Dyes and Pigments **23** (1993) 91–120

Some Recent Advances in Kinetic Studies in Dye Chemistry

Zhu Zhenghua

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

(Received 21 January 1993; accepted 15 March 1993)

ABSTRACT

The importance of kinetic studies in dye chemistry is emphasized. The high pressure liquid chromatographic method, thin layer chromatograph–double scanning and proton NMR technique used to determine the rates of chemical changes are reviewed.

1 INTRODUCTION

As Rys and Zollinger[1] pointed out some 20 years ago, dye chemistry was often regarded as closed, conservative and not readily amenable to new discoveries. In the period since then, many major innovative studies based on sound theoretical principles have been done. One area of significant development pertains to studies involving physical chemistry. Such studies yield valuable information on important areas such as rates of reaction, and on reaction mechanisms. In this review some kinetic studies in dye chemistry are emphasized, and recent investigations from our laboratories are reviewed.

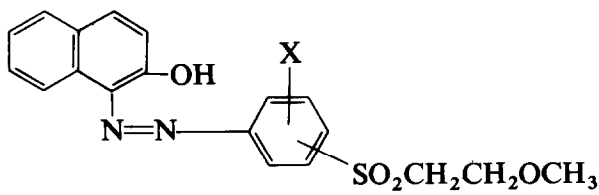
The general practice in chemical kinetics is to determine the concentration changes of the reactants or the products at a specific temperature. When the reactions are carried out in solutions, as is the case in the formation of most dyes, the concentration changes equate to the changes in weights of the reactants or of the products respectively. The essential problem is therefore to determine the changes in weight of the reactants or the products during dye formation. Different techniques pertinent to this are illustrated by the examples detailed below.

Dyes and Pigments 0143-7208/93/$06·00

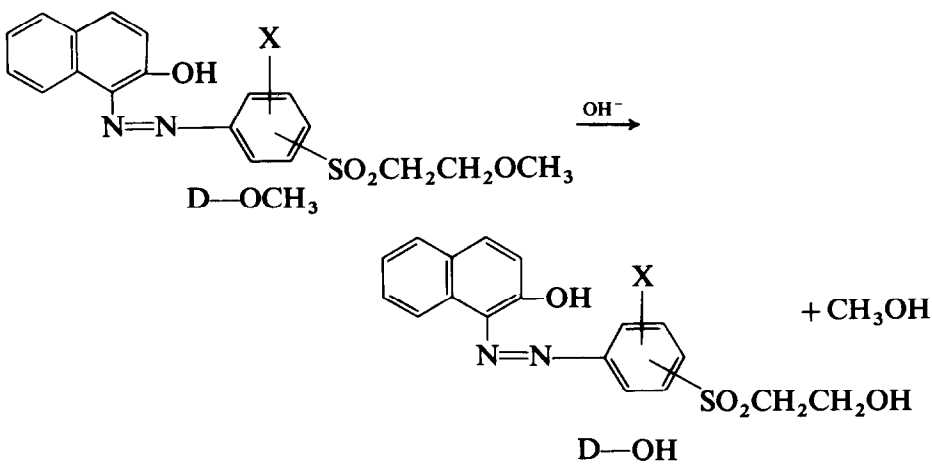
2 DETERMINATION OF THE RATES OF CHEMICAL CHANGES USING HIGH PRESSURE LIQUID CHROMATOGRAPHY (HPLC)

2.1 Determination of the rate constants of the alkaline hydrolysis of model vinyl sulfone dyes–cellulose compounds by reversed HPLC[2]

The model vinyl sulfonyl reactive dye-fiber compounds may be represented by $DOCH_3$, e.g.



The fading process of dyed fiber in alkaline medium may be determined by the rate of hydrolysis, viz.



In excess alkali, the kinetic equation of the hydrolysis is denoted by the following equation:

$$\ln \frac{[\text{D—OCH}_3]_o}{[\text{D—OCH}_3]_t} = kt$$

where k is the pseudo-first order rate constant of hydrolysis.

Since $[\text{D—OCH}_3]_o = [\text{DOCH}_3]_t + [\text{D—OH}]_t$ then

$$\frac{[\text{D—OH}]_t}{[\text{D—OCH}_3]_t} = \frac{W_{\text{DOH}} M_{\text{DOCH}_3}}{W_{\text{DOCH}_3} M_{\text{DOH}}} = \frac{A_{\text{DOH}} M_{\text{DOCH}_3}}{A_{\text{DOCH}_3} M_{\text{DOH}}}$$

and

$$\ln \frac{[DOCH_3]_o}{[DOCH_3]_t} = \ln\left(1 + \frac{A_{DOH} M_{DOCH_3}}{A_{DOCH_3} M_{DOH}}\right) = kt$$

where

W_{DOH} = weight of DOH at t
W_{DOCH_3} = weight of $DOCH_3$ at t
A_{DOH} = peak area of DOH at t
A_{DOCH_3} = peak area of $DOCH_3$ at t
M_{DOCH_3}, M_{DOH} = molecular weights of $DOCH_3$ and DOH respectively

In our experiments, the reversed HPLC method with a ODS packed column was used and methyl alcohol was employed as the mobile phase. The high pressure liquid chromatogram of the vinyl sulfone dye–fiber model compound at various times is presented in Fig. 1. From this figure, it is apparent that the peak area for the time of retention $t_R = 4{\cdot}22$ is reduced and the peak area at $t_R = 3{\cdot}72$ is increased. Since the hydrolysis product $—SO_2CH_2CH_2OH$ is more polar than the reactant $—SO_2CH_2CH_2OCH_3$, the former peak appears first, and the peak for the product appears last, i.e. the peak at $t_R = 4{\cdot}24$ is that for the unhydrolyzed dye and the peak at $t_R = 3{\cdot}72$ is for the hydrolyzed dye.

Standard solutions were then successively diluted to give concentrations from 1·068 to $9{\cdot}612 \times 10^{-7}$ g/ml. These solutions were subjected to HPLC

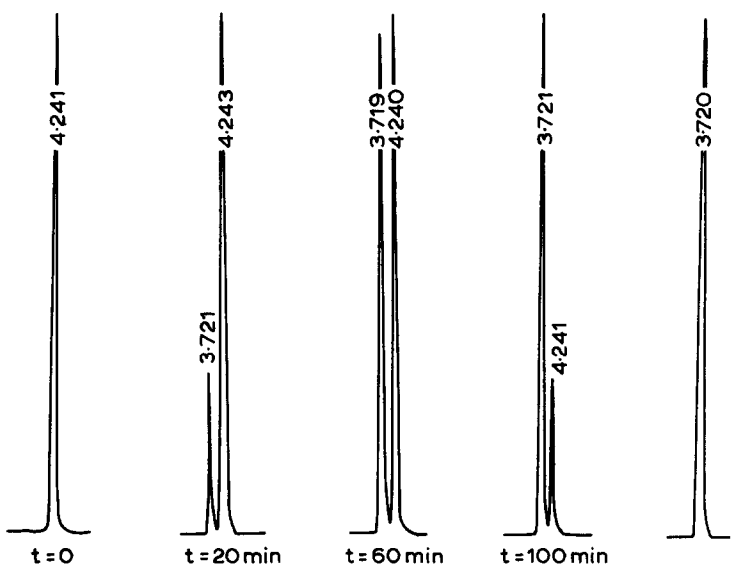


Fig. 1. High pressure liquid chromatogram of model dye D—OCH_3 reaction with alkali.

TABLE 1
Dosage Quantities of Peak Areas of $DOCH_3$

Solution taken (ml)	*Dosage quantity* ($\times 10^{-7}$ g)	*Peak area*[a]	*Observed weight* ($\times 10^{-7}$ g)	*Relative error (%)*
1	1·068	8 545	1·069	0·09
3	3·204	24 501	3·173	0·98
5	5·340	40 605	5·295	0·83
7	7·476	57 849	7·569	1·24
9	9·612	73 629	9·649	0·38

[a] Average value taken over three readings.

using a Shimidazu LC-6A Liquid Chromatograph. The peak areas observed are shown in Table 1.[3]

On plotting the dosage weights against peak areas, standard curves of unhydrolyzed and hydrolyzed dyes respectively can be obtained (Figs 2 and 3).

A plot for

$$\ln\left(1+\frac{A_{DOH}M_{DOCH_3}}{A_{DOCH_3}M_{DOH}}\right)$$

against time t (a straight line) is obtained (Fig. 4).

The model dye–fiber compound was dissolved in dioxane/water (9:1) and heated to 60°C for 30 min. A solution of 0·5% NaOH (5 ml) was added with good stirring. Samples were taken at intervals and added to dilute HCl, maintaining pH 5–6 to stop the reaction. The samples were analyzed using the Shimadazn LC-6A system. For each of the model compounds, the hydrolysis rate constants at 60°C are given in Table 2.

