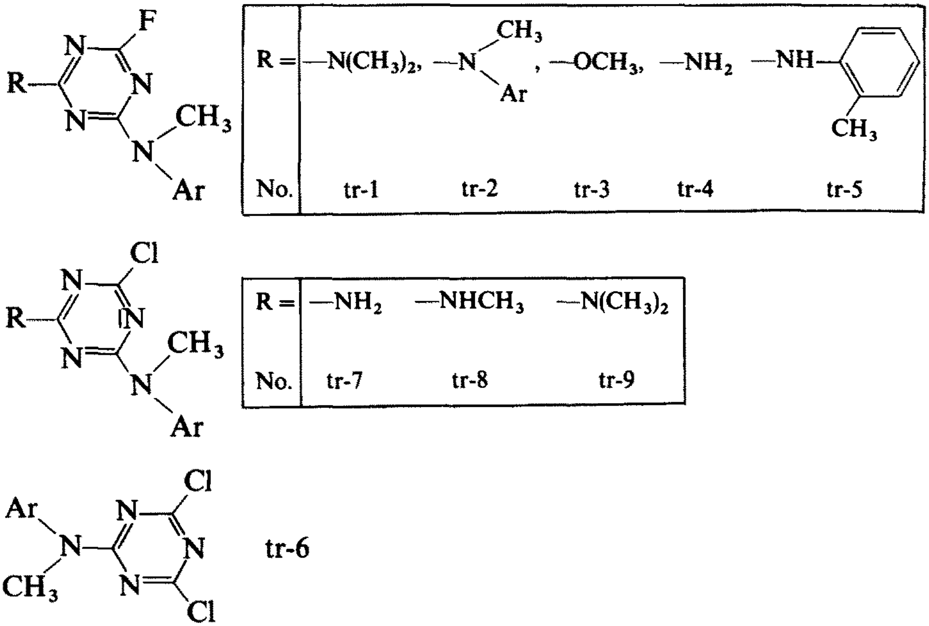
2 METHODS USED AND RESULTS

2.1 Model reactive dyes

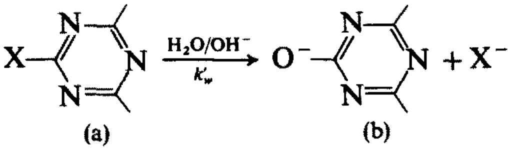
The following model reactive dyes (Structure 1) were synthesized, and their analytical data are shown in Table 1.



Structure 1

2.2 Kinetic equation of hydrolysis

The alkaline hydrolysis of the model dyes may be expressed as follows:



X = F or Cl

This is a second-order reaction, having the rate equation

$$\frac{d[D]}{dt} = k'_w[D][OH^-]$$

In excess alkali, it may be treated as a pseudo first-order reaction, i.e.

$$\frac{d[D]}{dt} = k_w[D], \qquad \ln\frac{[D_0]}{[D]} = k_w t \tag{1}$$

TABLE 1
The Analytical Data of Model Reactive Dyes

No.	*Mol wt*	*m.p. (°C)*	*Analysis N %*		*M+/e*
			Calculated	*Observed*	
tr-1	247·26	76·5–76·9	28·32	28·29	247
tr-2	309·32	70·2–70·6	22·64	22·42	309
tr-3	234·24	65·7–66·6	24·24	24·12	234
tr-4	219·25	148–150	31·95	31·78	219
tr-5	309·32	253–255	22·64	23·04	309
tr-6	255·21	72·5–73·8	21·96	21·96	255
tr-7	235·73	171–172	29·72	29·40	235
tr-8	249·76	156–160	28·05	27·94	249
tr-9	263·78	120–122	26·56	26·53	263

If the fluoride- and chloride-ion-selective electrodes methods are employed, the concentration of F^- and Cl^- measured may be used to calculate k_w.

$[D_t]$ is equal to $[F^-]$ or $[Cl^-]$ at time t, the concentration of compound B is equal to $[D_t]$, and the concentration of A that is $[D_a]$ is equal to $[D_0] - [D_t]$.

Equation (1) can thus be written as

$$\ln \frac{[D_0]}{[D_0] - [D_t]} = k_w t$$

If $\ln [D_0]/([D_0] - [D_t])$ is plotted against t, a straight line is obtained, the slope of which is k_w (see Fig. 1).

The rate constants of hydrolysis of the various model dyes are shown in Table 2.

2.3 Kinetic equation of alcoholysis

The reaction between a reactive dye and cellulose fiber may be compared to the reaction between the model reactive dye and a polyhydric alcohol.

