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Study of Competitive Alcoholysis and Hydrolysis of Vinylsulfonyl Reactive Dyes

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ABSTRACT

The competitive reactions of a model vinylsulfonyl reactive dye with aqueous n-*propanol and isopropanol were studied. The respective alcoholysis rates were compared with the hydrolysis rate of the same reactive dye. It was found that the rate of alcoholysis, with either* n-*propanol or isopropanol, was much larger than the rate of hydrolysis. The relative rates of alcoholysis with* n-*propanol and isopropanol were studied at different pH and alcohol concentrations. These relative rates of alcoholysis are used to estimate the relative amounts of primary and secondary ethers formed in the reaction of the vinylsulfonyl reactive dye with cellulose fibre, and a corresponding kinetic equation is derived.*

1 INTRODUCTION

The dyeing behaviour of vinylsulfonyl reactive dyes with cellulose was concluded by Bhagwanth[1] and Chekalin[2] to proceed with the site of reaction being the C6 primary OH group of the glucose residues in the cellulose molecule. However Stamm[3] and Hagen *et al.*[4] considered that it was the secondary OH group of the glucose residues where the vinylsulfonyl dye molecules mainly reacted. Actually, the reactions between vinylsulfonyl dye and cellulose fibre are very complex and it is rather difficult to determine the position of the attack by direct means. In order to verify the dyeing behaviour of the different hydroxyl groups in the glucose residues, the competitive alcoholysis and hydrolysis reactions under various alkaline

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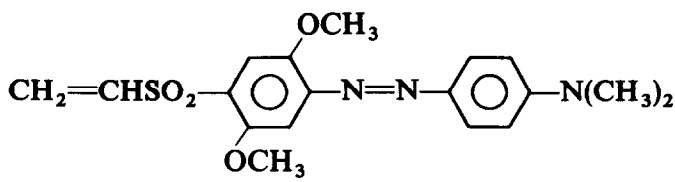
conditions were studied in the homogeneous phase. *n*-Propanol and isopropanol were selected to represent the primary and secondary hydroxyl groups of the glucose residues. Thus the competitive reaction of aqueous *n*-propanol or aqueous isopropanol with vinylsulfonyl dye was studied. The reaction products were separated by HPLC and purified. The corresponding standard curves of hydrolysed dye and of the *n*- or isopropyl ethers of the reactive dyes were obtained. The rate of hydrolysis and rate of alcoholysis (both in *n*-propanol and isopropanol) may thus be determined. These rates were used to estimate the relative reactivities of the primary or secondary hydroxyl group of the glucose unit in the cellulose molecules. The relative amounts of primary to secondary ether formed in the dyeing of vinylsulfonyl reactive dye to cellulose fibre may also be estimated.

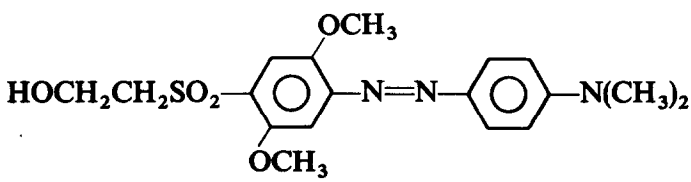
2 EXPERIMENTAL

2.1 Synthesis

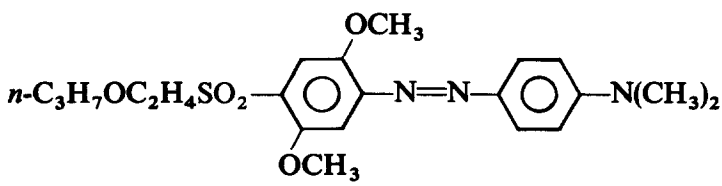
The vinylsulfonyl dye, its hydrolysed product and its *n*-propyl and isopropyl ether were prepared by known methods.[5,6] The structures of the compounds used are listed below:



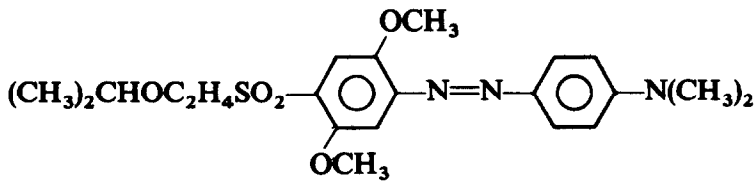
Dye 1 (or VDN)



Dye 2 (or HDN)



Dye 3 (or NDN)



Dye 4 (or IDN)

The analytical data of the dyes are given in Table 1.

