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Kinetics of Hydrolysis of some Model Bifunctional Reactive Dyes

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ABSTRACT

The hydrolysis in alkaline solution of some model bifunctional reactive dyes has been studied using ^{1}H-NMR. The kinetics of the hydrolysis of the monochlorotriazine group and the vinylsulfone group were studied by the chloride ion-selective electrode method and by ^{1}H-NMR respectively. HMO theory was used to calculate the reactive indices on the two reactive sites and a very good relationship was found between ln k and superdelocalizability, S_r^N:

For the monochlorotriazine group, $T \ln k_1(\times 10^{-3}) = 1{\cdot}397 S_{r_1}^N - 3{\cdot}957$

and

For the vinylsulfone group, $T \ln k_2(\times 10^{-3}) = 0{\cdot}777 S_{r_2}^N - 3{\cdot}287$

1 INTRODUCTION

There are numerous ways in which an increase in the fixation rate of reactive dyes on cellulose can be attained and recently, efforts have been made in introducing two similar or dissimilar reactive groups into the dye molecule. Bifunctional reactive dyes containing monochlorotriazine and vinylsulfonyl groups have been produced and these have excellent properties. A study of the kinetics of the hydrolysis of these bifunctional reactive dyes is thus important with respect to improving dyeing properties and to develop this type of reactive dye.

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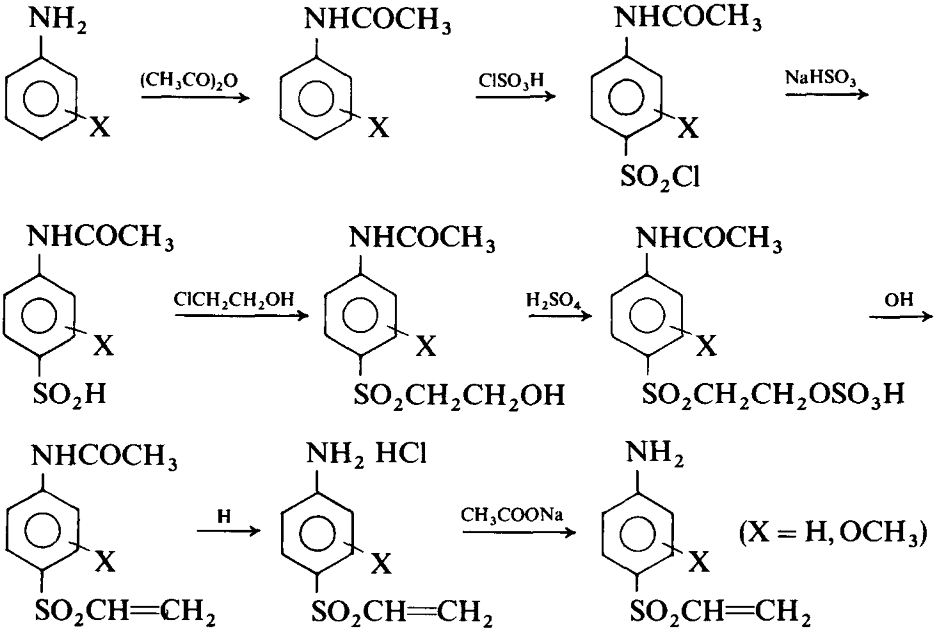
In this paper, some model bifunctional reactive dyes were synthesized and ^{1}H-NMR was used to follow the hydrolytic reaction path. The specific rate constants of hydrolysis were determined by the chloride ion-selective electrode method and by ^{1}H-NMR. The HMO method was used to calculate the reactive indices at the reaction sites, and ln *k* was correlated with some of the calculated indices.

2 EXPERIMENTAL

2.1 Preparation of reactive intermediates and of model bifunctional reactive compounds

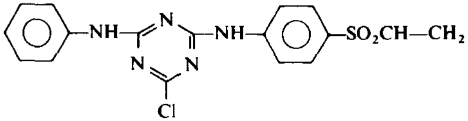
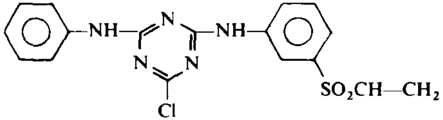
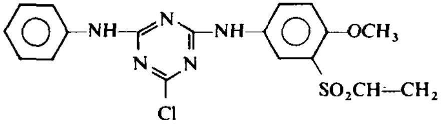
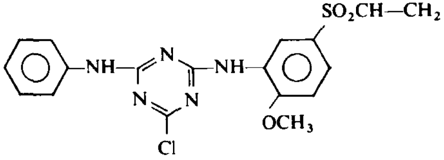
The reactive intermediates used were prepared according to Scheme 1.[1]



Scheme 1.

These intermediates were dissolved in acetone at 0–5°C and then reacted with cyanuric chloride. The reaction temperature was then raised to 55–60°C, and the initial condensation product further reacted with aniline. The final products were purified by chromatography and recrystallization to give the pure model bifunctional reactive compound, data for which are shown in Table 1.

TABLE 1
Analytical Data of Model Compounds

No.	*Structure*	*Mol. wt*	*Melting pt (°C)*	*Calculated (%)*			*Found (%)*			*m/e*
				C	*H*	*N*	*C*	*H*	*N*	
BI-1		387·5	204–206	52·65	3·61	18·06	52·84	3·62	17·88	387
BI-2		387·5	170–171	52·65	3·61	18·06	53·15	3·86	17·92	387
BI-3		417·5	226–228	51·74	3·83	16·77	51·46	3·85	16·58	417
BI-4		417·5	212–214	51·74	3·83	16·77	51·32	3·85	16·58	417

2.2 ^{1}H-NMR studies of hydrolysis mechanism

According to transition theory, the reactants in a chemical reaction must surmount an energy barrier, i.e. they must pass through an activated state. Knowledge of the structure of the activated state is usually taken from the nearby intermediate, but the intermediate is comparatively short-lived and changes rapidly to the final product. The so-called mechanism of reaction is a study of the formation and transformation of the intermediates and in this respect evidence of formation of the intermediate is thus very important in mechanism elucidation. In this paper, ^{1}H-NMR is used to study the hydrolytic mechanism of bifunctional reactive dyes. Instruments used were a WP-100SY NMR spectrometer (Spectrospin, Switzerland) and B-VT1000 adjustable-temperature equipment (Bruker, FRG).