TABLE 2
The Rate Constants of Hydrolysis and Their Relative Ratio
($T = 323$K)

No.	*tr-1*	*tr-2*	*tr-3*	*tr-4*	*tr-5*	*tr-6*	*tr-7*	*tr-8*	*tr-9*
$k_w \times 10^{3a}$	0·602	1·077	7·692	2·703	1·493	30·2	1·136	0·867	0·430
Ratio	1·4	2·5	17·9	6·3	3·5	93·5	2·7	2·0	1

[a] The unit of the rate constant (k) is $\min^{-1}$.

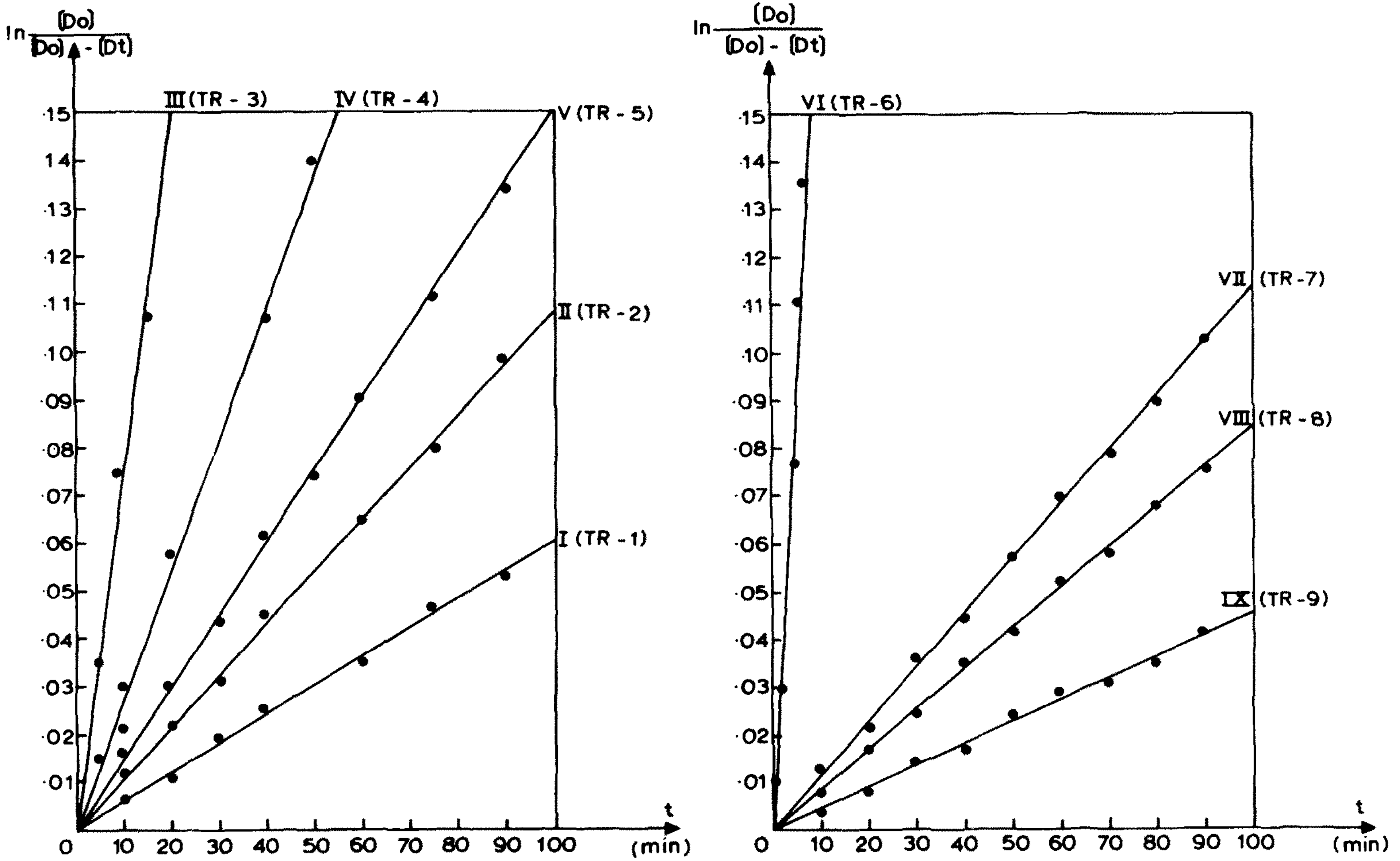
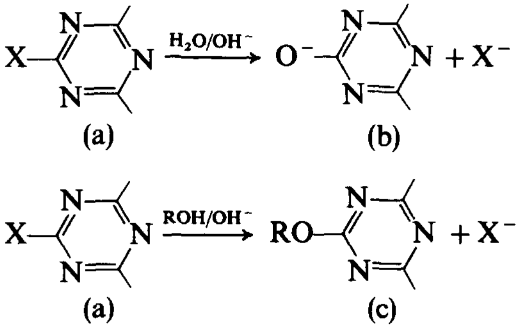


Fig. 1. Plot of $\ln [D_0]/([D_0]-[D_t])$ against *t*.

