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A Kinetic Study of the Formation of Some Pyrylium and Thiopyrylium Polymethine Cyanine Dyes

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ABSTRACT

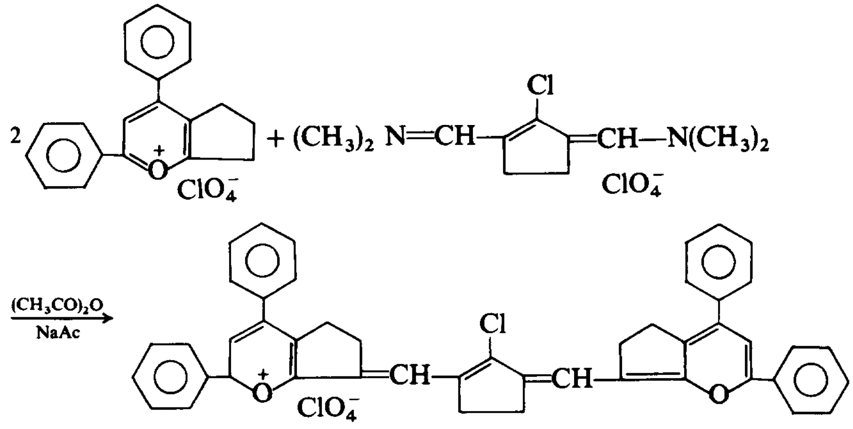
The mechanism of formation of some heptamethine pyrylium and thiopyrylium cyanine dyes has been studied using the TLC-double scanning method. The dyes are formed through a consecutive reaction route, with different rate constants at a given temperature. The function of added catalyst (sodium acetate) is also studied. The mechanism of the reaction is described on the basis of the kinetic study.

1 INTRODUCTION

Polymethine cyanine dyes are important dyes for use in photography and dye-lasers. Their structures are closely related to cationic dyes used as textile dyes. But so far as the mechanism of the polymethine dye formation is concerned, current knowledge is largely derived from general electronic theory.[1] In this paper, kinetic studies of the formation of pyrylium and thiopyrylium polymethine cyanine dyes were carried out using the TLC-double scanning method in order to illustrate details of the reaction pathway.

The general practice in a kinetic study of a reaction is to determine the concentration changes of the reactants or of the products at a specific temperature. In this present case, the reactions were carried out in solution and, therefore, the concentration changes are related to changes in the weights of the reactants or of the products respectively. Since the

TLC-double scanning method was used, the spots of reactants, intermediates and products at various times of reaction were separated and the peak areas of the spots measured, and hence correlated with weights. A number of standard curves relating peak areas and weights of spots were thus obtained. From these standard curves, the concentration changes during the reaction of either the reactants or the products may be determined from the corresponding changes in weights.[2] The formation of a polymethine cyanine dye may be represented by the following example:



In general, the formation of symmetrical polymethine cyanine dyes may be expressed as follows:

$$2A + B \longrightarrow D \qquad (1)$$

This is a termolecular reaction, usually taking place by two consecutive bimolecular reactions following one another, i.e.

$$A + B \longrightarrow C \qquad (2)$$

$$A + C \longrightarrow D \qquad (3)$$

where C denotes the intermediate formed from A and B. Once C is formed, C reacts further with another molecule of A to yield the final product D.

For reaction (2), where the concentrations of A and B are equal, then

$$C_A + C_B$$

and the kinetic equation of reaction (2) is:

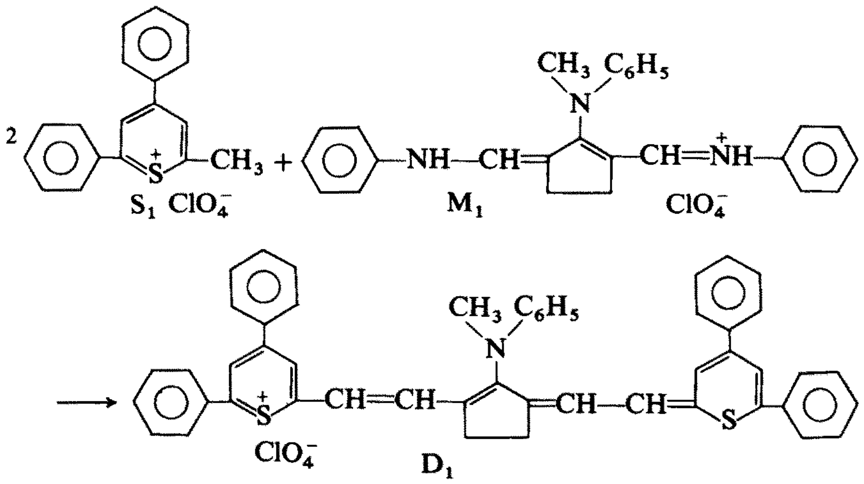
$$1/C_A - 1/C_{A0} = k_2t$$

where C_A is the concentration of A at time t, C_{A0} is the initial concentration of A and k_2 is the rate constant of reaction (2).