In a sample tube ($d = 5$ mm), 0·5 ml CD_3COCD_3, 0·01 ml alkaline solution (30 g NaOH/0·1 litre H_2O) and 0·09 mol dye sample were mixed and reacted at 30°C. Samples were computer-analysed at specific time intervals, thus providing information on the reaction pathway.

3 RESULTS AND DISCUSSION

3.1 ^{1}H-NMR spectra

Figure 1 shows the ^{1}H-NMR spectrum of the model bifunctional compound **BI-3** in CD_3COCD_3. In the spectrum, the two multiple peaks 6·8 and 7·8 ppm are due to H of the phenyl group, and the peak 3·8 ppm is due to H of the methoxy group.

Figure 2 shows the ^{1}H-NMR spectrum of the NaOH–CD_3COCD_3–H_2O

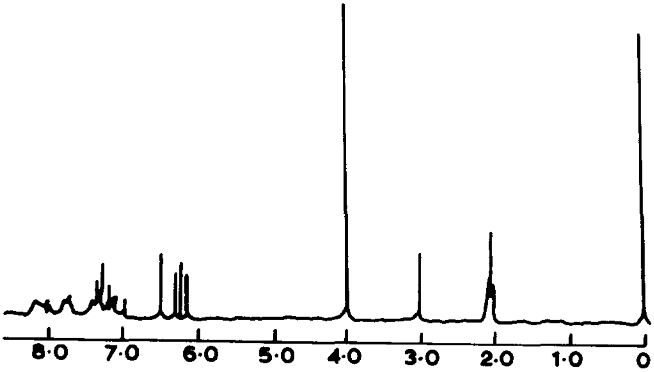


Fig. 1. ^{1}H-NMR spectrum of model bifunctional compound **BI-3** in CD_3COCD_3.

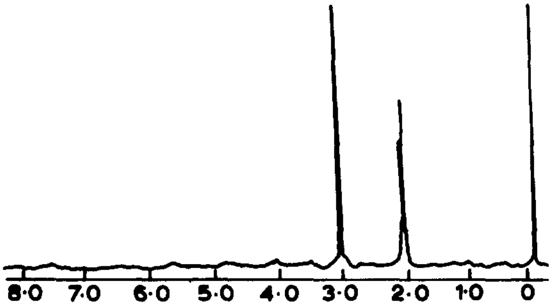


Fig. 2. ^1H-NMR spectrum of the $NaOH$–CD_3COCD_3–H_2O system.

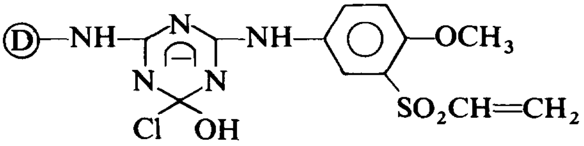
system. In the spectrum, the peak at 3·0 ppm is due to H of water, and the multiple peaks about 2·0 ppm are due to H of acetone.

Figure 3 shows the ^1H-NMR spectrum of the model bifunctional compound **BI-3** in H_2O–CD_3COCD_3–$NaOH$ at different times. Compared with Fig. 1 and Fig. 2, it is apparent that in Fig. 3, eight new peaks, from 4·0 to 9·0 ppm, occur, of which those at 8·77, 8·22, 6·69, 5·52, 4·99 and 4·44 ppm appear after 5 min. The intensities of these six new peaks then gradually decrease and completely disappear after 20 min. If the reaction is carried out in $NaOD$–D_2O–CD_3COCD_3 (see Fig. 4), the six resonance signals are not formed. The two peaks at 3·95 and 4·09 ppm increase as the reaction progresses. Even when the reaction was carried out in completely deuterated medium, these two peaks still occurred and increased in intensity with progression of the reaction.

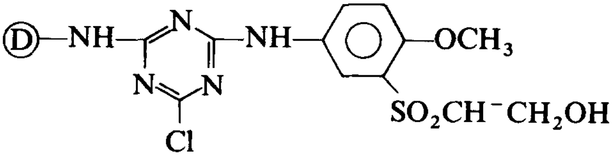
Thus, it can be concluded that the six peaks from 4·44 to 8·77 ppm are formed due to active H and the other two peaks from 3·95 to 4·09 ppm are the resonance absorption peaks from the final product. The mechanism of hydrolysis may thus be elaborated as follows.

3.2 Structure deduction of intermediates

It can be presumed that the six new peaks from 4·44 to 8·77 ppm are due to the formation of the intermediates **A** and **B** during hydrolysis. The protons in the —OH and (—CH^-—) are active hydrogens and therefore the resonance absorption peaks disappear in deuterated medium.



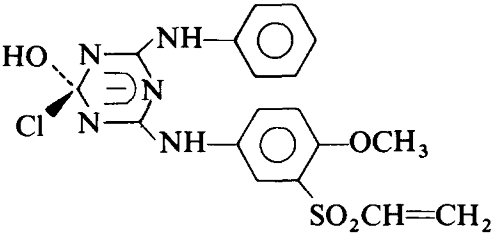
A



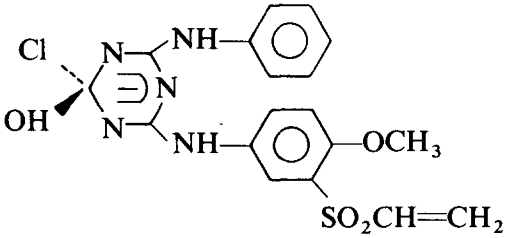
B

In the initial stage of the reaction, the model compound is attacked by OH^- with the formation of **A** and **B**. As the reaction progresses, the concentration of the intermediates **A** and **B** gradually decreases and they finally disappear, the associated six peaks in the ^1H-NMR spectrum also gradually disappearing.

The reactive site of the triazinyl ring may be attacked by OH^- in the direction from above or below the ring-plane and thus two stereoisomers, **A-1** and **A-2**, are formed.



A-1



A-2

Since the OH is attached to the triazinyl ring (and is thus similar to phenolic OH in nature), its resonance peaks will appear in low field. The two peaks at 8·77 and 8·22 ppm are thus due to the active hydrogen in the stereoisomers **A-1** and **A-2**.