Sorbitol was chosen to study the kinetics of the alcoholysis of the model dyes in homogeneous solution. The measurement of rate constants and the ratio of k_{alc}/k_w may then be used to study the selectivity of various reactive groups to the cellulose fiber.

In water–polyhydric alcohol solution, the hydrolysis and alcoholysis may be expressed as follows:



X = F or Cl

In excess alkali and sorbitol, these are first-order reactions kinetically. If $[D_t]$ denotes the concentration of ions in solution at time t, then $[D_t] = [D_b] + [D_c]$. Therefore

$$[D] = [D_0] - [D_b] - [D_c] \qquad [D] = [D_0] - [D_t]$$

and hence

$$\ln \frac{[D_0]}{[D_0] - [D_t]} = k_{total} t$$

If $\ln [D_0]/([D_0] - [D_t])$ is plotted against t, a straight line will be obtained, the slope of which is k_{total}, and hence k_{alc}/k_w can be obtained using the relationship

$$k_{alc}(\text{sorbitol}) = k_{total} - k_w$$

The rate constants of alcoholysis in sorbitol and k_{alc}/k_w are tabulated in Table 3.

TABLE 3
The Rate Constants of Alcoholysis and the Ratio of k_{alc}/k_w ($T = 323$ K)

No.	*tr-1*	*tr-2*	*tr-3*	*tr-4*	*tr-5*	*tr-6*	*tr-7*	*tr-8*	*tr-9*
k_{alc} (min^{-1})	0·0194	0·0285	0·0473	0·0626	0·0385	0·392	0·0177	0·0135	0·0679
k_{alc}/k_w	32·9	26·4	23·1	23·2	25·8	12·0	15·6	15·6	15·8

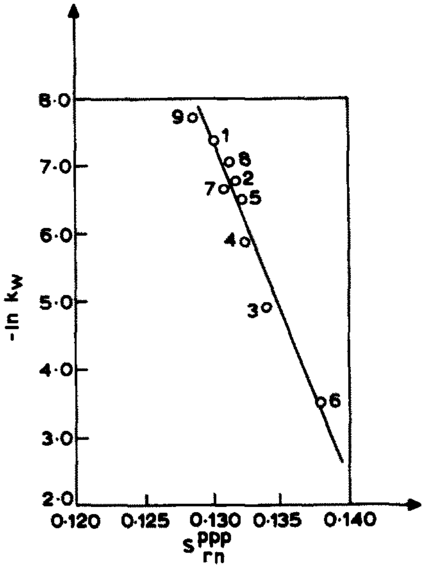


Fig. 2. Correlation of $\ln k_w$ with S_{rn}^{ppp}.

2.4 SCF–PPP MO calculation[2,3]

The SCF–PPP MO method was used to calculate the electron densities, localization energies and superdelocalizabilities on the reaction sites of various model dyes. The obtained reactive indices were then used to correlate with $\ln k_w$.

The superdelocalizability, originally defined by Fukui, may be represented as follows:

$$S_{rn}^{PPP} = \sum_{i}^{\text{unocc}} \frac{2(C_r^i)^2}{|E_i - E_0|}$$

The parameter values of the heteroatoms for use in HMO and PPP

TABLE 4
The Parameter Value of HMO

Group	$(ph)\!-\!\ddot{N}=$	$\overset{R'}{\underset{R}{>}}N$—	*RNH*—	—NH_2	—CH_3	—*Cl*	—*F*	—OCH_3
h_x	0·5	1·0	1·4	1·5	2·0	2·0	3·0	1·9
$\text{Bond}_{x\text{-}y}$	C—N	N—C	N—C	N—C	C—C	C—Cl	C—F	O—C
$k_{x\text{-}y}$	1·0	1·0	0·9	0·8	1·0	0·8	0·7	0·9