2.2 Hydrolysis and reaction products of VDN (dye 1)[6,7]

The vinylsulfonyl dye VDN ($2{\cdot}7 \times 10^{-3}$ g mol) was dissolved in 5 ml of acetone, NaOH (0·1 N 20 ml) was added and the mixture refluxed for 2 h. Water (40 ml) was then added to stop the reaction; the liquor was cooled and filtered. The precipitate was washed and dried (crude yield 90%). The crude product was purified by column chromatography or thin plate chromatography. The pure hydrolytic product had λ_{max} (acetone) at 465 nm, mol wt 393·46, *m/e* 393. The infrared spectrum had an additional 3500 cm^{-1} peak when compared with the original vinylsulfonyl dye, and the characteristic absorption peaks of the sulfone group at 1115 and 1315 cm^{-1} were still present. The elemental analysis corresponded to $C_{18}H_{23}N_3O_5S$ and in the PMR spectrum, the ethylenic proton peak was absent.

2.3 Reactions of vinylsulfonyl dye VDN with *n*-propyl and isopropyl alcohol

The vinylsulfonyl dye VDN ($2{\cdot}7 \times 10^{-3}$ g/mol) was dissolved in *n*-propyl alcohol (1·1 g/mol), 30% NaOH solution (1·4 g, $1{\cdot}05 \times 10^{-3}$ g/mol) was added and the mixture refluxed for 1 h. Then 0·01 N HCl was added to give pH 7. Part of the solvent was distilled and on dilution with water, a precipitate separated. This was filtered, washed, recrystallized, and finally

TABLE 1
Analytical Data of Dyes

Dye	*MP*	*MW*	*m/e*	*Calculated*			*Found*			λ_{max} (*nm*)
				C	*H*	*N*	*C*	*H*	*N*	
1	156	375	376	57·58	5·64	11·19	57·81	5·59	11·45	465
2	175	393	393	54·95	5·89	10·68	55·15	5·81	10·70	465
3	146	435	435	57·91	6·71	9·56	57·52	6·71	9·61	465
4	126	435	435	57·91	6·71	9·65	57·92	6·69	9·50	465

purified by column chromatography to give a product having satisfactory elemental analysis and mass spectrum.

2.4 Competitive reaction of vinylsulfonyl dye with aqueous *n*-propyl or isopropyl alcohol

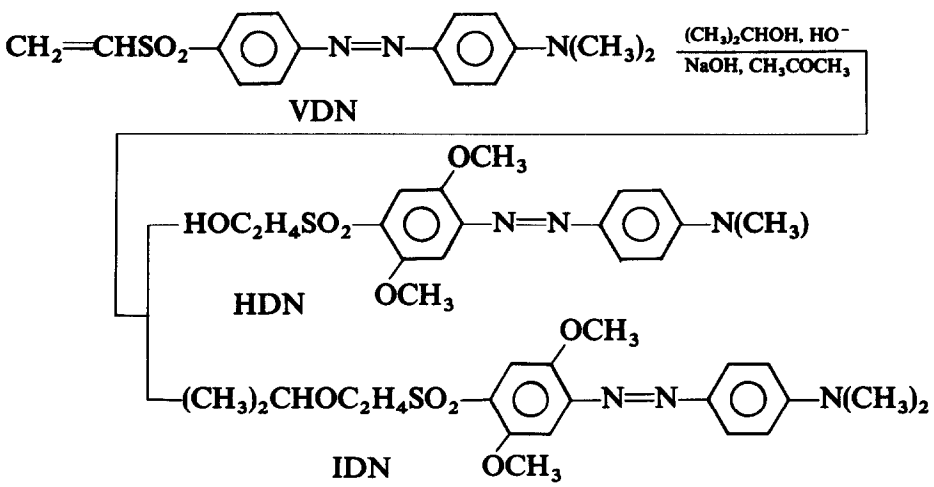
The kinetic determination was homogeneously carried out in aqueous propyl alcohol and maintained at a definite temperature. After mixing with good stirring, samples were taken every 5 min to determine the concentration change of unreacted, hydrolysed dye and reaction products with propyl alcohol during the reaction. The temperature of reaction was controlled by a precision thermostat. Using a kinetic equation (see below), the corresponding reaction rate constant was thus determined.

2.5 Separation by HPLC

By using HPLC, the concentrations of unreacted dye, hydrolysed dye, *n*-propyl and isopropyl reaction products may be determined simultaneously. The ratio of the rate constants of alcoholysis and hydrolysis thus obtained at various temperatures were determined more accurately than by other methods.

A Waters 510 HPLC with a C_{18} column was used. Flow phase: $CH_3OH/H_2O = 90–75/10–25$. Temperature: 25–40°C. Flow rate: 0·5–1 ml/min. Wavelength for detection: 465 nm.

Taking the competitive reaction of VDN with aqueous isopropyl alcohol as an example: NaOH solution is $1·576 \times 10^{-2}$ mol/l, isopropyl alcohol is of 3·328 mol/l. Isopropyl alcohol: $H_2O:CH_3COCH_3 = 1:1:2$ (by volume), reaction temperature 50°C.