The four other peaks are attributed to the different modes of nucleophilic addition of OH^- to the vinylsulfone double bond. Thus formation of a hydrogen bond between OH and the oxygen atom of the vinylsulfonyl group can occur, formation of **B-1**, or if such a hydrogen bond is not formed, then structure **B-2** will result. In either case, the $—CH^-—$ in the $—SO_2CH_2—$

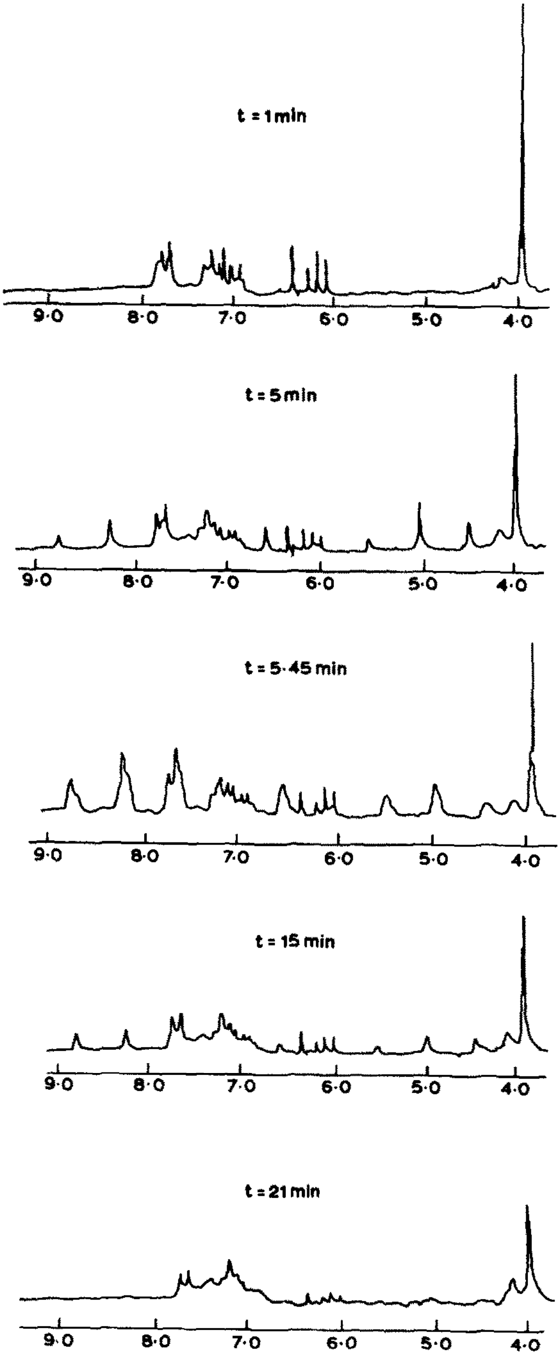


Fig. 3. ^{1}H-NMR spectrum of **BI**-3 in H_2O–CD_3COCD_3–NaOH at various times.

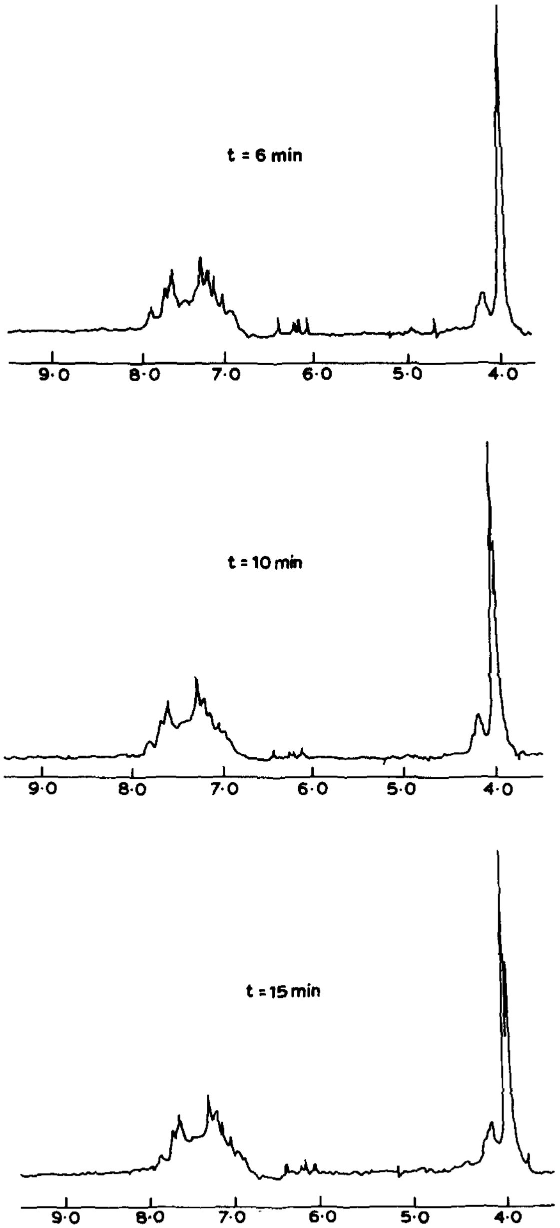


Fig. 4. ^{1}H-NMR spectrum of **BI-3** in NaOD–D_2O–CD_3COCD_3 at various times.

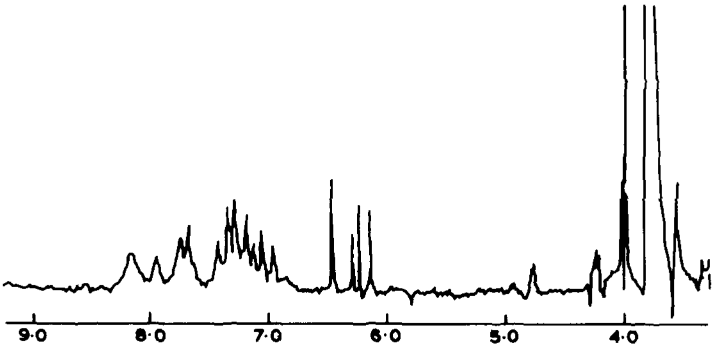
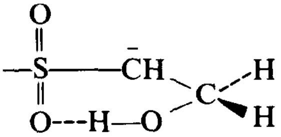
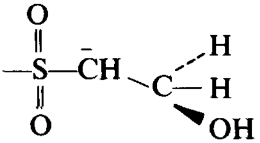


Fig. 5. ^{1}H-NMR spectrum after addition of trifluoroacetic anhydride.