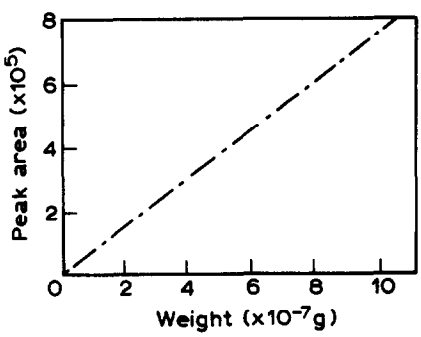


Fig. 2. Standard curve of unhydrolyzed dye D—OCH_3.

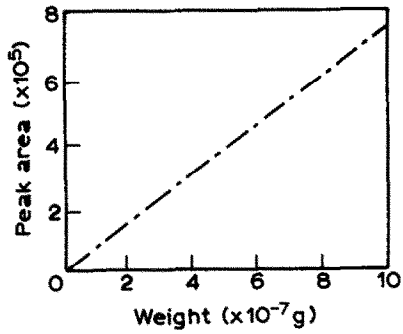


Fig. 3. Standard curve of hydrolyzed dye D—OH.

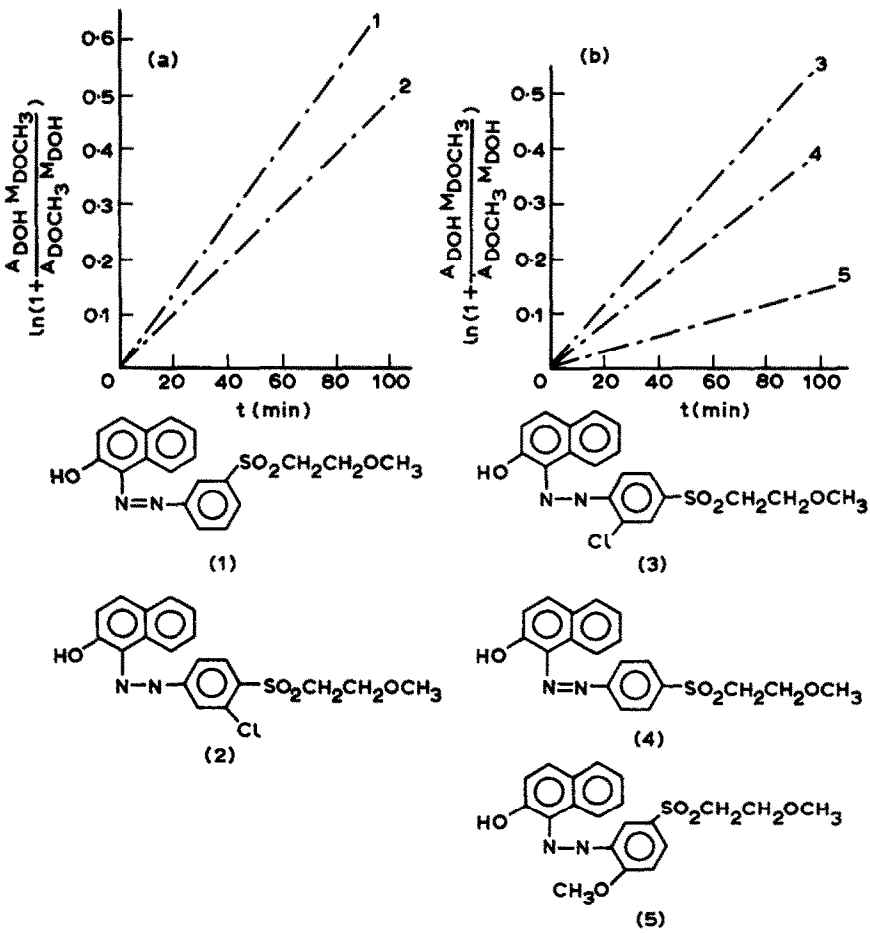


Fig. 4. Hydrolysis kinetic plots of model dye–fiber compound.

TABLE 2
The Rate of Hydrolysis of Model Dyes $DOCH_3$

Structure	k' (min^{-2})	r	λ (*nm*)
(1)	$3{\cdot}843 \times 10^{-3}$	0·9998	476
(2)	$6{\cdot}825 \times 10^{-3}$	0·9999	465
(3)	$1{\cdot}343 \times 10^{-3}$	0·9996	482
(4)	$5{\cdot}439 \times 10^{-3}$	1·0000	482
(5)	$4{\cdot}899 \times 10^{-3}$	0·9997	473

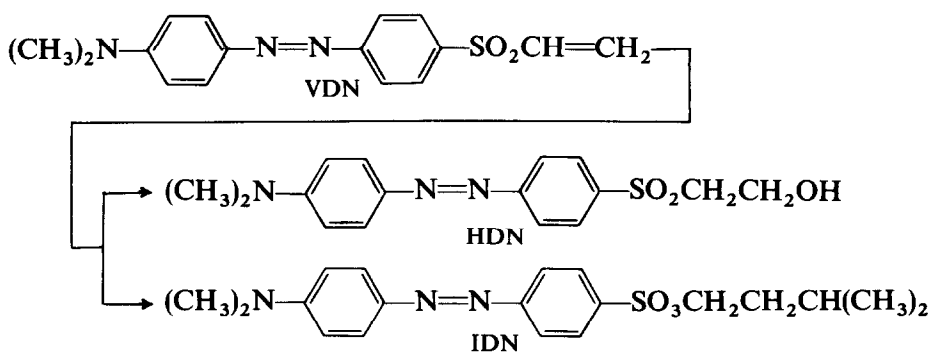
From the kinetic data, the structure of the model dye–fiber compounds may be quantitatively correlated to the ease of hydrolysis of these compounds.

2.2 Determination of the rate constants of the competitive reactions of a vinyl sulfone dye with aqueous *n*-propyl or isopropyl alcohol[4]

The kinetic determination was homogeneously carried out in aqueous propyl alcohol and maintained at a specific temperature. After mixing with good stirring, samples were taken every 5 min to determine the concentration change of unreacted dye, hydrolyzed dye, and the reaction products with propyl alcohol during the reaction.

By using HPLC, the concentrations of unreacted dye and hydrolyzed dye can be determined simultaneously. A Water 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: 0·5–1·0 ml/min. Wavelength for detection 465 mn.)

Taking the competitive reaction of dye VDN with aqueous isopropyl alcohol as an example (Scheme 1), the NaOH solution used was $1{\cdot}576 \times 10^{-2}$ mol/liter and isopropyl alcohol 3·328 mol/liter; isopropyl alcohol:H_2O:acetone = 1:1:2 (by volume), reaction temperature 50°C.



Scheme 1

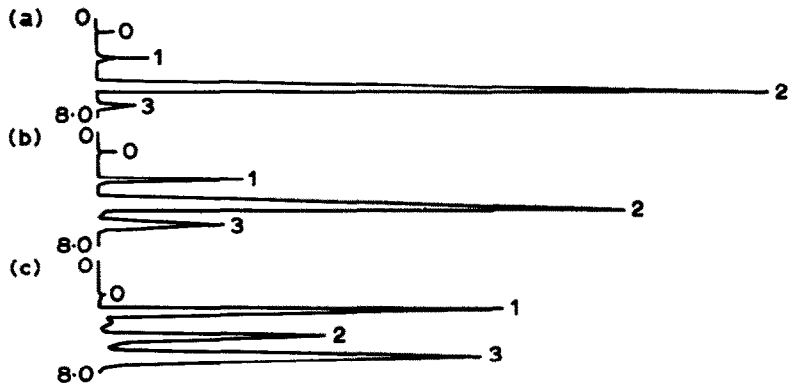


Fig. 5. High pressure liquid chromatogram of the competitive reaction of VDN with isopropyl alcohol–H_2O: (a) after 2 min; (b) after 4·8 min; (c) after 12·15 min.

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. 5: peak 1, retention time 4·26 min, is for 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.

The standard curve determination was carried out as follows: a standard sample of VDN (34·36 mg) was dissolved in acetone (100 ml); 25 ml of this

TABLE 3
Dosage Quantities to HPLC and Peak Areas of a VDN Standard Dye Samples

Name of dye	*Conc. of standard solution (mg/liter)*	*Dosage quantity (ml)*	*Peak area ($\times 10^5$)*	*Dosage weight ($\times 10^{-7}$ g)*	*Dosage quantity ($\times 10^{-7}$ mol)*
VDA	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

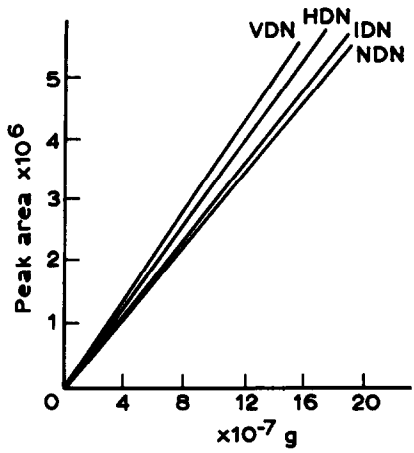


Fig. 6. Standard curves of VDN, HDN, IDN and NDN.

was diluted to 50 ml to give a standard solution of 171·8 mg/liter. Aliquots (1, 2, 3, 4, 5, 6, 7, 8, 9 ml, respectively) were made up to 10 ml in acetone to give a further nine standard solutions of different concentrations. Into the Waters 510, fitted with a C_{18} column, were injected 10 μl of solution. The peak areas and weight of dosaged VDN solutions are listed in Table 3. Plots of peak areas and dosage quantities are given in Fig. 6.