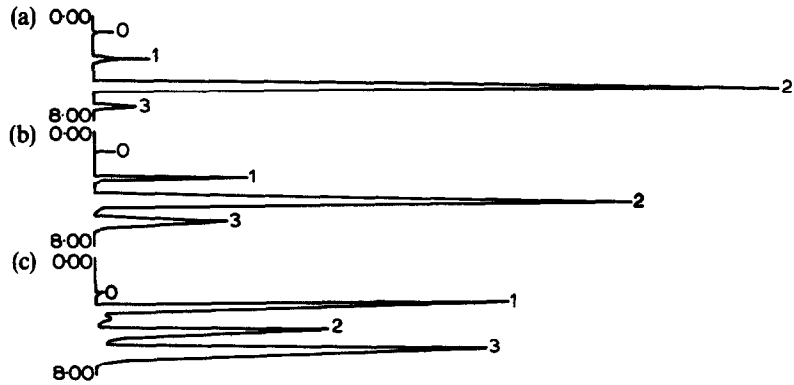


Fig. 1. High pressure liquid chromatogram of the competitive reaction of VDN with isopropyl alcohol-H_2O: (a) after 2 min; (b) after 48 min; and (c) after 12·15 min. Peak 1, retention time 4·26 min, is of dye HDN; peak 2, dye VDN, retention time 5·72 min; peak 3, dye IDN, retention time 7·14 min; peak 0, impurities in solvent.

After reaction, the reaction products were injected into the HPLC column. The separation was by the gradient elution method. $CH_3OH/H_2O = 95/5$ (0 min), 85/15 (1 min), 78/22 (1·5 min), 75/25 (2·5 min). Temperature: 25°C. Dosage quantity 10 μl. Results are shown in Fig. 1. Peak 1, retention time 4·26 min, is of dye HDN; peak 2, dye VDN, retention time 5·72 min; peak 3, dye IDN, retention time 7·14 min; peak 0, impurities in solvent.

2.6 Standard curve determination

An accurately standard sample of VDN (34·36 mg), was dissolved in acetone (100 ml); 25 ml of this was diluted to 50 ml to give a standard solution of 171·8 mg/l. Aliquots (1, 2, 3, 4, 5, 6, 7, 8, 9 ml respectively) were made up to 10 ml in acetone to give a further 9 standard solutions of different concentrations.

Into the Waters 510, fitted with a C_{18} column, were injected 10 ml of solution. The peak areas and weight of dosaged **VDN** solutions are listed in Table 2. Plots of peak area and dosage quantities are given in Fig. 2.

If Y represents the peak areas and X ($\times 10^{-7}$ g) represents the dosage weight of the dye sample then the following equations are obtained:

$$\text{VDN dye: } Yv = 3{\cdot}445 \times 10^5 Xv + 875 \quad (1)$$

$$\text{HDN (hydrolysed dye): } Yh = 3{\cdot}254 \times 10^5 Xh + 786 \quad (2)$$

$$\text{IDN (isopropyl ether): } Yi = 3{\cdot}001 \times 10^5 Xi + 423 \quad (3)$$

$$\text{NDN (}n\text{-propyl ether): } Yn = 2{\cdot}935 \times 10^5 Xn + 895 \quad (4)$$

Since the λ_{max} of VDN, HDN, IDN and NDN are similar and there is no

TABLE 2
Dosage Quantities to HPLC and Peak Areas of a VDN Standard Dye Sample

Name of dye	*Concentration of standard solution (mg/l)*	*Dosage quantity (ml)*	*Peak area ($\times 10^6$)*	*Dosage weight ($\times 10^{-7}$ g)*	*Dosage quantity ($\times 10^{-0}$ mol)*
VDN	0·0	10	0·0	0·0	0·0
	57·3	10	1·91	5·73	1·53
	85·9	10	2·99	8·59	2·29
	114·5	10	3·96	11·46	3·05
	143·1	10	5·04	14·31	3·81
	171·8	10	6·10	17·18	4·58
HDN	0·0	10	0·0	0·0	0·0
	65·9	10	2·02	6·59	1·68
	98·8	10	3·22	9·88	2·51
	115·3	10	3·75	11·57	2·93
	131·8	10	4·36	13·18	3·33
	164·7	10	5·15	16·47	4·19

light absorption density change detected, we may consider that the ratio of peak areas is equal to their molecular ratios.