CH_2OH group results in two new peaks in addition to two different peaks of the OH group and therefore, resonance absorption peaks appear, e.g. 6·69, 5·52, 4·99 and 4·44 ppm.[2]

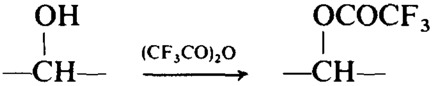


B-1



B-2

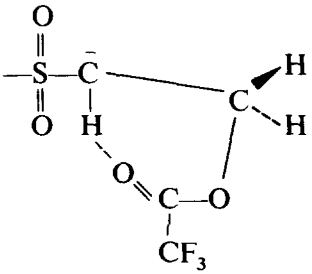
In order to verify this conclusion, trifluoroacetic anhydride was added. For reaction at the OH group,[3] viz., the proton peak due to OH should



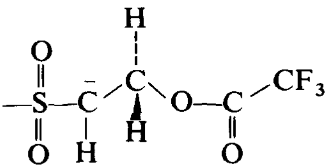
$$\overset{\displaystyle OH}{\overset{|}{—CH—}} \xrightarrow{(CF_3CO)_2O} \overset{\displaystyle OCOCF_3}{\overset{|}{—CH—}}$$

disappear and the —CH— proton peak will be shifted to low field. Figure 5 shows that the original six peaks disappear completely and two new peaks around 8·00 ppm appear.

It is apparent that four of the six peaks are from OH and the two new peaks result from another two of the six peaks shifting to low field, possible structures being **C-1** and **C-2**.



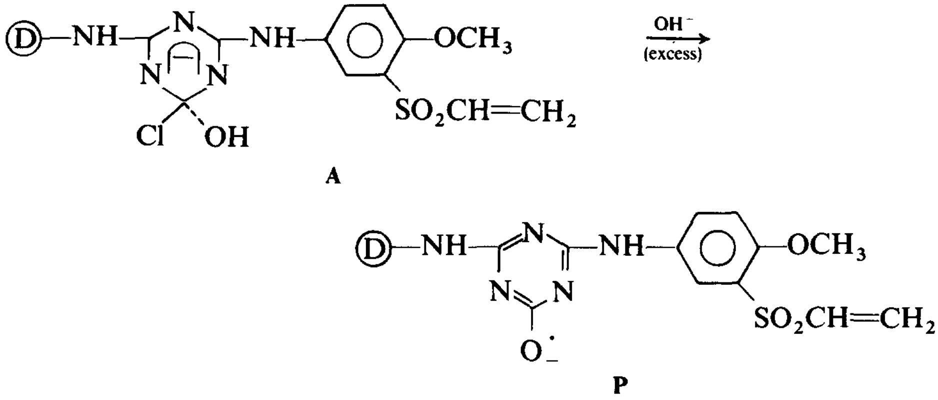
C-1



C-2

3.3 Structure confirmation of the reaction product formed by nucleophilic substitution

When the intermediate **A** is formed after nucleophilic substitution in the triazinyl ring in presence of excess alkali, **A** reacts further with formation of the final product **P**.



Therefore, the peaks at 8·77 and 8·22 ppm disappear.

3.4 Structure confirmation of the reaction product formed by nucleophilic addition

Figures 3 and 4 show that the two peaks at 3·95 and 4·09 ppm gradually increase. This may be due to the increase in concentration of —CH_2CH_2— in the hydroxyethylsulfonyl group (—$SO_2CH_2CH_2OH$) resulting from nucleophilic addition of OH^- to the vinylsulfonyl double bond.

In order to verify this, $(CF_3CO)_2O$ was added to the reaction mixture when the reaction was complete. It was found that the peak at 3·95 ppm

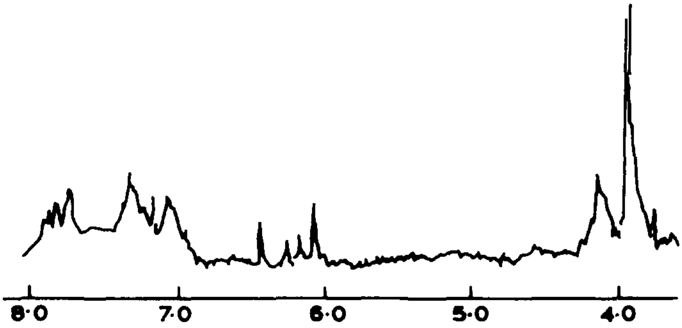


Fig. 6. ^{1}H-NMR spectrum at the end of reaction.

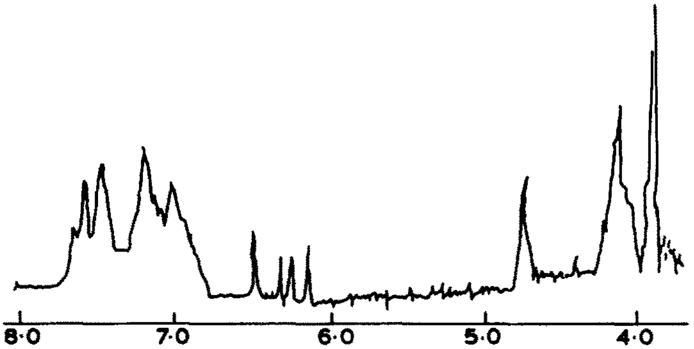
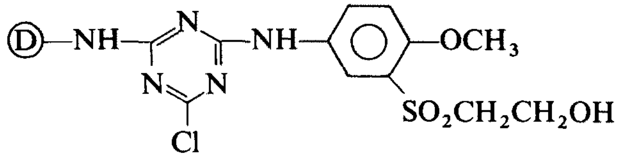


Fig. 7. ^{1}H-NMR spectrum of reaction mixture when $(CF_3CO)_2O$ is added.

disappeared and a new peak around 4·88 ppm appeared (Figs 6 and 7). This indicates that:

(a) an OH group is present in the final products;
(b) this OH group is linked to an aliphatic carbon atom;
(c) the protons in $—SO_2CH_2—C—$ appear at 4·09 ppm, and the protons in $—SO_2—C—CH_2$ appear at 3·95 ppm.