TABLE 5
The Parameter Value of PPP

$Bond_{x\text{-}y}$	$-\dot{N}=(ph)$	$\begin{matrix}R' & \\ & N- \\ R & \end{matrix}$	$RNH-$	$-NH_2$	$-OCH_3$	$-Cl$	$-F$	$-CH_3$
I_p (eV)	16·96	21·22	22·00	22·60	26·73	25·07	30·24	23·49
A_p (eV)	4·51	8·24	8·20	8·15	12·16	15·50	16·37	12·65
$R_{x\text{-}y}$ (A)	1·39	1·40	1·39	1·38	1·35	1·77	1·38	1·52
Z_n^*	1	2	2	2	2	2	2	2

TABLE 6
S_{rn}^{ppp} and N_r on the Reaction Sites

No.	*tr-1*	*tr-2*	*tr-3*	*tr-4*	*tr-5*	*tr-6*	*tr-7*	*tr-8*	*tr-9*
S_{rn}^{ppp}	0·1302	0·1320	0·1337	0·1325	0·1322	0·1379	0·1315	0·1312	0·1289
N_r	0·5555	0·5516	0·5451	0·5514	0·5515	0·5425	0·5525	0·5532	0·5579

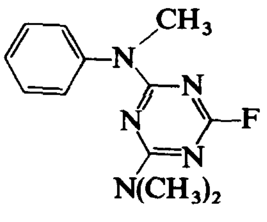
methods are given in Tables 4 and 5 respectively and the calculated S_{rn}^{ppp} and N_r values are collated in Table 6.

If the various reactive indices are plotted against $\ln k_w$, only S_{rn}^{ppp} is found to show a linear relationship to $\ln k_w$ (Fig. 2), the correlation being defined by:

$$T \ln k_w(\times 10^{-3}) = 166{\cdot}65 S_{rn}^{ppp} - 24{\cdot}06$$

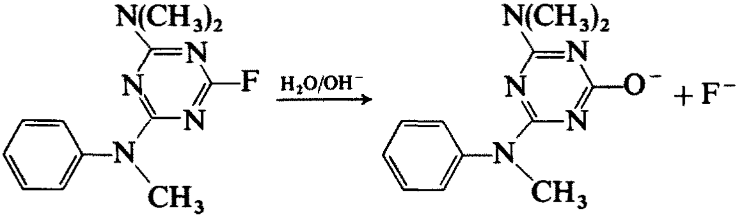
2.5 Mechanism of hydrolysis of model monofluorotriazine reactive dyes by ^{1}H NMR

The structure of the selected model monofluorotriazinyl dye used was



The ^{1}H NMR spectrum in *d*-acetone is shown in Fig. 3, the chemical shifts in which are $\delta = 7{\cdot}4$ ppm, phenyl ring protons; $\delta = 3{\cdot}5$ ppm, methyl protons in *N*-methyl group; $\delta = 3{\cdot}1$ ppm, protons of the $N(CH_3)_2$ group; and $\delta = 2{\cdot}3$ ppm, acetone.

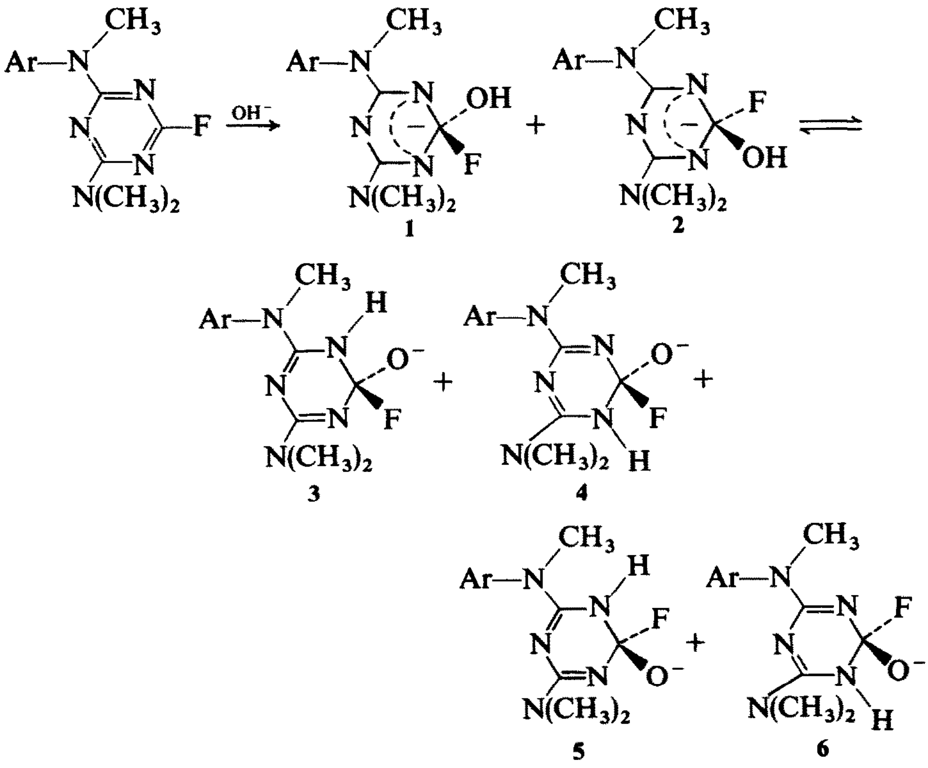
The hydrolysis reaction of the model dye is