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

VDN: $Y_v = 3{\cdot}445 \times 10^5 X + 875$
HDN: $Y_h = 3{\cdot}254 \times 10^5 X + 286$
IDN (isopropyl ether): $Y_i = 3{\cdot}001 \times 10^5 X + 423$
NDN (*n*-propyl ether): $Y_n = 2{\cdot}935 \times 10^5 X + 895$

TABLE 4
Competitive Alcoholysis (Isopropyl Alcohol) and Hydrolysis of VDN at 50°C

Time (*s*)	*Conc. of dye*	*Conc. of alcohol*	*Conc. of hydrolyzed dye*	$\ln(D_o/D_t)$
0	99·02	—	—	0·0000
36	94·05	3·36	2·55	0·0515
66	89·62	5·84	4·54	0·0997
84	86·28	7·56	6·16	0·1377
112	83·48	9·03	7·49	0·1707
134	83·04	9·53	7·43	0·1760
167	80·35	10·87	8·78	0·2089
205	76·86	12·81	10·33	0·2533
362	72·63	15·02	12·35	0·3099

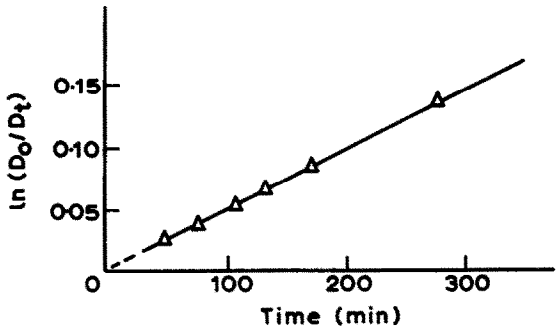


Fig. 7. Plot of $\ln(D_0/D_t)$ against time t.

The rate equation for the hydrolysis of VDN is:

$$\frac{d[\text{Dye}]}{dt} = k'_{\text{total}}[\text{Dye}]$$

where k'_h is rate constant of pseudo-first order hydrolysis.

$$k_{\text{total}} = k'_h + k'_{\text{ROH}}$$

The competitive alcoholysis (isopropyl alcohol) and hydrolysis of VDN at 50°C are shown in Table 4.

On plotting $\ln(D_0/D_t)$ against time (in seconds), a straight line is obtained.

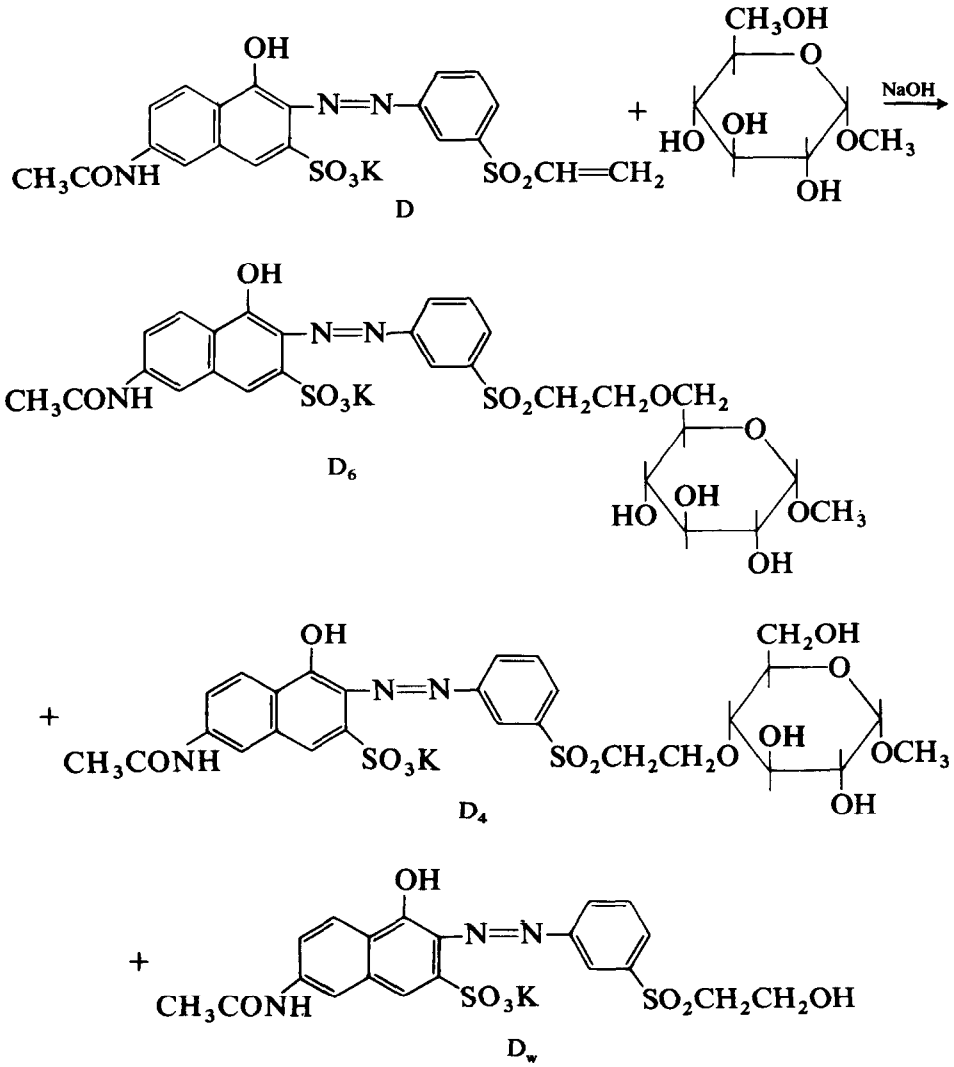
From Fig. 7, $k_{\text{total}} = 7{\cdot}27 \times 10^{-2}\,\text{min}^{-1}$ by calculation, $k'_{\text{ROH}} = 4{\cdot}05 \times 10^{-2}\,\text{min}^{-1}$ and $k'_h = 3{\cdot}22 \times 10^{-2}\,\text{min}^{-1}$.

3 DETERMINATION OF RATES OF CHEMICAL CHANGES BY THIN LAYER CHROMATOGRAPH-DOUBLE SCANNING

3.1 Reaction between a vinyl sulfonyl reactive dye and methyl-αD-glucoside (Scheme 2)

D, D_w, D_6 and D_4 (10 mg of each) were dissolved in a 100 ml volumetric flask to give standard solutions of dye with concentration 0·1 mg/ml. Aliquot portions of the solution were then diluted to give a series of solutions with concentrations of 1–7 mg/ml.

The samples were applied to chromatographic plates, developed and zig-zag scanned. The peak areas of the spots (spot 1 was shown to be D, spot 2 D_w, spot 3 D_4 and spot 4 D_6) were obtained (Table 5), and plots were then produced for the peak areas versus the corresponding dosage quantities (Fig. 8).



Scheme 2

From Fig. 8, $A = r_p D$, $A_D = k_D D$, $A_w = k_w D_w$, $A_6 = k_6 D_6$ and $A_4 = k_4 D_4$. Since

$$\ln \frac{D_o}{D_t} = kt$$

then

$$\ln \frac{A_o}{A_t} = kt$$

TABLE 5
Peak Areas and Dosage Quantities of D, D_w, D_6 and D_4

Dosage quality ($D \times 10^{-7}$ g)	*0*	*1*	*2*	*3*	*4*	*5*	*6*	*7*
A_6	0	2 498·26	5 512·95	9 236·87	11 765·25	14 446·18	15 863·96	18 684·11
A_6	0	3 735·5	7 524·31	11 982·72	15 378·79	19 044·23	21 025·41	25 784·2
A_W	0	4 858·45	8 036·52	15 855·81	18 604·23	23 654·9	27 824·89	31 328·55
A_D	0	5 515·23	10 720·6	16 739·38	23 320·16	27 652·21	30 344·71	36 780·92

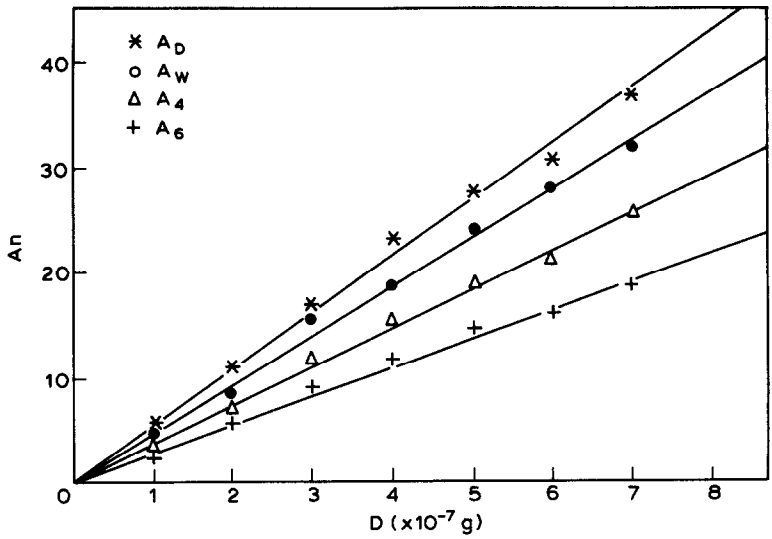


Fig. 8. Standard curves of D, D_w, D_6 and D_4.