Thus, the structure of the final product formed after nucleophilic addition at the vinylsulfonyl double bond is:



3.5 General observations

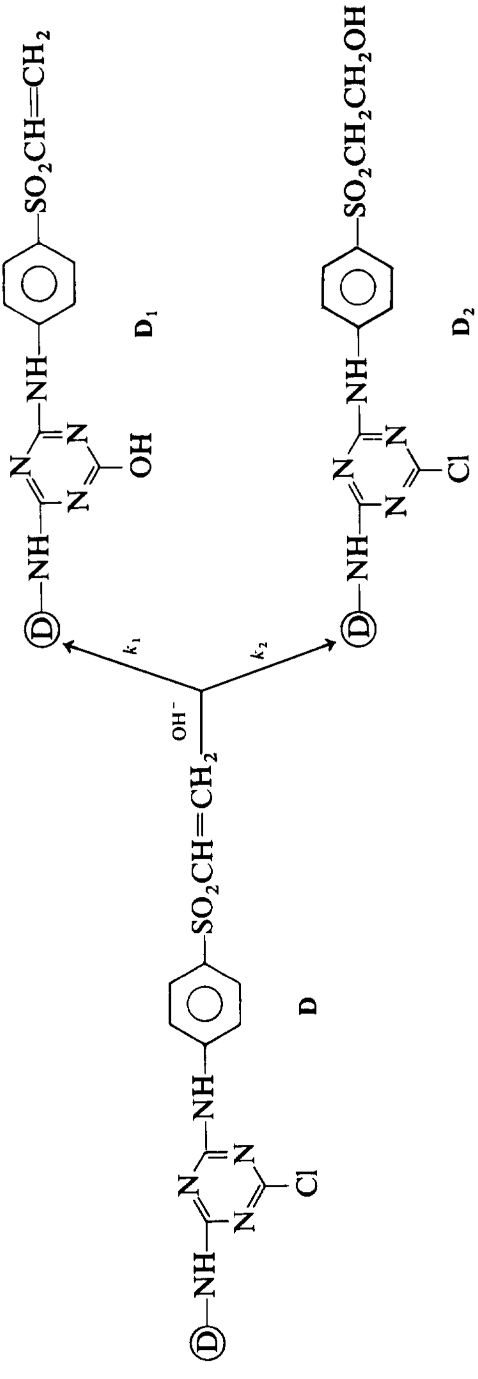
Figure 3 shows that the six resonance absorptions appear concurrently and are of different peak areas only. Therefore, the hydrolytic reaction of the model compounds is a parallel reaction in which nucleophilic substitution and nucleophilic addition take place at the same time.

The hydrolysis of the other three model compounds was also followed by ^{1}H-NMR and similar results were obtained.

3.6 Hydrolysis kinetics study of the model bifunctional compounds by ^{1}H-NMR and chloride ion-selective electrode methods

3.6.1 Establishment of hydrolytic kinetic equation

The alkaline hydrolysis of the model bifunctional reactive dyes may be expressed by



Scheme 2.

If [D], $[D_1]$ and $[D_2]$ represent the corresponding concentrations of **D**, $\mathbf{D_1}$ and $\mathbf{D_2}$, then

At time 0, $[D] = [D_0]; [D_1] = [D_2] = 0$

At time *t*, $[D] = [D_0] - [D_1]_t - [D_2]_t$

$[D_1] = [D_1]_t, [D_2] = [D_2]_t$

so

$$-\frac{d[D]}{dt} = k_1[D][OH] + k_2[D][OH] \tag{1}$$

$$= (k_1 + k_2)[D][OH] \tag{2}$$

The integrated form is:

$$-\ln[D] = k\int_0^t [OH]\,dt + C \tag{3}$$

where $k = k_1 + k_2$.

Plotting $-\ln[D]$ against $\int_0^t [OH]\,dt$ thus gives the total rate constant of the second-order parallel reaction.

Similarly, the following equations may also be obtained:

$$\frac{d[D_1]}{dt} = k_1[D][OH] \qquad \frac{d[D_2]}{dt} = k_2[D][OH]$$

so

$$\frac{d[D_1]}{d[D_2]} = \frac{k_1}{k_2} \quad \text{or} \quad \frac{[D_1]}{[D_2]} = \frac{k_1}{k_2} \tag{4}$$

From eqns (2), (3) and (4), k_1 and k_2 may be calculated.

3.6.2 Determination of rate constants k_1 and k_2 by chloride ion-selective electrode method and by ^{1}H-NMR

In the parallel process of hydrolysis, the concentration of Cl^- will increase and the concentration of $—SO_2CH{=}CH_2$ will decrease gradually. The standard curve method, utilizing the chloride ion-selective electrode, may be used to determine the concentration of Cl^- in solution. The peak area of the vinyl double bond in the ^{1}H-NMR spectrum may be used to determine the concentration of $—SO_2CH{=}CH_2$. The total change in concentration of OH^- in solution may be determined by potentiometric titration.

(*a*) *Quantitative determination by ^{1}H-NMR spectroscopy.* The weight of the unknown is calculated by the internal standard method using the following equation:[4]

$$W_u = W_s\frac{N_sA_uM_u}{N_uA_sM_s}$$

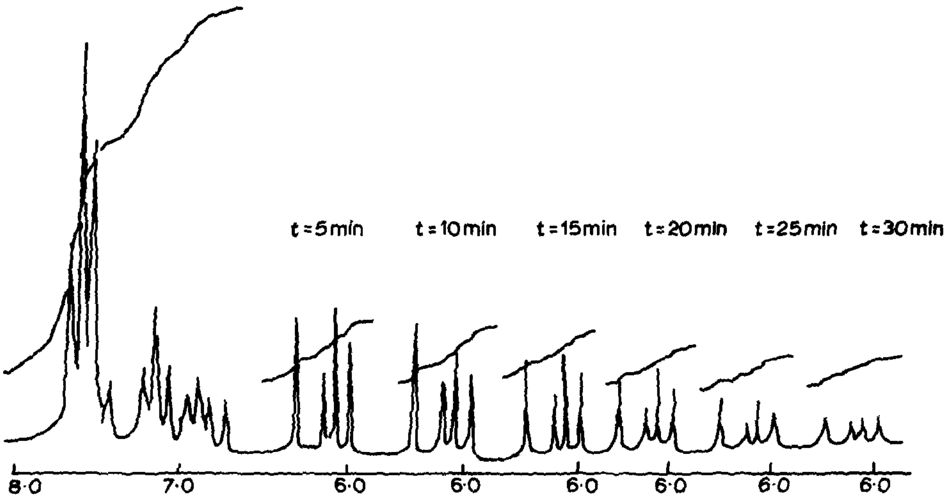


Fig. 8. ^{1}H-NMR spectrum of ethylene goup of **BI-3** after different times.

where

W_u, W_s = weight of unknown and weight of reference standard, respectively;
N_u, N_s = number of protons in unknown and reference standard, respectively;
A_u, A_s = peak areas of unknown and reference standard, respectively;
M_u, M_s = molecular weight of unknown and reference standard, respectively.

