Dyes and Pigments **14** (1990) 157–163

A Study of the Hydrolytic Stabilities of *n*- and iso-Propyl Ethers of Some Vinylsulfone Reactive Dyes

Zhu Zhenghua, Chen Kongchang & Yu Ronggeng

East China University of Chemical Technology, Shanghai 200237,
People's Republic of China

(Received 19 September 1989; accepted 24 November 1989)

ABSTRACT

The rate of alkaline hydrolysis of a series of n-*propyl and isopropyl ethers derived from some vinylsulfone reactive dyes has been measured. The ethers were used as model dye-fibre compounds on the basis that there are both primary and secondary OH groups in each glucose unit in the cellulose molecule. The ratio of the rate constants of the* n-*propyl ether to that of the isopropyl ether of the vinylsulfone dyes was determined. It was found that this ratio was nearly constant within the experimental conditions used. This result was used to explain the fact that the rate of hydrolysis of dyed fibre is linearly related to that of a model dye-fibre compound, as found previously.*

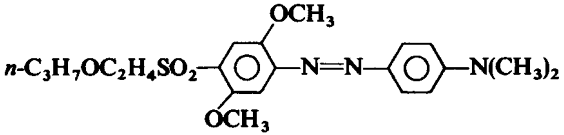
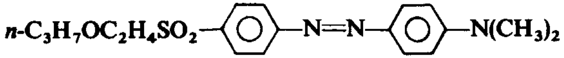
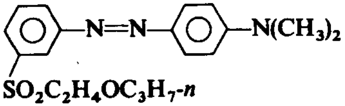
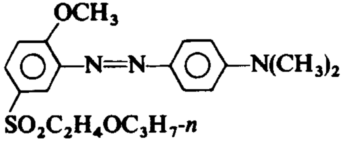
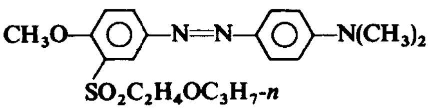
1 INTRODUCTION

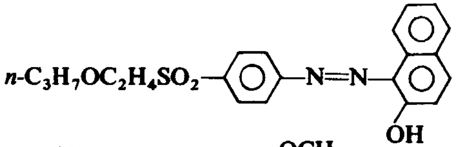
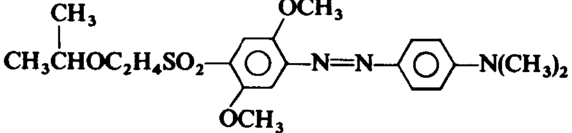
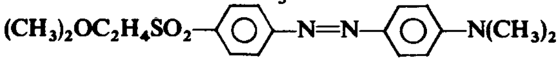
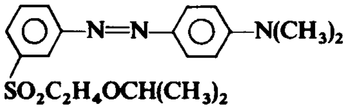
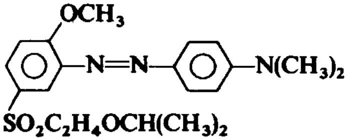
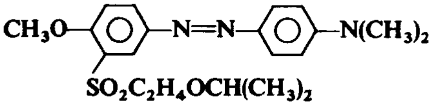
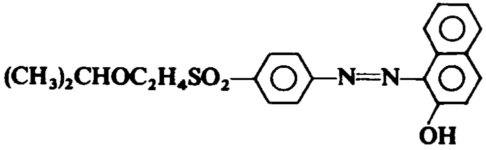
In a previous paper,[1] we observed that the hydrolysis behaviour of a vinylsulfone dye-fibre system could be simply represented by its methyl ether. In the cellulose fibre, there are both primary and secondary OH groups in each glucose unit. In order to obtain deeper understanding, a series of *n*- and iso-propyl ethers of various vinylsulfone reactive dyes were synthesized. The rates of hydrolysis of these model compounds were measured and compared.

Dyes and Pigments 0143-7208/90/$03·50 © 1990 Elsevier Science Publishers Ltd, England. Printed in Great Britain

TABLE 1

Analytical Data of *n*-Propyl Ether Derived from Vinylsulfone Dyes

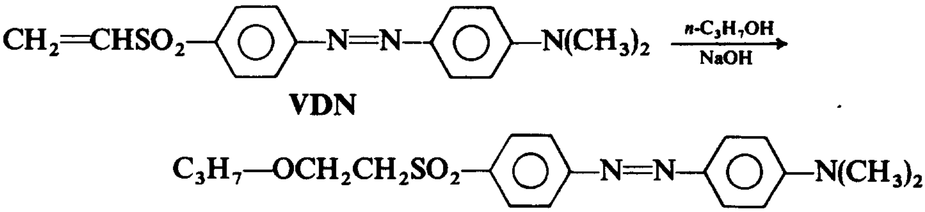
Name	*Formulae*	*MP (°C)*	*Mw*	*m/e*	*N%*		λ_{max} *(nm)* *(in acetone)*
					Cal.	*Found*	
NDN		110	435·5	435	9·65	9·61	465
NPN		149	375·5	375	11·19	11·12	420
NMN		110	375·5	375	11·19	11·12	418
NMoN		108	405·5	405	10·36	10·69	455
NMpN		135	405·5	405	10·36	10·53	420