A plot of

$$\ln \frac{D_o}{D_t}$$

against time t is shown in Fig. 9. The slope of the straight line is k, the total constant of the reaction rate. Since $k = k_w + k'_6 + k'_4$, and $k'_6 : k'_4 : k_w = D_6 : D_4 : D_w$, k'_6, k'_4 and k_w can thus be calculated (Table 7).

3.2 Determination of the rates of alkaline hydrolysis of dye–glucoside[4]

The alkaline hydrolysis of D_6 may be represented by Scheme 3. The rate equation of the hydrolysis of D_6 may be represented as follows:

$$\ln \frac{[D_6]_o}{[D_6]_t} = k_6 t$$

where $k_6 = k'_1 + k'_2$.

D_6 (0·02 g) was dissolved in 30 ml of distilled water. The solution (7·5 ml) was transferred to a 50 ml conical flask. The solution was stirred and maintained at 50°C for 1 h, and 0·025 ml of 2 N NaOH solution was then added. Aliquots were removed at intervals, cooled immediately and dilute HCl added to give a pH of 5–6. A microinjector was used to inject 1 μl onto a chromatographic plate (Silica Gel G + 0·2% CMC), which was then developed (using as eluant an appropriate phase, viz. butanol or iso-butanol/methanol/acetic acid/water, 60/10/1/20; isobutanol/ethyl/acetate/ammonia,

TABLE 6

Experimental Data and Calculated Results of the Reaction by the Dye and Methyl-α-D-glucoside at 50°C and pH 12·821

Time (min)	*0*	*0·5*	*1·0*	*1·5*	*2*	*2·5*	*3·0*	*5·0*	*7·0*	*9·0*	*12·0*
A_5	0	6 240	12 110	16 122	19 110	20 095	20 095	20 704	27 041	29 023	26 928
A_4	0	890	1 840	2 294	2 548	2 943	3 114	4 823	5 569	6 531	5 183
A_W	0	2 490	5 130	62 331	73 312	7 865	8 223	12 160	14 299	17 751	17 058
A_D	108 871	95 224	82 908	66 839	48 771	40 791	30 826	24 679	18 365	15 707	11 453
D_6/D_W	—	0·424	3·995	4·378	4·422	4·323	4·466	4·424	3·205	2·767	2·671
D_4/D_W	—	0·454	0·455	0·467	0·442	0·459	0·480	0·5031	0·495	0·467	0·3856
$\ln(D_o/D_t)$	—	0·134	0·272	0·488	0·803	0·982	1·262	1·484	1·780	1·963	2·252

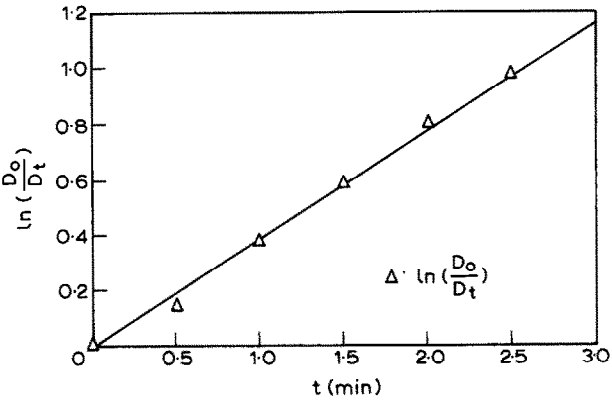


Fig. 9. Plot of $\ln(D_0 D_t)$ versus reaction time t (min) of reaction 1 at 50 ± 1 C and pH = 12·824.

6/6/4; butanol/ethylacetate/water/ammonia, 60/30/10/2) and scanned. The chromatogram of D_6 during the hydrolysis at 50°C showed that there were two reaction products formed, D_w and D. The standard curves for D_6, D and D_w were obtained (Table 8).

On plotting

$$\ln \frac{[D_6]_o}{[D_6]_t}$$

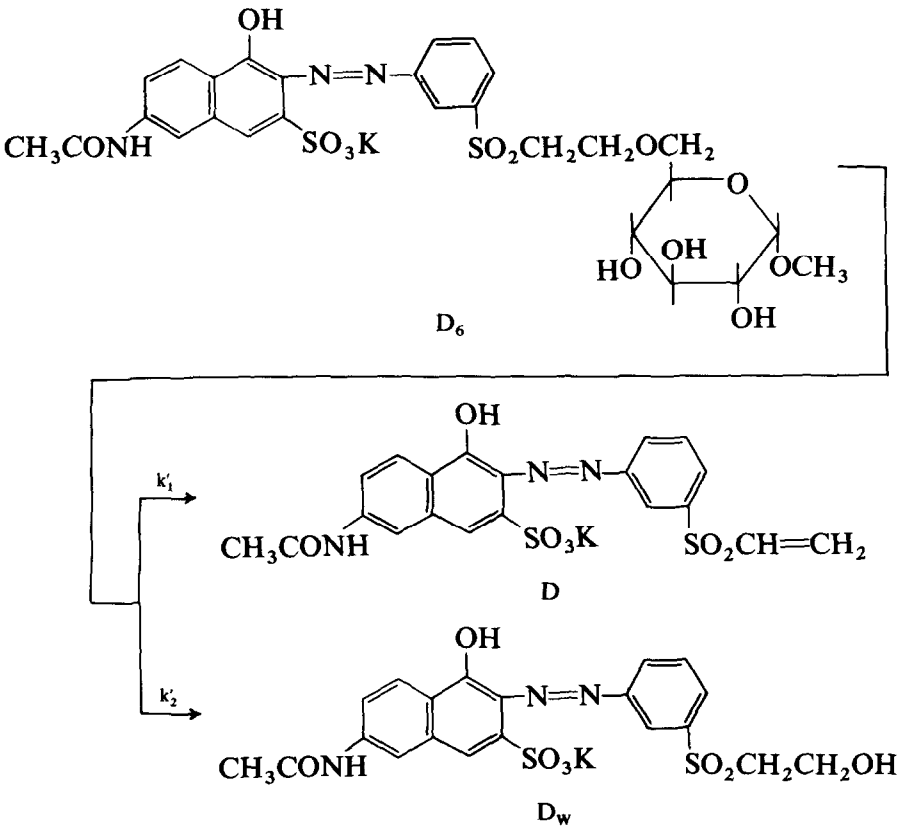
against time t, a straight line is obtained (Fig. 10); the slope of line is $k_6 = 0{\cdot}11424\ \text{min}^{-1}$.