The ^{1}H NMR spectra of the model dye, after different times t(min) of hydrolysis are shown in Fig. 4.

Thus, during the course of the hydrolysis, six additional peaks appear, having chemical shifts at 4·5, 5·2, 5·8, 7·8, 8·5 and 9·2 ppm respectively. If the hydrolysis is carried out in deuterated medium, these peaks are not formed. If the hydrolysis is carried out with addition of a small amount of trifluoroacetic anhydride, the peaks at $\delta = 4{\cdot}5$ ppm and $\delta = 5{\cdot}2$ ppm disappear and hence these two peaks are due to the two OH groups formed during the reaction (see Fig. 3).

From the above results, the mechanism of hydrolysis of the model monofluorotriazinyl reactive dyes may be depicted as follows:[5]



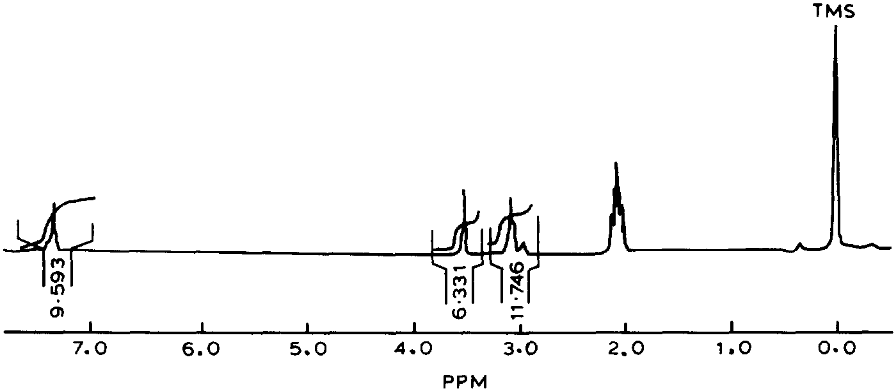


Fig. 3. ^{1}H NMR spectra of the model dye in *d*-acetone.