NPβ		148	398	398	7·03	7·11	470
IDN		126	435·5	435	9·65	9·50	465
IPN		154	375·5	375	11·19	10·98	420
IMN		120	375·5	375	11·19	11·05	418
IMoN		124	405·5	405	10·36	10·24	455
IMpN		142	405·5	405	10·36	10·05	420
IPβ		162	398	398	7·03	7·01	470

2 EXPERIMENTAL

2.1 Preparation of *n*- and iso-propyl ether of vinylsulfone dyes

In neutral or acidic conditions, a vinylsulfone reacts with difficulty with primary or secondary alcohols, but in alkaline conditions, the reaction takes place easily, e.g.



VDN

NDN

In all, 2·7 × 10^{-3} mol of **VDN** dye and 1·1 mol of *n*-propanol were heated to obtain a solution then 30% NaOH (1·4 g, 1·05 × 10^{-2} mol) was added and the solution refluxed for 1 h. Dilute HCl was then added to neutralize the solution and part of the solvent was distilled off.

On addition to water, a precipitate was formed. This was filtered, washed and dried to give orange-red crystals (yield 90%). These were recrystallized from acetone and petroleum ether mixture to give a product (m.p., 110°C, λ_{max} 465 nm). The crude dye was further purified on a silica G plate, developing with CH_3Cl:$CH_3COOC_2H_5$ (30:2 by volume) occurred. The spot of $R_f = 0{\cdot}88$ was the *n*-propyl ether, the spot of $R_f = 0{\cdot}25$ was the hydrolysed product. The spot of $R_f = 0{\cdot}85$ was separated and extracted with acetone. The acetone extract was concentrated, and the dye separated by adding *n*-hexane.

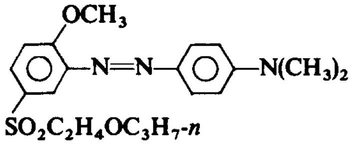
The other *n*- or iso-propyl ethers were prepared similarly; relevant data are given in Table 1.

2.2 Alkaline hydrolysis of model dye-fibre compounds

The alkaline hydrolysis of the model dye-fibre compound was carried as previously described.[1] HPLC can be used to determine the concentrations of the original dye-fibre compound and the hydrolysed dye, as described recently by Zhu and others in a study of competitive alcoholysis and hydrolysis of vinylsulfone reactive dyes (unpublished work).

The hydrolysis product is the β-hydroxy-ethyl sulfone dye. Trace impurities were mainly sulfonic acid and polymeric material, as shown by mass spectra data. Typical data are given in Tables 2 and 3.

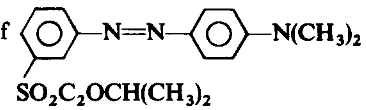
TABLE 2

Alkaline Hydrolysis of  at 60°C

Reaction time (min)	0	15·45	38·97	60·20	80·02	142·58
Concentration of dye (%)	98·97	95·85	91·35	88·75	85·70	78·95
ln(D_o/D_t)	0	0·032	0·0801	0·109	0·144	0·226

$\ln(D_o/D_t) = 0{\cdot}0101 + 1{\cdot}573 \times 10^{-3}t,\ r = 0{\cdot}99.$

TABLE 3

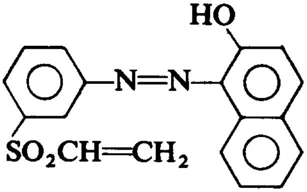
Alkaline Hydrolysis of  at 60°C

Reaction time (min)	0	14·67	21·77	40·05	60·15	81·25
Concentration of dye (%)	99·02	86·86	82·71	71·98	62·38	50·12
ln(D_o/D_t)	0	0·131	0·180	0·319	0·462	0·681

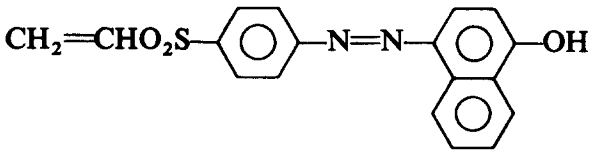
$\ln(D_o/D_t) = 6{\cdot}38 \times 10^{-4} + 8{\cdot}1196 \times 10^{-3}t.$

From plots of ln (D_0/Dt) against time, t (in min) (Figs 1–4), the k_H values of the various dye-fibre systems were obtained from the slopes of these plots. Values thus obtained are given in Table 4.