In the course of hydrolysis, the proton peak of the phenyl ring is not changed and the proton peak of the vinyl double bond is gradually decreased (Fig. 8). The proton peak of the phenyl ring may thus be considered as the reference standard, and the proton peak of the vinyl double bond in the vinylsulfonyl group can be used to determine the product of hydrolysis quantitatively.

Therefore

$$W_u = W_s \frac{N_s A_u}{N_u A_s}$$

or

$$M_u = W_s \frac{N_s A_u}{N_u A_s} \cdot \frac{1}{MV} \tag{5}$$

where

M_u = mole concentration of the unknown;
M = molecular weight of the unknown;
V = volume of reaction solution.

(*b*) *Experimental method.* The model dye and sodium hydroxide were mixed in 1:4 mole ratio at 30°C. The dye was dissolved in acetone: H_2O (1:1, v/v) and the NaOH in de-ionized water and both solutions were preheated for 0·5–1 h. After mixing with good stirring, samples were taken every 5 min. The volume of sample was 2 ml, of which 1 ml was added to standard HCl solution, and back-titrated with standard NaOH solution. The total alkalinity of the reaction solution was thus obtained. The other 1 ml was added to 5·00 ml of 0·1M-KNO_3 solution (at 0°C) and the Cl^- determined by the chloride ion-selective electrode method. This method of determining the vinylsulfonyl group is similar to those mentioned above in the mechanism determination.

(*c*) *Results.* From eqn (5), M_u, the mole concentration of vinylsulfone, may be obtained, and $[D_2]$, the mole concentration of the product of hydrolysis, may be calculated from the relationship $[D_2] = [D] - M_u$.

The concentration of Cl^-, measured by the chloride ion-selective electrode method, is equal to $[D_1]$, the concentration of hydrolyzed model reactive dye.

Plotting the total alkalinity from the potentiometric titration against time, $\int_0^t [OH]\,dt$ is obtained (Fig. 9). Finally, from eqn (3), plotting $-\ln [D]$ against $\int_0^t [OH]\,dt$, a kinetic curve of hydrolysis of the model dye is obtained

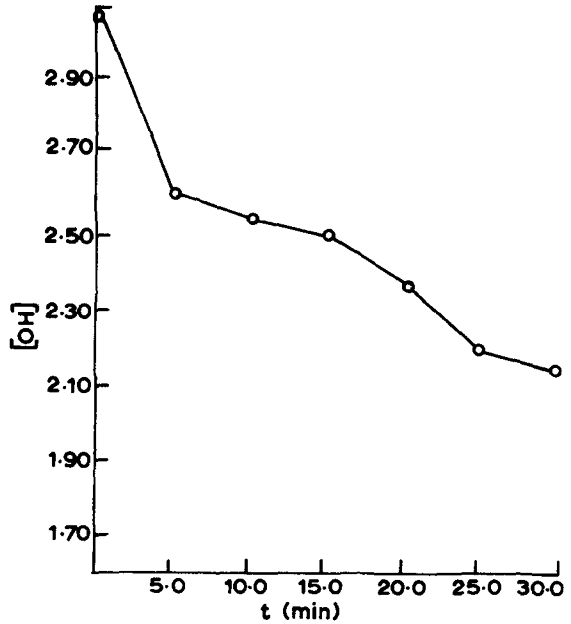
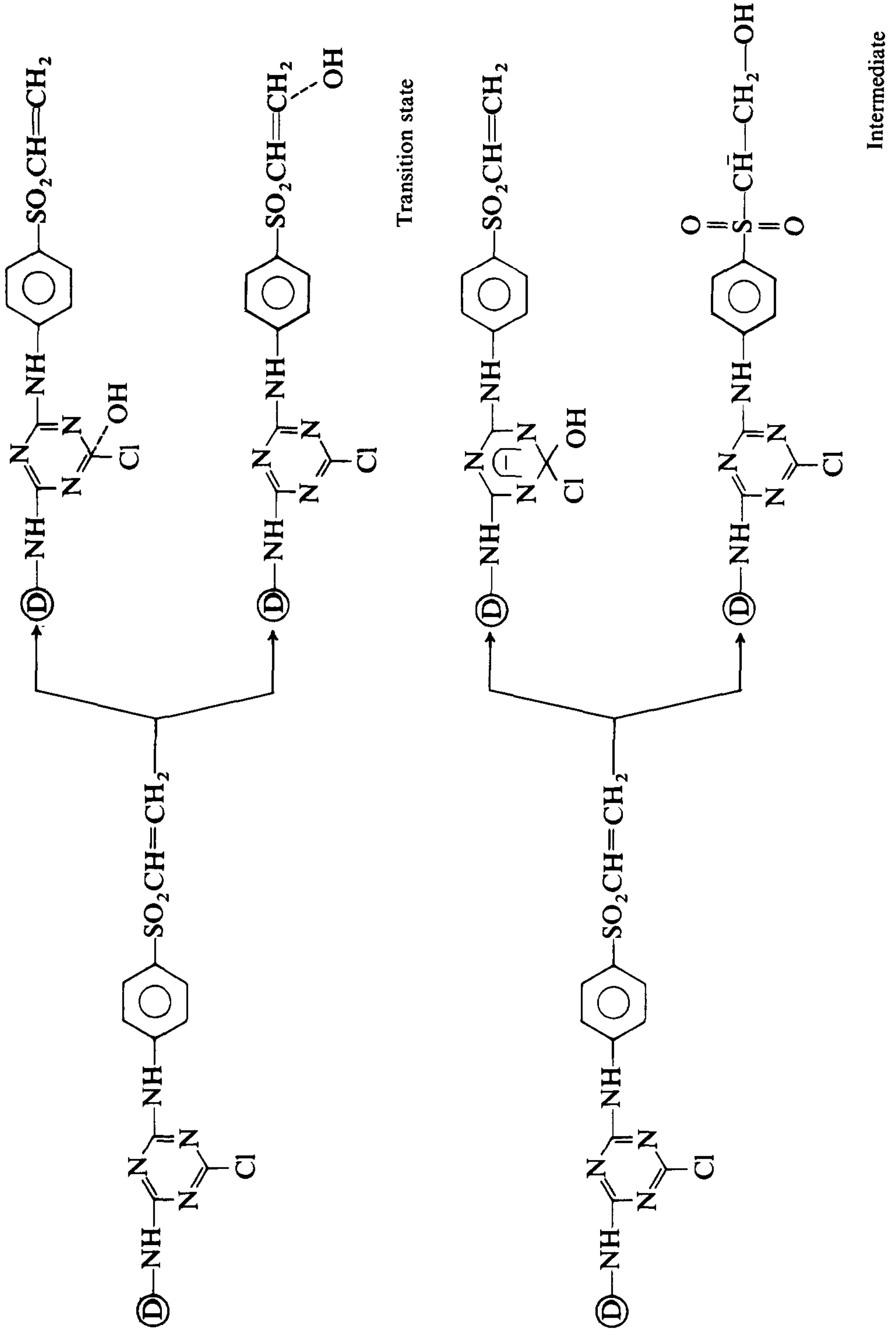
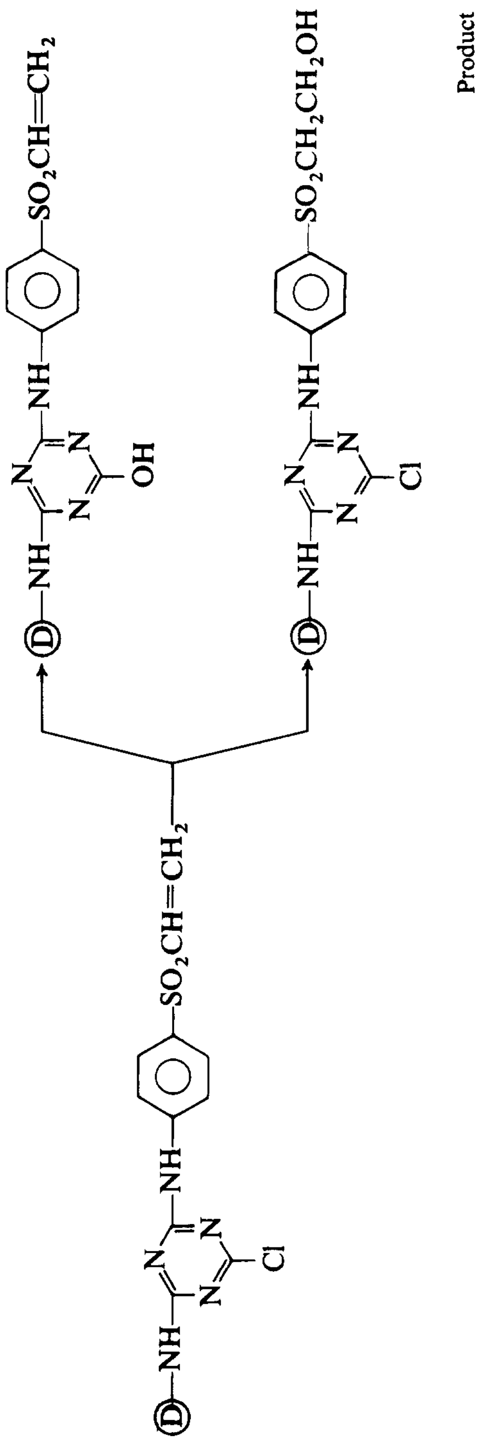