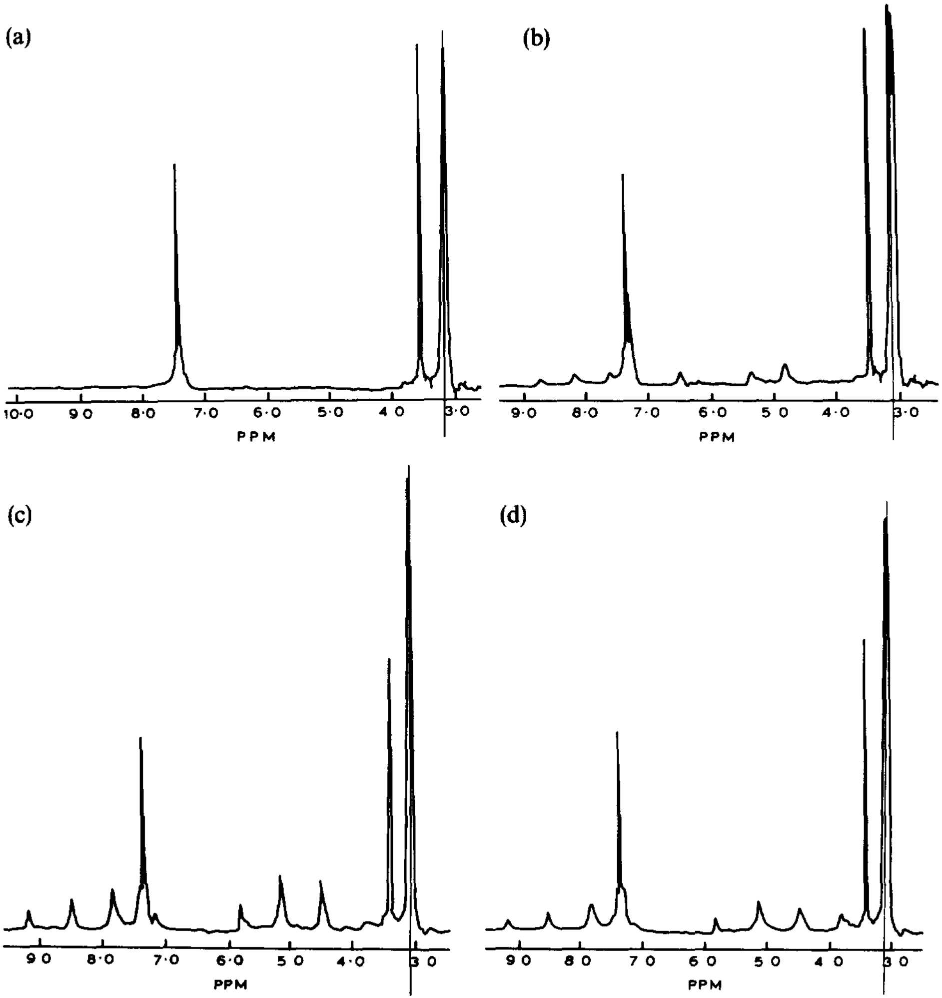


Fig. 4. ^{1}H NMR spectra of the model dye after different times (t) of hydrolysis. (a) $t = 30$ s, (b) $t = 3$ min, (c) $t = 4$ min, (d) $t = 5$ min, (e) $t = 10$ min, (f) $t = 20$ min, (g) $t = 4$ min; T = 303K in each instance.