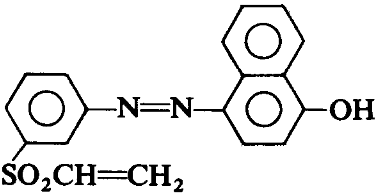
The structures of dyes **Vmβ**, **Vpα** and **Vmα** are



Vmβ



Vpα



Vmα

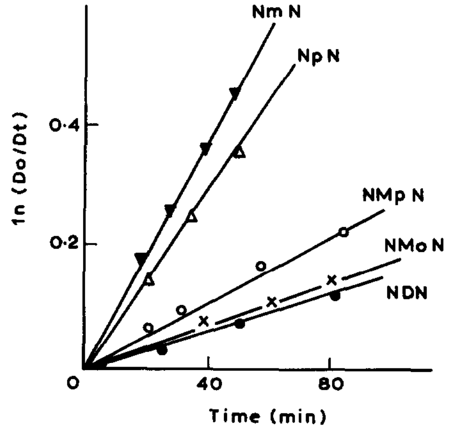


Fig. 1. Plot of $\ln(D_0/D_t)$ against time t of dyes NmN, NpN, NMpN, NMoN and NDN.

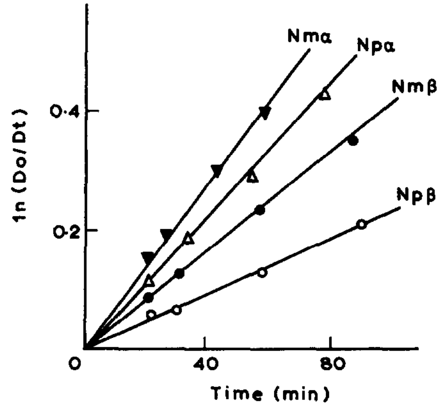


Fig. 2. Plot of $\ln(D_0/D_t)$ against time t of dyes Nmα, Npα, Nmβ and Npβ.

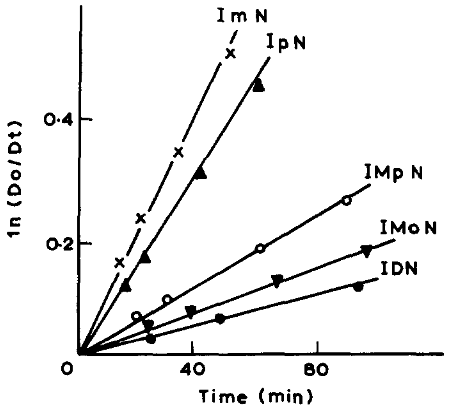


Fig. 3. Plot of $\ln(D_0/D_t)$ against time t of dyes ImN, IpN, IMpN, IMoN and IDN.

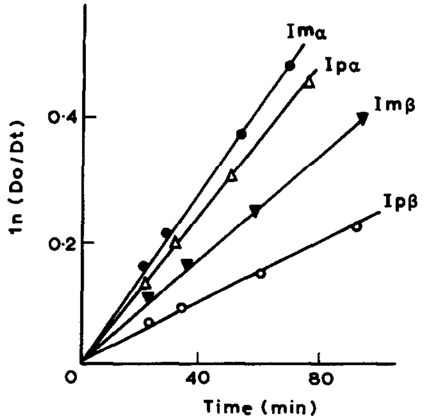


Fig. 4. Plot of $\ln(D_0/D_t)$ against time t of dyes Imα, Ipα, Imβ and Ipβ.

TABLE 4
The Specific Rate Constants of the Hydrolysis of Various Dye-Fibre Compounds at 60°C

Dye	VpN	VmN	VDN	VMoN	VMpN	VPβ	Vmβ	Vpα	Vmα
kH (n-propyl ether) (rn) $\times 10^{-3}\,min^{-1}$	7·15	8·37	1·51	1·57	2·66	2·42	4·29	5·70	6·81
kH (iso-propyl ether) (ri) $\times 10^{-3}\,min^{-1}$	8·12	8·94	1·62	2·00	3·10	2·62	4·41	6·36	7·12
rn/ri	0·88	0·93	0·93	0·79	0·86	0·92	0·97	0·90	0·96

The results show that the ratio of the specific rate constants of the alkaline hydrolysis of the *n*-propyl ether and the isopropyl ether is constant within a wide structural variation of the vinylsulfone reactive dyes. The mean value of *rn*/*ri* is 0·90. This is the reason why the methyl ether of a vinsulfonyl dye, when used as a model dye-fibre compound, is linearly correlated to dyed fibre kinetically. This experimental conclusion is in accord with previously reported conclusions.[1]

3 CONCLUSION

A series of *n*- and iso-propyl ether formed from various vinylsulfone dyes has been synthesized. The specific rates of alkaline hydrolysis were measured by HPLC to obtain the concentration of unreacted dye at different reaction times.

Comparison of the results from both *n*- and iso-propyl ether shows that the ratio between them varies only within a narrow range. This result explains the fact that the rate of hydrolysis of the dyed fibre is linearly correlated to the rate of hydrolysis of the model dye-fibre compound, despite the presence of both primary and secondary OH groups in each glucose unit in cellulose fibre.

REFERENCE

1. Jian Wen, Zhu Zhenghua & Chen Kongchang, *Dyes and Pigments*, **10** (1989) 217–37.