Fig. 9. Total change in concentration of OH in a solution of **BI-3** after different times.



Transition state

Intermediate



Scheme 3.

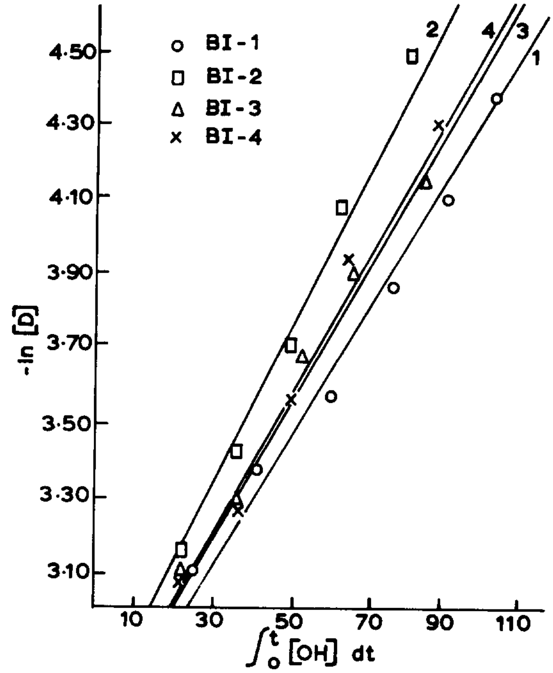


Fig. 10. Kinetic curve of hydrolysis of model dyes.

(Fig. 10). From k, the total rate constant of hydrolysis, k_1 and k_2 may also be obtained (Table 2).

3.7 Mechanism of hydrolysis of the model reactive compounds

This can thus be formulated as shown in Scheme 3.

3.8 Use of molecular orbital theory in the study of hydrolysis kinetics

The calculations were carried out using an IBM-PC-XT microcomputer, by HMO theory.

TABLE 2
Rate Constants of Hydrolysis of Model Dyes

	BI-1	BI-2	BI-3	BI-4
k (min^{-1})	$1{\cdot}677 \times 10^{-2}$	$1{\cdot}915 \times 10^{-2}$	$1{\cdot}756 \times 10^{-2}$	$1{\cdot}780 \times 10^{-2}$
k_1 (min^{-1})	$3{\cdot}672 \times 10^{-3}$	$3{\cdot}662 \times 10^{-3}$	$3{\cdot}658 \times 10^{-3}$	$3{\cdot}655 \times 10^{-3}$
k_2 (min^{-1})	$1{\cdot}300 \times 10^{-2}$	$1{\cdot}549 \times 10^{-2}$	$1{\cdot}390 \times 10^{-2}$	$1{\cdot}414 \times 10^{-2}$

TABLE 3
The Parameter Values for Heteroatoms

Substituted group X	*Atom integral* h_x	*X—Y*	*Bond integral* $K_{X—Y}$	*Reference*
—Cl—	2·0	C—Cl	0·8	5, 6
—OCH—	1·9	C—O	0·8	7
—N=	0·5	C—N	1·0	8
B—NH—	1·0	C—N	0·8	9
=S=	0·2	C—S	0·6	5, 8
=O	1·6	S—O	1·0	

By HMO theory, some theoretical indices, e.g. electron densities (Q_r) and superdelocalizabilities (S_r^N) on the reactive sites are calculated. The parameter values for heteroatoms h_X and bond integral $k_{X—Y}$ are listed in Table 3 and the results of the calculation, together with $T \ln k$, are tabulated in Table 4. The results show that there is no relationship between $T \ln k$ and Q_r, but it is found that $T \ln k_1$ and $T \ln k_2$ are correlated with $S_{r_1}^N$ and $S_{r_2}^N$ respectively. The results are shown in Figs 11 and 12. The correlated equations are as follows.