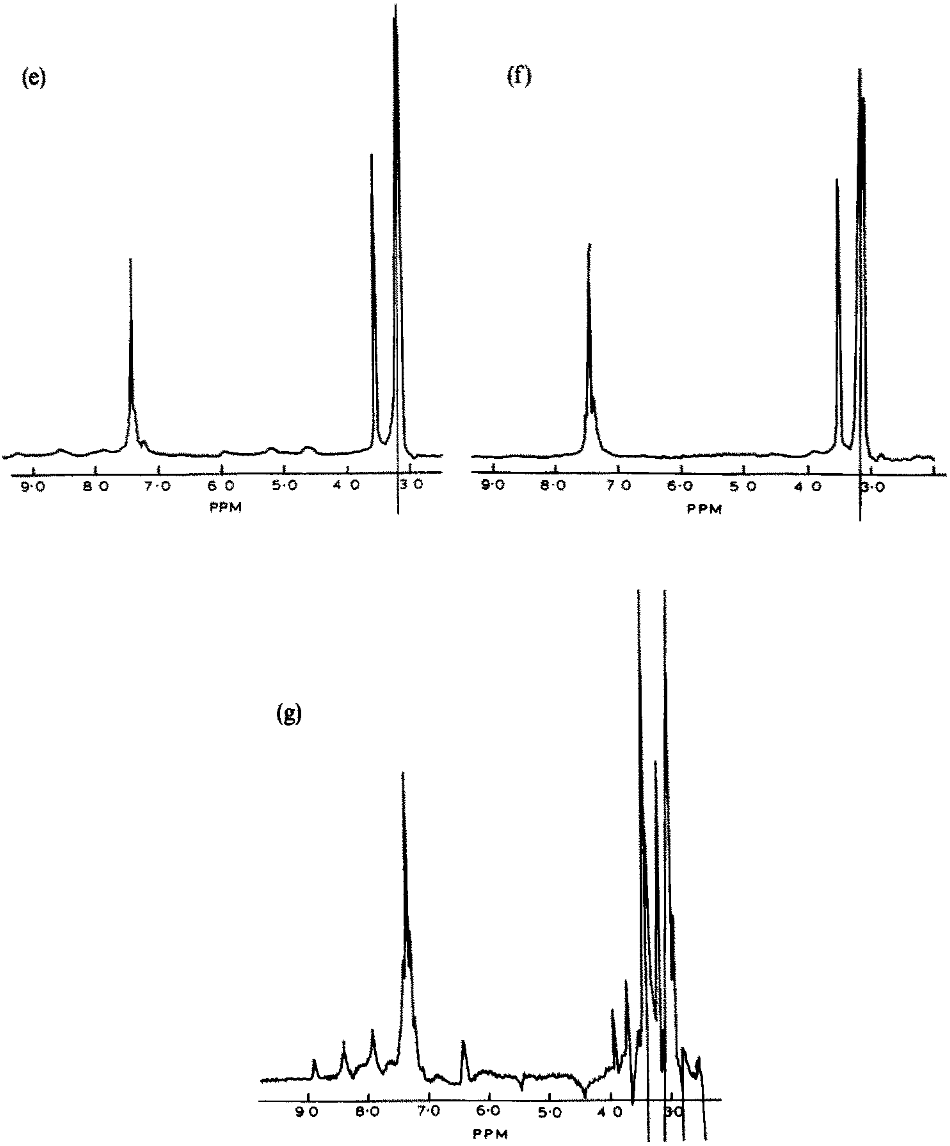


Fig. 4.—*contd.*

2.6 General observations

There are two factors to consider when comparing the specific properties of reactive dyes, viz. the reactivity and the fixation rate. Using only the rate constants of the hydrolysis, it is difficult to rationalize these two factors. However, if k_w is used as a measure of reactivity and k_{alc}/k_w is used as a measure of fixation rate, then the results of the kinetic study give a more satisfactory explanation of the practical results, viz.

(1) Order of k_w: dichlorotriazine > monofluorotriazine > monochlorotriazine.
(2) Order of k_{alc}/k_w: monofluorotriazine > monochlorotriazine > dichlorotriazine.

Actually, k_{alc}/k_w reflects the selectivity of the reactive group to alcoholysis. The fixation rate is dependent on the selective behaviour of the dye to cellulose and to OH^-. The properties of actual reactive dyes may be approximated by the study of the model reactive dyes.

The dyeing of monochlorotriazine reactive dyes involves four successive stages: (1) adsorption of dye molecules by fiber, (2) addition of alkali with the formation of cellulose O^-, (3) fiber reaction and (4) elimination of Cl^-. The reaction between the reactive dye and cellulose O^- is the most important. In the third step, the O^- of the cellulose fiber will attack the chlorine or fluorine atom from below. The atomic radius of fluorine (1·39 Å) is smaller than that of chlorine (1·77 Å) and the fluorine atom is therefore more readily attacked by O^- and is more readily eliminated. Therefore the model monofluorotriazine dyes have higher selectivity than the model monochlorotriazine dyes towards alcoholysis.

3 EXPERIMENTAL

3.1 Synthesis of model monofluorotriazine reactive dyes (tr-1)

Acetone (70 ml) was cooled to below −10°C and cyanuric fluoride (6–8 g) was added with stirring. A solution of *N*-methylaniline (5·3 g) in acetone (30 ml), was then added, maintaining pH 3–4 by addition of 10% KOH solution gradually until the pH remained unchanged. The reaction was continued for a further 1 h. Acetone (30 ml) containing 33% dimethylamine solution (0·05 mol) was then added to 0–5°C, with addition of a small amount of 10% KOH to maintain the pH at 6–7. After the solution pH was unchanged, the reaction was continued for a further 0·5 h. The mixture was then poured slowly onto ice-water (400 ml) and the white precipitate was filtered, washed with ice-water and then twice with cold ethanol. The filter cake was vacuum dried, and the crude product was recrystallized from benzene, giving a white powder, with m.p. 76·5–76·9°C.

Other model compounds were similarly prepared.