3.3 Determination of the rates of formation of polymethine dyes[6]

The rates of formation of polymethine dyes have not been fully studied kinetically. The mechanisms in polymethine dye formation have only been explained by the general electronic theory.[7]

TABLE 7
The Rate Constants of the Reaction between Dye and Methyl-α-D-Glucoside

No. of reaction	*Reaction conditions*	$\bar{K}_n$	k'_w	k'_6	k'_r	$k'_6/(k'_e+k'_4)$
1	50 ± 1°C [GOH]:[D] = 4:1	0·1411	0·01674	0·1081	0·01628	0·8691
2	60 ± 1°C [GOH]:[D] = 4:1	0·1607	0·03470	0·1096	0·01856	0·8553



Scheme 3

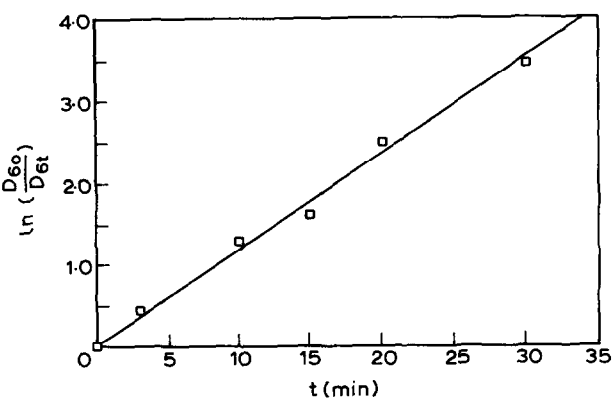
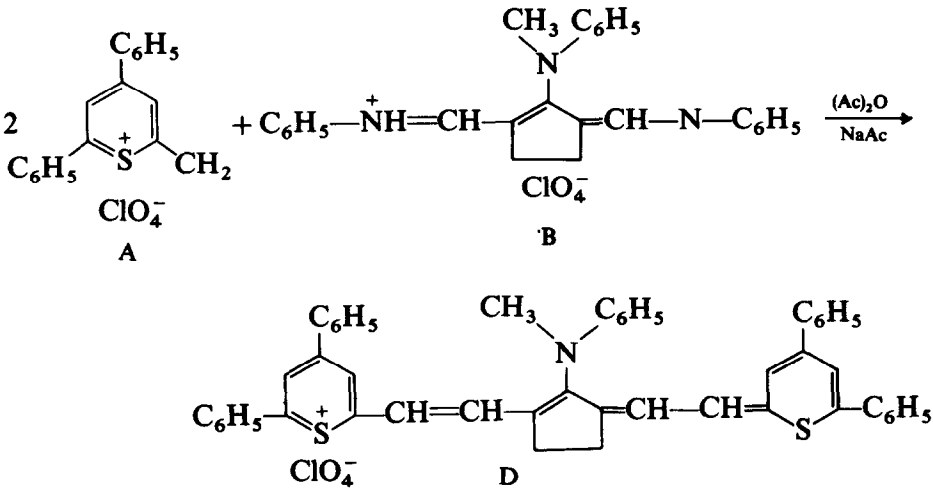


Fig. 10. Plot of $\ln([D_6]_0/[D_6]_t)$ against time t (min).

TABLE 8
Peak Areas of A_D, A_W and A_6 During Hydrolysis

Time (min)	*0*	*3·0*	*5·0*	*10·0*	*15·0*	*20·0*	*30·0*
A_D	0	9 498·52	6 814·44	4 146·85	2 965·05	1 408·57	644·23
A_W	0	6 463·65	9 826·11	14 809·32	17 009·04	18 637·64	21 003·09
A_6	31 458·22	20 114·39	13 435·69	8 736·58	5 344·34	2 627·65	996·41
$\ln [D_6]_o/[D_6]_6$	0	0·447	0·8507	1·281	1·601	2·483	3·452

We have recently carried out kinetic studies by using the TLC-double scanning method.



Scheme 4

A thiopyrylium near infrared lasing dye was prepared as outlined in Structure 4. After reaction, the samples were applied to a chromatographic plate, developed and zig–zag scanned. The spots were identified as the reactants A and B, the intermediate C, and the final product D. The concentration changes in A, B, C and D, are shown in Table 9. From Table 9, the possible reaction sequences in the presence of the catalyst NaAc at 125°C are A + B → C (reaction 1) and A + C → D (reaction 2) (Scheme 5). The kinetic treatment is therefore very difficult to carry out. In our study, the reaction occurred in two steps. The first step is a reaction of A and B (mole ratio of A : B is 1 : 1) to form the intermediate C at 125°C, without NaAc. The peak areas and dosage quantities of A, B and C, respectively, were determined. The experimental data and the calculated results of reaction (1) were obtained (Table 10).

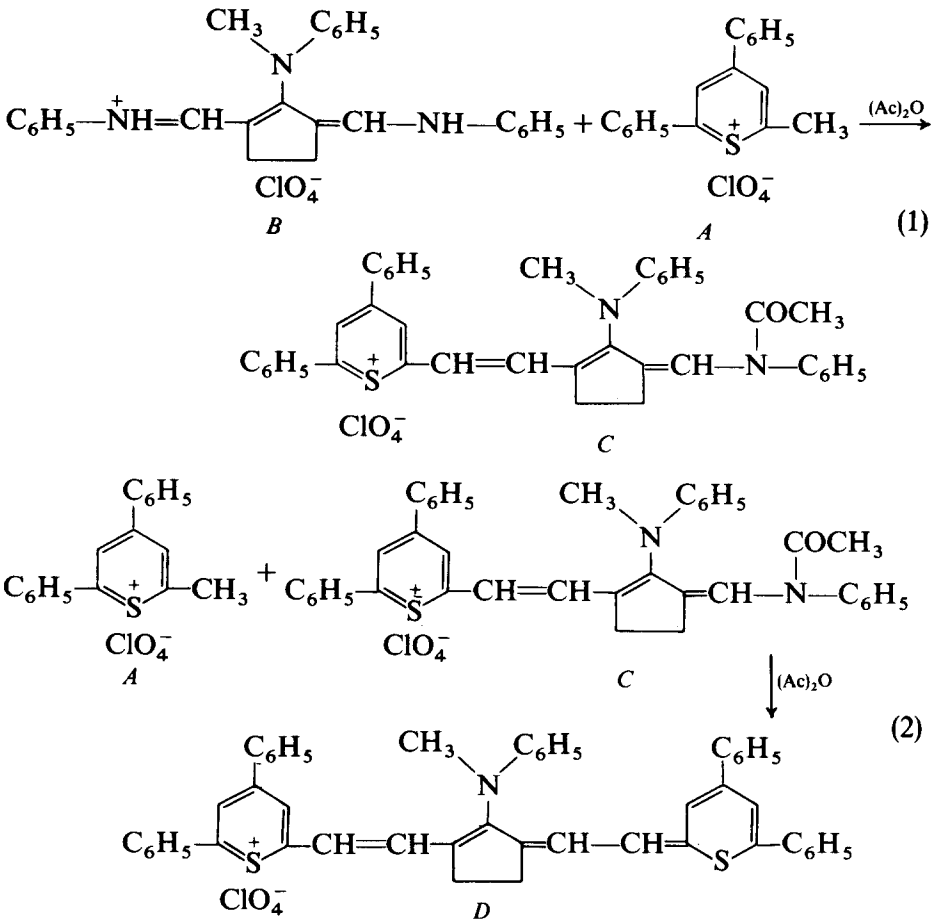
The plot of $1/C_B$ against time t (min) of reaction (1) at 125°C without NaAc is shown in Fig. 11. From Fig. 11, the straight line fits the second order rate equation $1/C_B = k_1 t + 1/C_{B_0}$; k_1 is the specific rate constant of reaction (1), i.e. 2·89 liter/mol/min at 125°C.

The second step is the reaction between A and C to form D (1 : 1 mol ratio). The temperature of this reaction was also kept at 125°C, and alliquot portions applied to the chromatographic plate, which was then developed and scanned. The experimental data and the calculated results of reaction (2) were thus obtained (Table 11).

A plot of $1/C_C$ against time t at 125°C, without catalyst NaAc, gives a

TABLE 9
Experimental Data and Calculated Results of the Reaction by $2A + B \rightarrow C + D$ at 125°C with NaAc

t_{min}	0	1	2	3	4	5	6	7	8	9	10	11	12
A_A	2584 68	2175·42	1990·25	1697·39	1599·53	1543·87	1491·12	1337 97	1133·71	1018·56	875 5	738·44	638·03
W_A (μg)	0·7340	0·6215	0·5706	0·4901	0·4632	0·4479	0·4334	0·3913	0·3434	0·3035	0·2650	0·2265	0·1989
C_A ($\times 10^{-2}$ m)	10 11	8·56	7·86	8 75	6·38	6·17	5·97	5·39	4·73	4·18	3·65	3 12	2 74
$1/C_A$	9·89	11·68	12·72	14 81	15·67	16·21	16 75	18·55	21·14	23·92	27·40	32·05	36·50
A_B	6835·63	4637 58	3721·83	2637·11	2282·81	1983·01	1773·15	1602·82	1432 48	1198·09	1079·53	1753·64	1027·75
W_A (μg)	0·5011	0 3398	0·2726	0·1930	0·1670	0·1450	0·1296	0 1171	0·1046	0·0874	0 0787	0·0768	0·0749
C_B ($\times 10^{-2}$ m)	5·22	3·54	2·84	2·01	1·74	1·51	1·335	1·22	1·09	0·91	0·82	0·80	0·78
$1/C_B$	19 23	28·25	35·21	49·75	57·47	66·23	74·07	81·97	91·74	109·89	121 95	125·00	128·21
A_C	0	818·34	1077 06	1483·84	1654·80	1742 56	1599 27	1544 34	1478·27	1252·98	1049·19	834·65	680·62
W_C (μg)	0	0·1921	0·2571	0·3593	0·4022	0·4243	0·3883	0·3745	0·3579	0·3013	0 2501	0 1962	0·1575
C_C ($\times 10^{-2}$ m)	0	1·39	1·88	1 86	2·60	3·07	2·81	2·71	2·59	2·18	1·81	1·42	1 14
$1/C_C$		71 94	53·76	38·46	34·36	32·57	35·51	36·90	38·61	45·87	55·25	70·42	87·72
A_D	0	7·795	96·14	178·39	354·36	430·86	463·90	548·30	759·83	1042 11	1306·43	1675·51	1811·74
W_D	0	0·098	0·0344	0 0573	0 1063	0 1276	0·1358	0·1603	0·2192	0·2978	0 3714	0 4466	0·5121
C_D ($\times 10^{-2}$ m)	0	0 06	0·21	0·35	0·65	0·78	0·83	0·98	1·34	1·82	2·27	2·73	3 13
$1/C_D$		166 67	476·19	285 71	153 85	128·21	120·48	102·04	74·61	54·95	44·05	36 03	31 95



Scheme 5

linear relationship (Fig. 12). Therefore, reaction (2) is also a second order reaction with $k = 0{\cdot}432$ liter mol^{-1} min.