2.7 Derivation of kinetic equation of hydrolysis

$$\mathrm{ArSO_2CH{=}CH_2 + OH^- \longrightarrow ArSO_2CH_2CH_2OH}$$

$$-\frac{d[\mathrm{Dye}]}{dt} = k_h''[\mathrm{Dye}][\mathrm{OH^-}] = k_h'[\mathrm{Dye}] \tag{5}$$

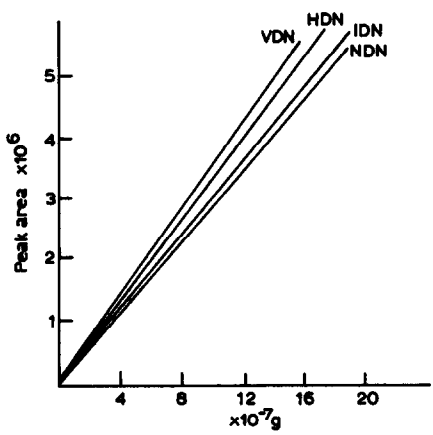


Fig. 2. The relation between peak areas and dosage quantities of various standard dye samples.

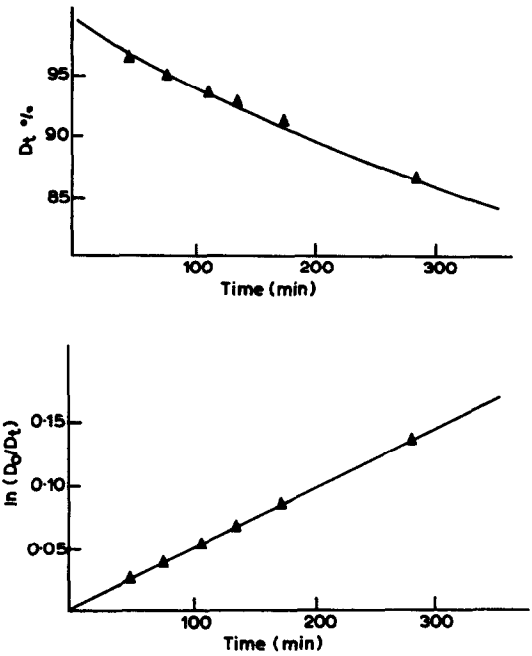


Fig. 3. $[\text{Dye}]_t \sim t$ and $\ln [\text{Dye}]_o/[\text{Dye}]_t \sim t$.

Integrating

$$\ln \frac{[\text{Dye}]_o}{[\text{Dye}]_t} = k'_h t \tag{6}$$

On plotting $\ln [\text{Dye}]_o/[\text{Dye}]_t$ against t, a straight line is obtained (Fig. 3) and the slope of the plot is the pseudo-rate constant k'_h.

2.8 Derivation of kinetic equation of alcoholysis

$$\text{ArSO}_2\text{CH}{=}\text{CH}_2 + \text{ROH} \longrightarrow \text{ArSO}_2\text{CH}_2\text{CH}_2\text{OR}$$

$$-\frac{d[\text{Dye}]}{dt} = k''_h[\text{OH}^-][\text{Dye}] + k''_{\text{ROH}}[\text{RO}^-][\text{Dye}]$$

$$= \frac{d[\text{ArOH}]}{dt} + \frac{d[\text{ArOR}]}{dt} \tag{7}$$

The following equilibrium exists between alcohol, alkali and water.

	ROH	$+\text{OH}^-$	$\rightleftharpoons \text{RO}^-$	$+\text{H}_2\text{O}$	
Initial	$[\text{ROH}]_o$	$[\text{OH}^-]_o$	O	$[\text{H}_2\text{O}]_o$	(8)
inequilibrium	$[\text{ROH}]_e$	$[\text{OH}^-]_e$	$[\text{RO}^-]_e$	$[\text{H}_2\text{O}]_o + [\text{RO}^-]_e$	

In our experiments, $[ROH]_o > 1{\cdot}5$ mol/l, $[OH^-]_o < 0{\cdot}03$ mol/l, the ionization constants of *n*- or isopropyl alcohol $< 8 \times 10^{-17}$, $[H_2O]_o > 13$ mol/l, so $[ROH]_o \gg [OH^-]_o$, $[H_2O]_o \gg [OH^-]_o$.

Since

$$\frac{[RO^-][H^+]}{[ROH]} = K_{ROH} \tag{9}$$

and

$$\frac{[H^+][OH^-]}{a_{H_2O}} = K_{H_2O} \tag{10}$$

where K_{ROH} and K_{H_2O} are ionization constants of ROH and H_2O respectively, a_{H_2O} is the activity coefficient. From eqns (9) and (10) we obtain:

$$\frac{[RO^-]_e}{[OH^-]_e} = \frac{K_{ROH}}{K_{H_2O}} \frac{[ROH]}{a_{H_2O}} \tag{11}$$

In dilute solution, a_{H_2O} is equal to 1. In a fixed system [ROH] is not changed, so $[RO^-]_e/[OH^-]_e$ is a constant and $[RO^-]_e + [OH^-]_e = [OH^-]_o$.