For monochlorotriazine group: $T \ln k_1(\times 10^{-3}) = 1{\cdot}397 S_{r_1}^N - 3{\cdot}957$

For vinylsulfonyl group: $T \ln k_2(\times 10^{-3}) = 0{\cdot}777 S_{r_2}^N - 3{\cdot}287$

Therefore, S_r^N is a good theoretical index in explaining the mechanism of

TABLE 4
Results of the Calculation by HMO Theory

Model compd	*Temp. (K)*	*k (min⁻¹)*	*T ln k*	Q_r	S_r^N
For monochlorotriazine group					
BI-1	303	$3{\cdot}672 \times 10^{-3}$	−1 698·93	0·774 916	1·113 039
BI-2	303	$3{\cdot}662 \times 10^{-3}$	−1 699·75	0·774 957	1·112 456
BI-3	303	$3{\cdot}658 \times 10^{-3}$	−1 700·08	0·775 052	1·112 169
BI-4	303	$3{\cdot}655 \times 10^{-3}$	−1 700·33	0·775 070	1·112 019
For vinylsulfonyl group					
BI-1	303	$1{\cdot}300 \times 10^{-2}$	−1 315·87	0·782 426	2·541 724
B1-2	303	$1{\cdot}549 \times 10^{-2}$	−1 262·77	0·776 778	2·607 544
BI-3	303	$1{\cdot}390 \times 10^{-2}$	−1 295·59	0·780 261	2·559 692
BI-4	303	$1{\cdot}414 \times 10^{-2}$	−1 291·47	0·780 235	2·564 994

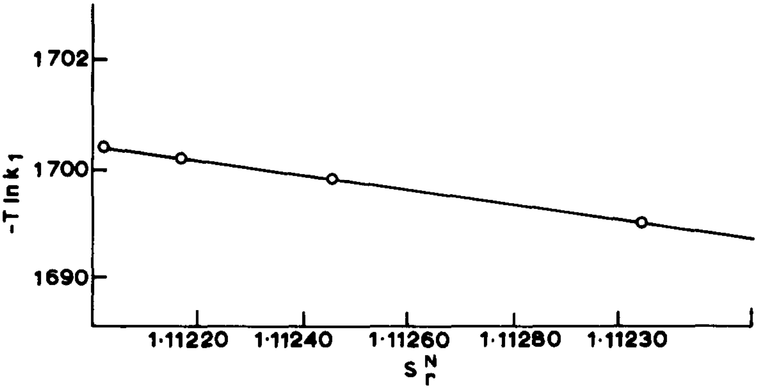


Fig. 11. The relationship between k_1 and S_r^N.

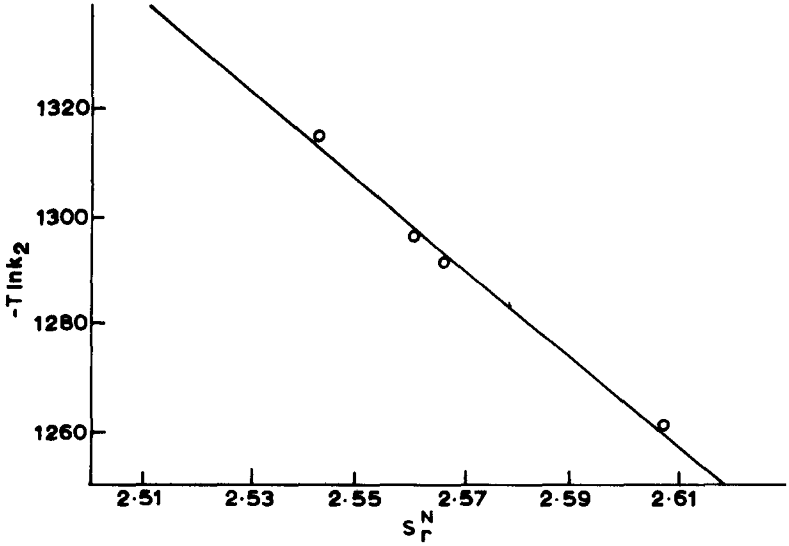
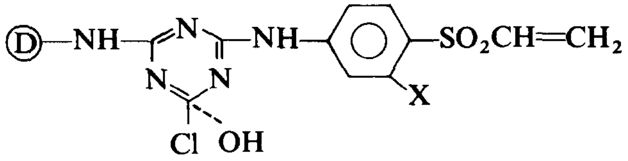
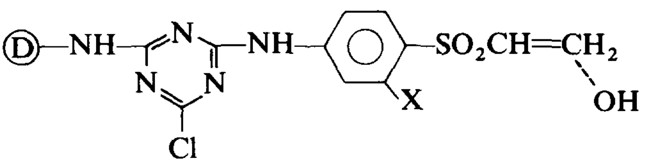


Fig. 12. The relationship between k_2 and S_r^N.

hydrolysis. The transition states for nucleophilic substitution and addition thus may be depicted within the model of superdelocalizability as





4 CONCLUSIONS

In order to study the kinetics and mechanism of hydrolysis, four model bifunctional reactive dyes were synthesized. ^{1}H-NMR spectroscopy was used to follow the reaction pathway in the hydrolysis. The results show that the hydrolysis of the model binfunctional reactive compounds is a parallel reaction. The chloride ion-selective electrode method combined with ^{1}H-NMR were used to determine the rate constants k_1 and k_2. The rate constant of hydrolysis of the vinylsulfonyl group is three to four times faster than that of the monochlorotriazines.

The HMO theory was used to study the mechanism of hydrolysis of the model dyes. The superdelocalizability proposed by Fukui is found to be a good reactive index correlating the logarithm of the rate constant of the hydrolysis with the structure of the model compounds.

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