The above two reactions were also carried out with addition of catalyst; at 75°C, k'_1 and k'_2 were determined in a similar manner, giving $k'_1 = 4{\cdot}334$ liter mol^{-1} min and $k'_2 = 1{\cdot}977$ liter mol^{-1} min.

$$k_1 > k_2, \quad k'_1 > k'_2, \quad k'_1 > k_1, \quad k'_2 > k_2$$

It is evident that the function of sodium acetate catalyst is to accelerate the rates of formation of the intermediate C and of dye D by enhancing the rate of formation of a methylene base from A. The rate of formation of intermediate C is greater than that of the final dye D. In general terms, the overall observed is:

$$2A + B \rightarrow D$$

TABLE 10
Experimental and Calculated Results of Reaction (1) at 125 C

Time (min)	*0*	*2*	*4*	*6*	*8*	*10*	*12*	*16*	*20*
A_A	1260·84	931·25	714·79	577·28	495·43	392·47	321·17	262·96	223·31
W_A (μg)	0·3701	0·2795	0·2200	0·1822	0·1597	0·1314	0·1118	0·0958	0·0849
C_A ($\times 10^{-2}$ m)	5·10	3·85	3·03	2·51	2·20	1·81	1·54	1·32	1·17
$1/C_A$	19·6	25·97	33·00	39·84	45·45	55·25	64·94	75·75	85·47
A_B	6548·1	5214·0	4141·55	3539·23	3120·88	2649·33	2231·03	1969·39	1733·64
W_B (μg)	0·4800	0·3821	0·3034	0·2592	0·2285	0·1939	0·1632	0·144	0·1267
C_B ($\times 10^{-2}$ m)	5·0	3·98	3·16	2·70	2·38	2·02	1·7	1·50	1·32
$1/C_B$	20	25·13	31·65	37·04	41·86	49·50	58·82	66·67	75·76
A_C	0	609·37	1038·45	1208·8	1440·06	1632·31	1808·63	1918·49	2078·1
W_C (μg)	0	0·1396	0·2474	0·2902	0·3483	0·3966	0·4409	0·4685	0·5086
C_C ($\times 10^{-2}$ m)	0	1·01	1·79	2·21	2·52	2·87	3·19	3·39	3·68

A is peak area, W is weight and C is the concentration.

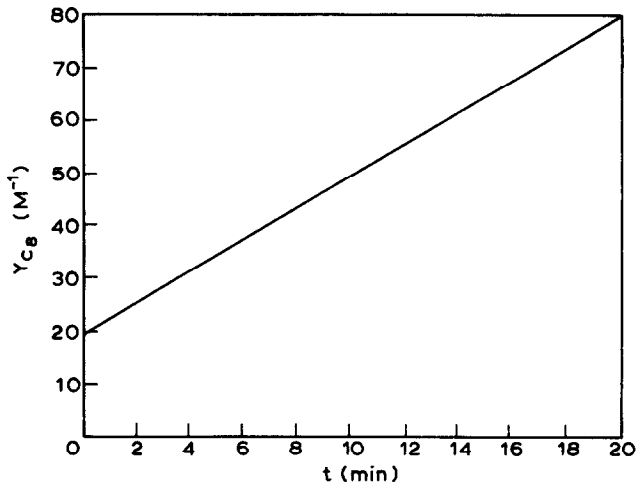


Fig. 11. Plot of $1/C_B$ against time t (min) of reaction (1) at 125°C without NaAc.

but it occurs in two steps, by forming the reaction intermediate C.

$$A + B \rightarrow C, \qquad A + C \rightarrow D$$

Since $k_1 > k_2$, C is found to be in excess. in the course of reaction. This is the reason why an asymmetric polymethine dye may be prepared by using this method.

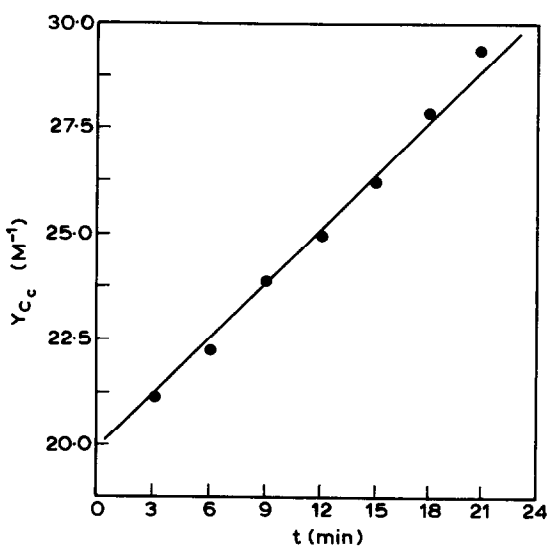


Fig. 12. Plot of $1/C_C$ against time t of reaction (2) without NaAc.

TABLE 11
Experimental Data and Calculated Results of Reaction (2) at 125°C without NaAc

t (min)	*0*	*3*	*6*	*9*	*12*	*15*	*18*	*21*	*24*
A_A	1240·47	1150·6	1079·31	1018·56	968·36	918·15	862·49	804·65	788·64
W_A (μg)	0·3645	0·3398	0·3202	0·3035	0·2879	0·2759	0·2606	0·2447	0·2403
C_A ($\times 10^{-2}$ m)	5·02	4·68	4·41	4·18	3·99	3·80	3·59	3·37	3·31
A_C	2804·08	2655·64	2501·6	2363·89	2265·17	2154·92	2033·92	1929·64	1891·03
W_C (μg)	0·6910	0·6537	0·6150	0·5804	0·5556	0·5279	0·4975	0·4713	0·4616
C_C ($\times 10^{-2}$ m)	5·0	4·73	4·45	4·20	4·02	3·82	3·60	3·41	3·34
$1/C_C$	20	21·14	22·47	23·81	24·88	26·18	27·78	29·33	29·94
A_D	0	137·08	307·67	448·46	554·4	677·59	812·62		953·76
W_D (μg)	0	0·0458	0·6933	0·1325	0·1620	0·1963	0·2339		0·2732
C_D ($\times 10^{-2}$ m)	0	0·28	0·57	0·81	0·99	1·20	1·43		1·67

4 DETERMINATION OF RATES OF CHEMICAL CHANGES USING ^{1}H NMR[8,9]

The hydrolysis in alkaline solution of some model bifunctional reactive dyes has been studied by using ^{1}H NMR. The kinetics of the hydrolysis of the monochlorotriazine group and the vinyl sulfonyl group were studied by the chloride ion-selective electrode method and by ^{1}H NMR respectively. The structure of the bifunctional reactive dye, and its hydrolysis reaction are shown in Scheme 6.