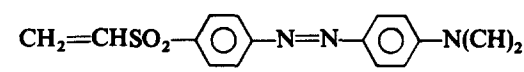
Therefore, from eqn (7)

$$-d[Dye]/dt = k'_h[Dye] + k'_{ROH}[Dye]$$
$$= [k'_h + k'_{ROH}][Dye] \tag{12}$$

$$-d[Dye]/dt = k'_{total}[Dye] \tag{13}$$

TABLE 3

Competitive Alcoholysis (Isopropylalcohol) and Hydrolysis of VPN Dye at 50°C



Time (s)	*Concentration of dye*	*Concentration of alcohol*	*Concentration of hydrolysed dye*	*ln(Do/Dt)*
0	99·02	—	—	0·000 0
36	94·05	3·36	2·55	0·051 5
66	89·62	5·84	4·54	0·099 7
84	86·28	7·56	6·16	0·137 7
112	83·48	9·03	7·49	0·170 7
134	83·04	9·53	7·43	0·176 0
167	80·35	10·87	8·78	0·208 9
205	76·86	12·81	10·33	0·253 3
362	72·63	15·02	12·35	0·309 9

Initial concentration of dye $3{\cdot}01 \times 10^{-3}$ mol/l [NaOH] = $1{\cdot}20 \times 10^{-2}$ mol/l [iso-PrOH] = 4·932.

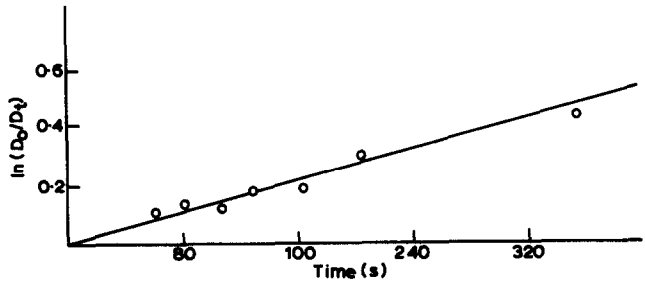


Fig. 4. $\ln([\text{Dye}]_o/[\text{Dye}]_t) - t$ diagram.

and

$$d[\text{ArOR}]/d[\text{ArOH}] = k'_{\text{ROH}}/k'_h = \Delta[\text{ArOR}]/\Delta[\text{ArOH}] \tag{14}$$

From eqn (13)

$$\ln([\text{Dye}]_o/[\text{Dye}]_t) = k'_{\text{total}}t \tag{15}$$

From the experimental results, by regressing $\Delta[\text{ArOR}]/\Delta[\text{ArOH}]$, we can obtain k'_{ROH}/k'_h. Similarly, by regressing $\ln[\text{Dye}]_o/[\text{Dye}]_t$ we can obtain k'_{total}. From $k'_{\text{total}} = k'_{\text{ROH}} + k'_h$, k'_{ROH} and k'_h can be obtained.

From Fig. 4, the slope of line k'_{total} is $7{\cdot}27 \times 10^{-2}\,\text{min}^{-1}$ since $k'_{\text{ROH}}/k'_h = 1{\cdot}26$: so $k'_{\text{ROH}} = 4{\cdot}05 \times 10^{-2}\,\text{min}^{-1}$; and $k'_h = 3{\cdot}22 \times 10^{-2}\,\text{min}^{-1}$.

3 RESULTS AND DISCUSSIONS

3.1 Calculation of the rate constants of hydrolysis and alcoholysis

The specific rate constants of hydrolysis and alcoholysis at 50°C are listed in Table 4.

TABLE 4
Rate Constants of Hydrolysis and Alcoholysis of VDN Dye

Compound	*Concentration of alcohol*	k'_{ROH} (min^{-1})	k'_{ROH}/k'_h	k'_h (min^{-1})	$k_{ionization}$
Water	—	—	—	$3{\cdot}80 \times 10^{-2}$	$1{\cdot}008 \times 10^{-14}$
N-Propanol	4·92	$2{\cdot}24 \times 10^{-1}$	5·89	$3{\cdot}80 \times 10^{-2}$	$7{\cdot}941 \times 10^{-17}$
Isopropanol	4·92	$4{\cdot}68 \times 10^{-2}$	1·26	$3{\cdot}81 \times 10^{-2}$	$7{\cdot}943 \times 10^{-18}$
Glucose	0·135	$2{\cdot}01 \times 10^{-1}$	5·28	$3{\cdot}81 \times 10^{-2}$	$8{\cdot}318 \times 10^{-13}$
Methylglucoside	0·137	$2{\cdot}24 \times 10^{-1}$	5·81	$3{\cdot}85 \times 10^{-2}$	$8{\cdot}245 \times 10^{-13}$