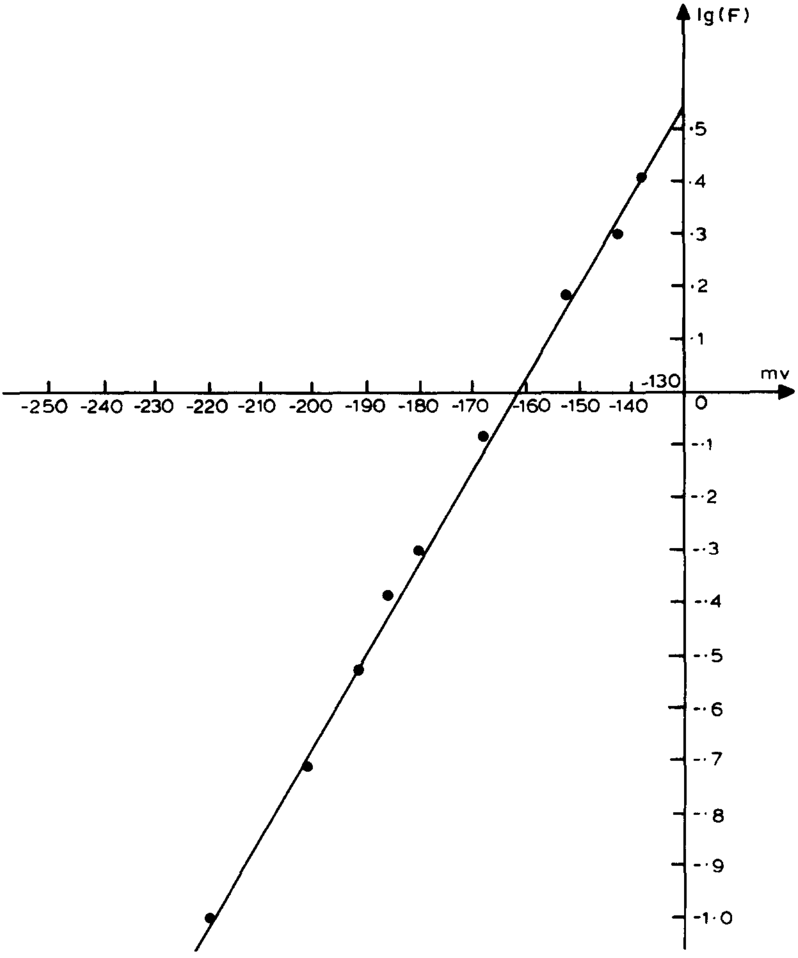


Fig. 5. Plot of $-\log[F^-]$ vs mV.

3.2 Kinetic measurement[4]

These were carried out in water–dioxane (1:1 v/v), using concentrations of NaOH and sorbitol in large excess with respect to the model reactive dyes, viz. water (50 ml), dioxane (50 ml), 1 M NaOH (10 ml), model reactive dye (5×10^{-4} mol), sorbitol (10^{-2} mol).

The liquors were thermostatted to the desired temperature and samples of the solution taken at selected times. They were added to ice-water, neutralized with HNO_3 and cooled to 0°C to stop the reaction. The halide ion concentration was measured by the ion-selective electrode method, using a pH meter model pH S-2, a pF-1 fluoride-ion-selective electrode and a 301 chloride-ion-selective electrode.

The standard curve was obtained by plotting $-\log[F^-]$ against mV (Fig. 5).

3.3 ^{1}H NMR measurements

A WP-100SY NMR spectrometer (Spectrospin, Switzerland) was employed, using, for hydrolysis: 0·5 ml deuterated alkaline solution (3 g/l NaOH) and 5×10^{-5} mol model dye, and for the alcoholysis: 0·5 ml deuterated acetone, 20 ml NaOD, 0·1 ml MeOH and 5×10^{-5} mol dye. A 5-ml sample tube was used directly in the NMR spectrometer. The temperature was raised to 30°C and kept constant, sampling, at different times, to follow the reaction pathway.

3.4 Measurement of kinetic data by fluoride-ion-selective electrode method

The measurement was carried out using the standard curve method. The following instruments were used: a (pH S-2) pH meter, a pF-1 fluoride-ion-selective electrode and a 301 chloride-ion-selective electrode.

The standard curve was obtained using the following method. Accurately weighed NaF (AR) (0·22 g) was dried for 2 h at 120°C and then dissolved in deionized water and diluted to 1 litre. Aliquots, viz. 0·06, 0·25, 0·50, 0·75, 1·00, 2·00, 3·00, 4·00 and 0·50 ml standard solution (1 ml $\approx$ 10 μg fluorine) were placed in a 50 ml volumetric flask and 1 drop of (0·1% Bromocresol Green added, followed by 2N NaOH until the colour of the solution changed from yellow to blue; 1N HNO_3 was then added until the yellow colour was restored. TISAB solution (10 ml) was added and the mixture diluted with deionized water to 50 ml, thus yielding a series of standard F^- solutions.

With stirring, the equilibrium potentials were recorded when they remained constant after 3 min. The standard curve was obtained on plotting $-\log[F^-]$ against mV.

The test sample was pipetted into a 50-ml volumetric flask and 1 drop of Bromocresol Green was added, followed by a few drops of 2N NaOH solution until the colour changed from yellow to blue, and then 0·1N HNO_3 was added to restore the yellow colour. TISAB solution (10 ml) was added and the solution was diluted with deionized water to 50 ml. After shaking, the potentials were measured and the F^- concentration was taken from the standard curve and thus calculated in the test sample.

4 CONCLUSIONS

Nine model reactive triazine dyes were synthesized, including five of monofluorotriazine derivatives. The hydrolysis and alcoholysis constants of these dyes were measured by ion-selective electrode methods and the measured values k_{alc}/k_w were used to interpret the high fixation value of monofluoro reactive dyes. The SCF–PPP MO theory was used to calculate the reactive indices and it was found that $\ln k_w$ showed good correlation with S_{rn}^{PPP}. The hydrolysis of a monofluoro reactive dye was followed using ^1H NMR. The mechanism of the hydrolysis is discussed. It is an addition–elimination reaction and the elimination of F^- is not involved in the rate-determining stage. Possible isomers which can be present in the reaction are also discussed.

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