If B and C are reactive intermediates, their concentrations are very low. By steady state theory

$$\frac{d[B]}{dt} = 0, \qquad \frac{d[C]}{dt} = 0$$

Then

$$\frac{d[B]}{dt} = k_1[A][OH^-] - k_{-1}[B] - k_3[B] = 0$$

and therefore

$$[B] = \frac{k_1}{k_{-1} + k_3}[A][OH^-]$$

and

$$\frac{d[C]}{dt} = k_2[A][OH^-] - k_3[C] - k_4[C] = 0$$

Therefore

$$[C] = \frac{k_2}{k_3 + k_4}[A][OH^-]$$

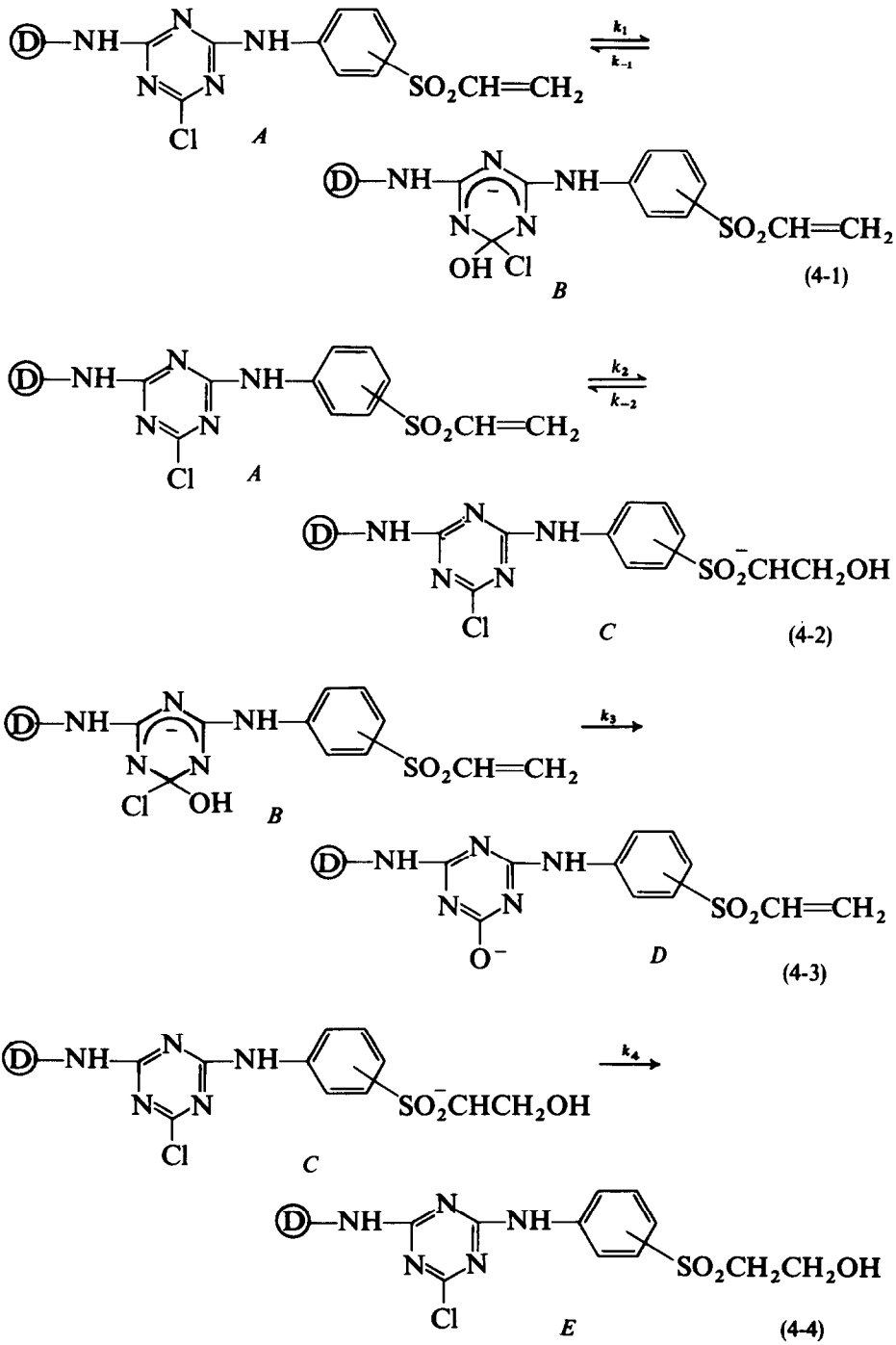
$$\frac{d[D]}{dt} = k_3[B]$$

$$\frac{d[R]}{dt} = k_4[C]$$

$$\frac{d[D]}{dt} = \frac{k_1 k_3}{k_{-1} + k_3}[A][OH^-] = k'_1[A][OH^-]$$

where

$$k' = \frac{k_1 k_3}{k_{-1} + k_3}$$



Scheme 6

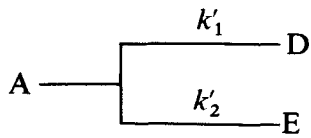
and

$$\frac{d[E]}{dt} = \frac{k_2 k_4}{k_{-2} + k_4}[A][OH^-] = k'_2[A][OH^-]$$

where

$$k'_2 = \frac{k_2 k_4}{k_2 + k_4}$$

From the above equations, the hydrolysis of the bifunctional reactive dye is a second order parallel reaction, and may be simplified as follows:



when

$t = 0 [A] = [A_o]$, $[D] = [E] = 0$

$t = t [A] = [A_o] - [D]_t - [E]_t$ $\quad [D] = [D]_t$, $\quad [E] = [E]_t$

$$-\frac{d[A]}{dt} = k'_1[A][OH^-] + k'_2[A][OH^-]$$

$$= (k'_1 + k'_2)[A][OH^-]$$

$$= k'[A][OH^-]$$

where

$$k' = k'_1 + k'_2$$

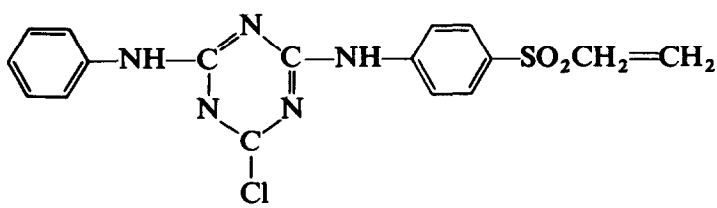
$$-\ln[A] = k' \int_0^t [OH]\, dt + C$$

and

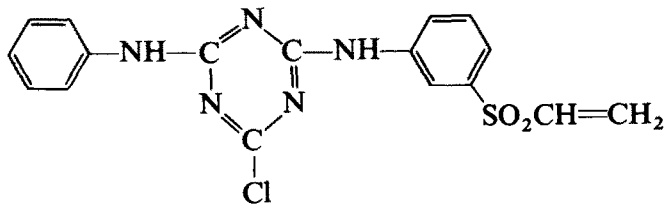
$$\frac{d[D]}{d[E]} = \frac{k'_1}{k'_2} \quad \text{or} \quad \frac{[E]}{[E]} = \frac{k'_1}{k'_2}$$

The total rate constant k' may be determined by potentiometric titration. By plotting $[OH^-]$ against time t, $\int_0^t [OH^-]\, dt$ is obtained and plots of $-\ln[D]$ versus $\int_0^t [OH^-]\, dt$ give the rate constant k' (Fig. 13).

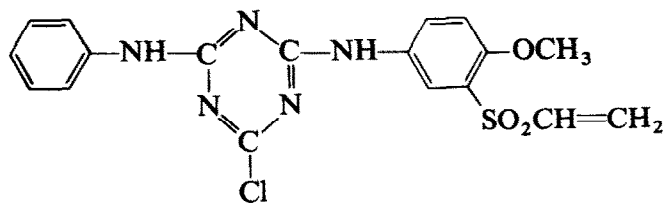
BI-1



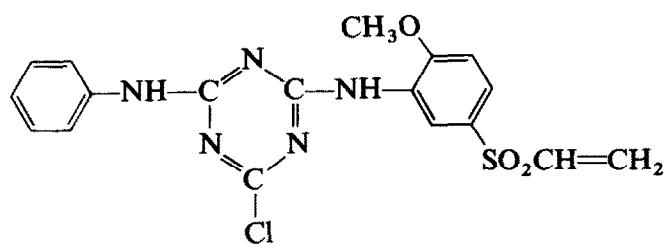
BI-2



BI-3



BI-4



In the course of hydrolysis, the proton peaks of the phenyl ring are not changed, but the proton peaks of the vinyl double bond gradually decrease.

The rate constants of the hydrolysis of the vinyl sulfonyl parts of the model dye may be determined by ^{1}H NMR. The weight of the unknown is calculated by the internal standard method using the following equation:

$$W'_u = W'_s \frac{N_s A_u M_u}{N_u A_s M_s}$$

where

W'_u, W'_s = weight of unknown and 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.

The proton peaks for the phenyl ring may thus be considered as the reference standard, and the proton peak of the vinyl double bond in the binyl sulfonyl group can be used to determine the products of hydrolysis quantitatively.

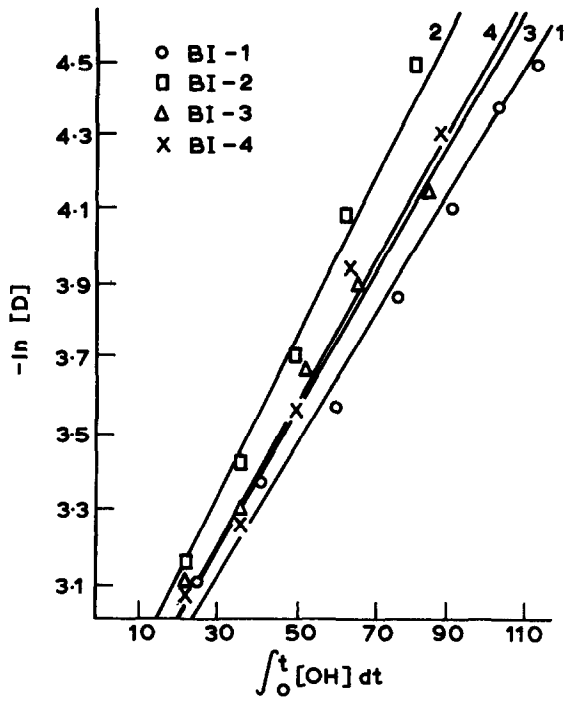


Fig. 13. Kinetic curves of the hydrolysis of model dyes.