TABLE 5
Effect of pH on the Competitive Reaction

No.	$[OH^-]_o$	*n-Propyl alcohol (mol/l)*	*Alkali used*	*pH (calculated)*	k'_n/k'_h C_3H_7OH	$k'_{n\text{-}C_3H_7OH}$ min^{-1}
1	$1{\cdot}541 \times 10^{-2}$	4·63	NaOH	12·19	14·6	$1{\cdot}03 \times 10^{-1}$
2	$7{\cdot}702 \times 10^{-3}$	4·63	NaOH	11·89	14·8	$6{\cdot}46 \times 10^{-2}$
3	$1{\cdot}698 \times 10^{-3}$	4·63	Na_2CO_3	11·23	16·1	$1{\cdot}51 \times 10^{-2}$
4	$1{\cdot}260 \times 10^{-6}$	4·63	Na borate	9·10	16·4	$5{\cdot}39 \times 10^{-4}$
5	$6{\cdot}92 \times 10^{-8}$	4·63	Na phosphate	6·84	16·2	$1{\cdot}16 \times 10^{-5}$

From Table 4, the rate of hydrolysis of VDN dye is seen to be smaller than its rate of alcoholysis. With the same dye, the rate of alcoholysis with *n*-propyl alcohol is 4–5 times larger than the rate of alcoholysis with isopropyl alcohol. The rates of alcoholysis of the VDN dye with *n*-propyl alcohol, glucose or α-methyl glucoside are similar in magnitude.

3.2 Effect of pH on competitive reaction

The competitive reaction of the vinylsulfonyl dye VDN with *n*-propyl alcohol is influenced by the different values of pH at which the reaction is carried out. The results are shown in Table 5.

The VDN dye was reacted at 40°C with *n*-propyl alcohol at different pH values in an acetone–water solution, (*n*-propyl alcohol + acetone)/water = 1·90/1 (v/v). Under this reaction condition, the rate constants of VDN with *n*-propyl alcohol change greatly, but the ratio of alcoholysis with respect to

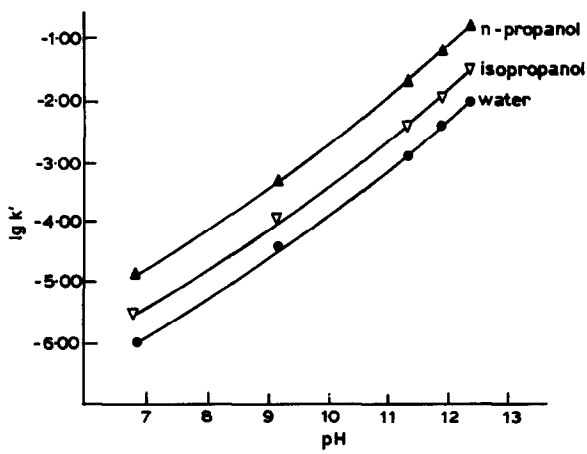


Fig. 5. Effect of pH on alcoholysis and hydrolysis.

TABLE 6
Effect of pH on Rate of Reaction of VDN to *n*- and Isopropyl Alcohol at 40°C

pH (calculated)	*12·19*	*11·89*	*11·23*	*9·10*	*6·84*
$k'_{n\text{-}C_3H_7OH}$ (min^{-1})	$1{\cdot}03 \times 10^{-1}$	$6{\cdot}49 \times 10^{-2}$	$1{\cdot}51 \times 10^{-2}$	$5{\cdot}39 \times 10^{-4}$	$1{\cdot}16 \times 10^{-5}$
$k'_{iso\text{-}C_3H_3OH}$ (min^{-1})	$2{\cdot}196 \times 10^{-2}$	$1{\cdot}40 \times 10^{-2}$	$3{\cdot}13 \times 10^{-3}$	$1{\cdot}13 \times 10^{-4}$	$2{\cdot}38 \times 10^{-5}$
$k'_{n\,so\text{-}C_3H_7OH}/k'_{iso\text{-}C_3H_7OH}$	4·75	4·67	4·82	4·72	4·90

the rate constant of hydrolysis changes within a narrow limit. By plotting the log values of the rate of alcoholysis of VDN dye against pH, the curves shown in Fig. 5 are obtained.

From Table 4, the ratio of the rate constant of alcoholysis to that of hydrolysis, over the pH range 7 to 12, is nearly a constant.

3.3 Effect of pH and alcoholic concentration on the relative rates of reaction of VDN with *n*- or isopropyl alcohol

Under different pH conditions and at 40°C the rates of alcoholysis of the VDN dye with neither *n*- nor isopropanol decrease when the pH of the reaction medium is lowered. The results are shown in Table 6.

The differences of alcoholic concentration are related to rate of reaction as shown in Table 7. The values of $k'_{n\text{-}C_3H_7O}/k'_{iso\text{-}C_3H_7OH}$ are equal to 4·38–4·50.

3.4 Salt effect on competitive reaction

The Debye–Hueckel limiting rate equation is:

$$\lg k = \lg k_o + 1{\cdot}02 Z_A Z_B \mu^{1/2} \qquad (16)$$
$$\mu = 1/2(C_i Z_i^2)$$

where Z_A and Z_B are the number of the charge of the reactant and the attacking ion.

TABLE 7
Effect of Alcoholic Concentration on Relative Rate of Reaction of VDN with Aqueous *n*- and Isopropyl Alcohol at 50°C

Concentration of alcohol (mol/l)	*[NaOH] (mol/l)*	*Acetone/ alcohol/ H_2O*	$k'_{n\text{-}C_3H_7OH}$ *(min)*	$k'_{iso\text{-}C_3H_7OH}$ *(min)*	$k'_{n\text{-}C_3H_7OH}/k'_{iso\text{-}C_3H_7OH}$
9·98	$5{\cdot}65 \times 10^{-3}$	15/75/10	$4{\cdot}12 \times 10^{-1}$	$9{\cdot}41 \times 10^{-2}$	4·38
3·33	$1{\cdot}576 \times 10^{-2}$	50/25/25	$3{\cdot}12 \times 10^{-1}$	$6{\cdot}94 \times 10^{-2}$	4·50

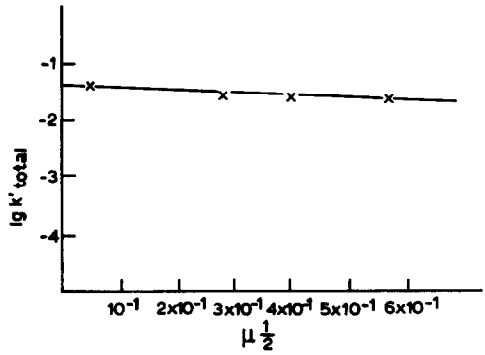


Fig. 6. Salt effect in the reaction of VDN dye with *n*-propyl alcohol.

At 40°C, with a concentration of VDN in *n*-propyl alcohol of 4·63 mol/l, and a concentration of NaOH $3{\cdot}856 \times 10^{-3}$ mol/l, by adding different amounts of NaCl in order to vary the ionic strength, the following curve is obtained (Fig. 6).

From Fig. 6, it is apparent that there is no kinetic salt effect present in the competitive reaction. Therefore it may be concluded that the dye is in the form of a neutral molecule when taking part in the reaction.

3.5 Estimation of relative amounts of primary and secondary ether formed in the actual dyeing of VDN dye to cellulose fibre

The dyeing of cellulose fibre by VDN dye is also a competitive reaction.

$$d[\text{Dye-O-cell}]/dt = d[\text{Dye-O-cell}_{\text{prim}}]/dt + d[\text{Dye-O-cell}_{\text{sec}}]/dt \quad (17)$$

$$d[\text{Dye-O-cell}_{\text{prim}}]/dt = k''_{\text{prim}}[\text{cell-O}^-_{\text{prim}}][\text{Dye}] \quad (18)$$

$$d[\text{Dye-O-cell}_{\text{sec}}]/dt = k''_{\text{sec}}[\text{cell-O}^-_{\text{sec}}][\text{Dye}] \quad (19)$$

In the actual dyeing process, the cellulose fibre and alkali are in excess and $[OH^-]$ and $[\text{cell-O}^-]$ are not changed, at least in the initial stage of reaction. The cellulose fibre may be regarded as a kind of alcohol, so

$$[\text{cell-O}^-_{\text{prim}}]/[OH^-] = (K_{\text{cell-OH}_{\text{prim}}}/K_{H_2O}) \times ([\text{cell-OH}_{\text{prim}}]/a_{H_2O}) \quad (20)$$

$$[\text{cell-O}_{\text{sec}}]/[OH^-] = (K_{\text{cell-OH}_{\text{sec}}}/K_{H_2O}) \times ([\text{cell-OH}_{\text{sec}}]/a_{H_2O}) \quad (21)$$

where $K_{\text{cell-OH}_{\text{prim}}}$, $K_{\text{cell-OH}_{\text{sec}}}$ and K_{H_2O} are ionization constants and a_{H_2O} is the activity coefficient, in dilute solution it is equal to 1. So

$$\begin{aligned} d[\text{Dye-O-cell}_{\text{prim}}]/d[\text{Dye-O-cell}_{\text{sec}}] &= k''_{\text{prim}}[\text{cell-O}^-_{\text{prim}}]/k''_{\text{sec}}[\text{cell-O}^-_{\text{sec}}] \\ &= (k''_{\text{prim}}K_{\text{cell-OH}_{\text{prim}}}/k''_{\text{sec}}K_{\text{cell-OH}_{\text{sec}}}) \\ &\quad \times ([\text{cell-OH}_{\text{prim}}]/[\text{cell-OH}_{\text{sec}}]) \end{aligned} \quad (22)$$

and the amount of primary ether/amount of secondary ether

$$= 1/2 \times k''_{\text{prim}} \times K_{\text{cell-OH}_{\text{prim}}}/k''_{\text{sec}} \times K_{\text{cell-OH}_{\text{sec}}} \tag{23}$$