Taking BI-1 as an example,

$$N_s = 9, \qquad N_u = 3 \quad [A_o] = 9{\cdot}662 \times 10^{-3}\ \text{mol/liter}$$

$$[\text{E}] = [A_o] - [A_t] = [A_o] - [A_o] \times \frac{9}{3} \times \frac{A_u}{A_s}$$

$$= [A_o] - 2{\cdot}899 \times 10^{-2} \frac{A_u}{A_s}$$

The experimental results in the case of BI-1 are shown in Table 12.

TABLE 12
Experimental Data of BI-1

t (min)	$[D] \times 10^3$	$[E] \times 10^3$	$[D]$	$-ln[A]$	$[OH^-] \times 10^2$	$\int_0^t [\text{OH}^-]\,dt$
5	1·149	4·113	3·58	3·126	2·614	24·15
10	1·388	4·863	3·50	3·378	2·550	43·80
15	1·528	5·335	3·49	3·567	2·506	62·40
20	1·681	5·880	3·50	3·863	2·369	79·20
25	1·746	6·287	3·61	4·091	2·183	92·72
30	1·845	6·549	3·55	4·366	2·144	104·20

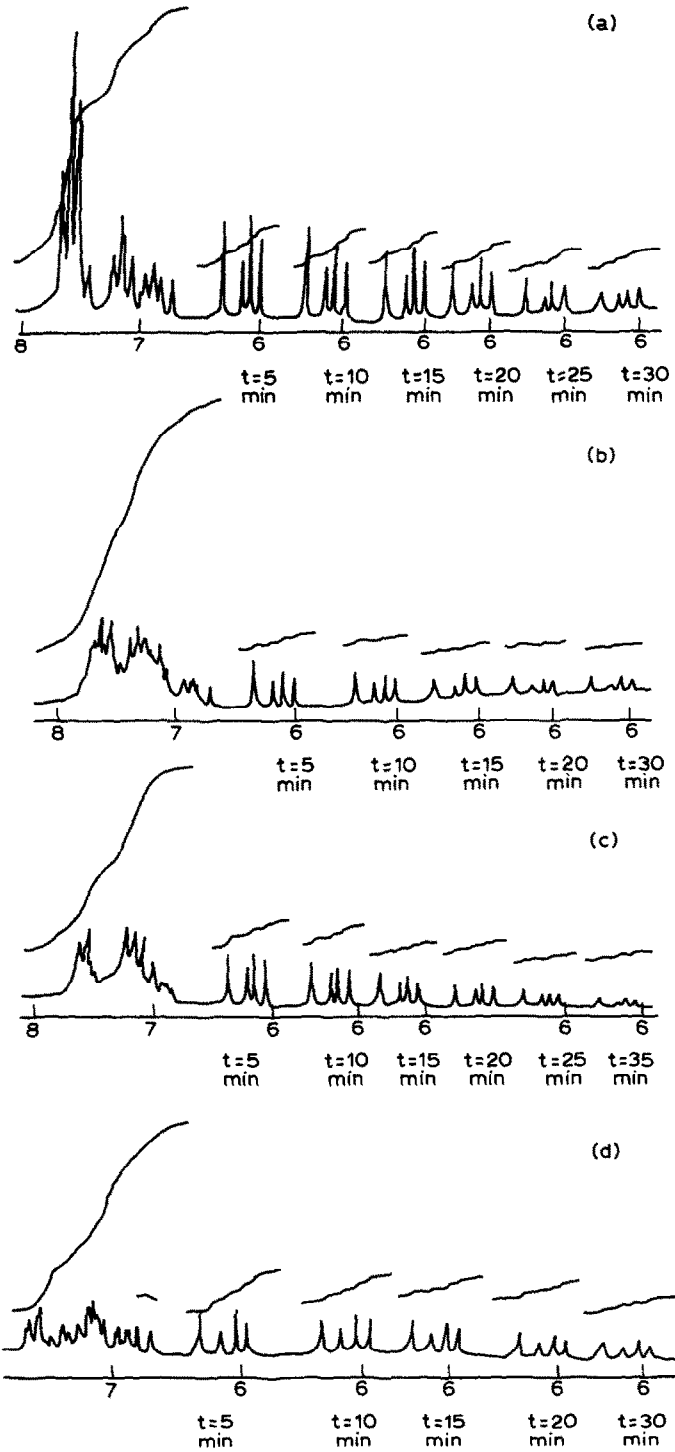


Fig. 14. ^{1}H NMR spectra for the ethylene group after different times: (a) BI-1; (b) BI-2; (c) BI-3; (d) BI-4.

TABLE 13
Experimental Data for BI-2

t (min)	$[D] \times 10^3$	$[E] \times 10^3$	$[E]/[D]$	$-ln[A]$	$[OH^-] \times 10^3$	$\int_0^t [OH^-]\,dt$
5	0·974	4·121	4·23	3·134	2·490	22·1
10	1·171	4·990	4·26	3·415	2·311	38·6
15	1·344	5·644	4·20	3·704	2·226	55·1
20	1·478	6·280	4·25	4·079	2·051	67·2
30	1·587	6·715	4·23	4·467	1·706	82·9

TABLE 14
Rate Constants of Hydrolysis of Model Dyes

	BI-1	*BI-2*	*BI-3*	*BI-4*
k	$1·677 \times 10^{-2}$	$1·915 \times 10^{-2}$	$1·756 \times 10^{-2}$	$1·780 \times 10^{-2}$
k'_1	$3·672 \times 10^{-3}$	$3·662 \times 10^{-3}$	$3·658 \times 10^{-3}$	$3·655 \times 10^{-3}$
k'_2	$1·300 \times 10^{-2}$	$1·549 \times 10^{-2}$	$1·390 \times 10^{-2}$	$1·414 \times 10^{-2}$

From Table 12, the average value of [E]/[D] = 3·54, and since $k' = 1·667 \times 10^{-2}$, so $k'_1 = 3·672 \times 10^{-3}$ min, $k'_2 = 1·300 \times 10^{-2}$ min.

For BI-2 $[A_0] = 9·450 \times 10^{-3}$ mol/liter, $N_s = 9$, $N_u = 3$, therefore

$$[\mathrm{E}] = [A_0] - [A_0] \times \frac{9}{3}\frac{A_u}{A_s} = [A_0] - 9·450 \times 10^{-3} \times 3\frac{A_u}{A_s}$$

$$= [A_0] - 2·835 \times 10^{-2}\frac{A_u}{A_s}$$

The average [E]/[D] is 4·23, and since $k' = 1·915 \times 10^{-2}\ \mathrm{min}^{-1}$, hence $k'_1 = 3·662 \times 10^{-3}\ \mathrm{min}^{-1}$ and $k'_2 = 1·549 \times 10^{-2}\ \mathrm{min}^{-1}$ (Table 13).

Similarly, the rate constants of the hydrolysis of the model dyes BI-3, BI-4 were obtained (Table 14).

5 CONCLUSIONS

Kinetic measurements in dye chemistry may be carried out using HPLC, TLC double-scanning and ^{1}H NMR methods. TLC double-scanning is considered to be the most convenient. All the methods can be considered as being relevant to the whole domain of dye chemistry.

REFERENCES

1. Rys, P. & Zollinger, H., *Fundamentals of the Chemistry and Application of Dyes.* Wiley-Interscience, London, 1972.
2. Jiang Wen, Zhu Zhenghua & Chen Kongchang, *Dyes and Pigments*, **10** (1989) 217–37.
3. Jiang Wen (Professor Zhu Zhenghua), Master thesis, East China University of Chemical Technology, 1980.
4. Zhu Zhenghua, Chen Kongchang & Yu Ronggen, *Dyes and Pigments*, **14** (1990) 129–42.
5. Zheng Yiadong (Professor Zhu Zhenghua), Doctor thesis, East China University of Chemical Technology, 1992.
6. Zhu Zhenghua & Zhang Jinglong, unpublished results, 1993.
7. Zhu Zhenghua, *Chemistry of Cyanine Dye* (in Chinese). East China University of Chemical Technology, 1964.
8. He Liqi, Zhu Zhenghua, Chen Kongchang & Zhao Paxiang, *Dyes and Pigments*, **10** (1989) 195–215.
9. He Liqi (Professor Zhu Zhenghua) Master thesis, East China University of Chemical Technology, 1987.