If *n*-propyl alcohol is used to represent the primary OH group and isopropyl alcohol to represent the secondary OH group in cellulose, the similarity of their physical and chemical properties leads us to suppose that the following equality exists approximately.

$$\frac{k''_{\text{n-C}_3\text{H}_7\text{OH}} \cdot K_{\text{n-C}_3\text{H}_7\text{OH}}}{k''_{\text{iso-C}_3\text{H}_7\text{OH}} \cdot K_{\text{iso-C}_3\text{H}_7\text{OH}}} \sim \frac{k''_{\text{prim}} \cdot K_{\text{cell-OH}_{\text{prim}}}}{k''_{\text{sec}} \cdot K_{\text{cell-OH}_{\text{sec}}}} \tag{24}$$

If the competitive reaction is carried out at same temperature, same $[OH^-]$ and alcohol concentration; the following equation may be obtained.

$$\frac{k'_{\text{n-C}_3\text{H}_7\text{OH}}}{k'_{\text{iso-C}_3\text{H}_7\text{OH}}} = \frac{k''_{\text{n-C}_3\text{H}_7\text{OH}}[\text{n-C}_3\text{H}_7\text{O}^-]}{k''_{\text{iso-C}_3\text{H}_7\text{OH}}[\text{iso-C}_2\text{H}_7\text{O}^-]}$$

$$= \frac{k''_{\text{n-C}_3\text{H}_7\text{OH}} K_{\text{n-C}_3\text{H}_7\text{OH}}[\text{n-C}_3\text{H}_7\text{OH}][OH^-]_e/K_{\text{H}_2\text{O}} \cdot a_{\text{H}_2\text{O}}}{k''_{\text{iso-C}_3\text{H}_7\text{OH}} K_{\text{iso-C}_3\text{H}_7\text{OH}}[\text{iso-C}_3\text{H}_7\text{OH}][OH^-]_e/K_{\text{H}_2\text{O}} a_{\text{H}_2\text{O}}} \tag{25}$$

The ionization constant of *n*- and isopropyl alcohol are very small, $[OH]_e$ is approximately equal to $[OH^-]_o$, so:

$$\frac{k'_{\text{n-C}_3\text{H}_7\text{OH}}}{k'_{\text{iso-C}_3\text{H}_7\text{OH}}} = \frac{k''_{\text{n-C}_3\text{H}_7\text{OH}} K_{\text{n-C}_3\text{H}_7\text{OH}}}{k''_{\text{iso-C}_3\text{H}_7\text{OH}} K_{\text{iso-C}_3\text{H}_7\text{OH}}} \sim \frac{k''_{\text{prim}} K_{\text{cell-OH}_{\text{prim}}}}{k''_{\text{sec}} K_{\text{cell-OH}_{\text{sec}}}} \tag{26}$$

By substituting eqn (26) into eqn (23) and taking the mean value of $k'_{\text{n-C}_3\text{H}_7\text{OH}}/k'_{\text{iso-C}_3\text{H}_7\text{OH}}$ in Table 6, then the amount of primary ether formed/amount of secondary ether formed

$$= 1/2(k'_{\text{n-C}_3\text{H}_7\text{OH}}/k'_{\text{iso-C}_3\text{H}_7\text{OH}})$$

$$= 2{\cdot}19 \text{ to } 2{\cdot}45 \tag{27}$$

Thus, the dye–cellulose bond is approximately 68–71% formed with the C6 primary OH group and the rest is formed with the other two secondary OH groups. This value also represents the relative reactivities of primary and secondary hydroxyl groups of the glucose unit in cellulose molecule.

4 CONCLUSION

The competitive reactions between alcoholysis and hydrolysis of vinylsulfonyl dyes and primary or secondary propyl alcohol are compared. The rate of alcoholysis of the vinylsulfonyl dye with primary propyl alcohol is four

times faster than that of the vinylsulfonyl dye with secondary propyl alcohol.

The relative rates of alcoholysis with primary and secondary propyl alcohol are used to estimate the actual dye–cellulose bond formation, 68–71% of the dye–cellulose bond being formed at the C6 OH group. This value may be compared with the 70% formation of the ether bond at C6 in the cellulose glucose unit with a sulfatoethylsulfonyl model compound previously noted.[8,9]

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