The kinetic equation of reaction (3) and k_3 may be obtained similarly. When C_A, C_{A0}, C_C and C_{C0} are experimentally determined, the rate constants k_2 and k_3 may then be calculated.

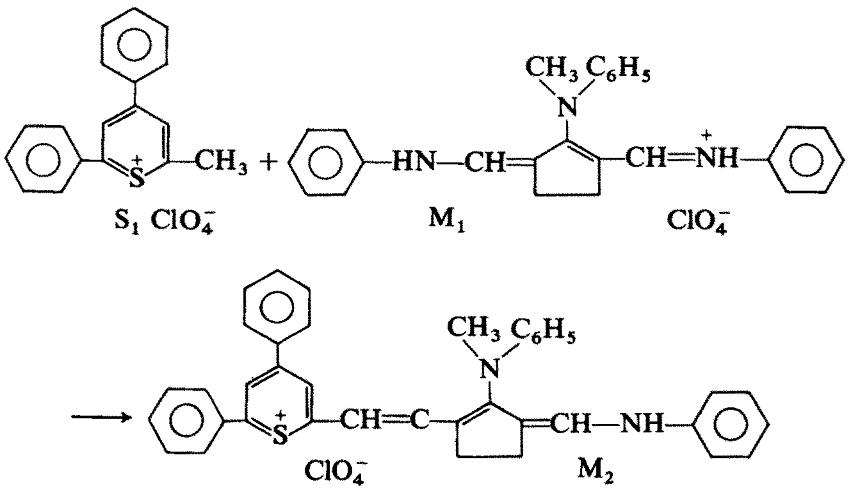
2 KINETIC STUDY OF THE FORMATION OF THE PYRYLIUM HEPTAMETHINE DYE D_1

The pyrylium heptamethine dye (D_1) is prepared according to eqn (4):

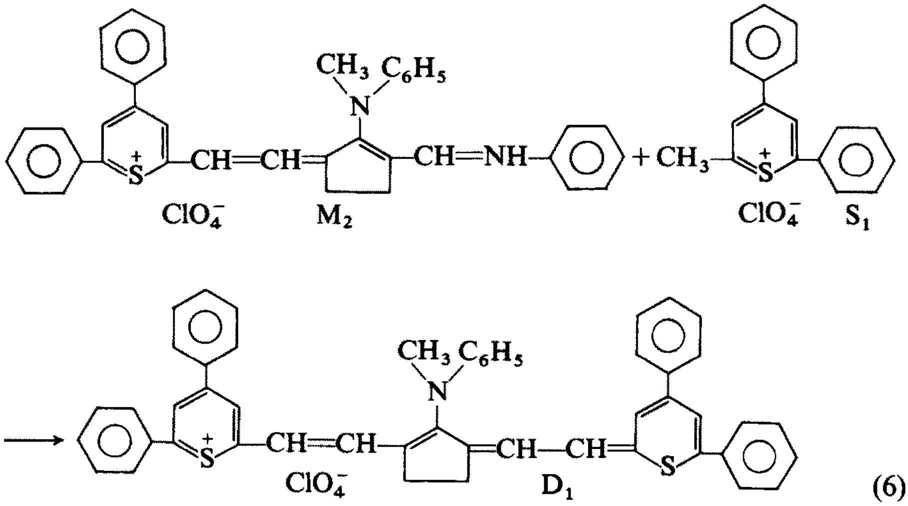


(4)

The overall reaction may be considered to comprise two consecutive reactions, i.e. (5) and (6):



(5)



(6)

2.1 Standard curve determination

The first step in the determination of the kinetic rates of the above reactions was to prepare and to purify the reactants (S_1), (M_1), the intermediate (M_2) and the final product (D_1) by repeated crystallization and finally by column chromatography. Accurately weighed S_1, M_1, M_2, D_1 (10 mg) were used to obtain a series of standard solutions of concentrations 0·01, 0·02, 0·03, 0·04, . . ., 0·08 A_n mg/ml. The samples were applied to chromatographic plates, developed and double-scanned, using a CS-930 instrument (Japan). The peak areas A_1, A_2, A_3 . . ., A_8 were obtained and by plotting A_n against dosage weights W_n (Table 1) standard curves of S_1, M_1, M_2 and D_1 were obtained.

The standard curves of S_1 and M_2, and of M_1 and D_1 are shown in Figs 1–3 respectively.

TABLE 1

Dosage Weights and the Peak Area Relationship of S_1, M_1, M_2 and D_1

W_n (×10 μg)	0	1	2	3	4	5	6	7	8
A_{S1}	0	306·25	632·15	899·75	1 443·63	1 752·23	2122·52	2 451·41	2 804·15
A_{M1}	0	1 333·72	2 613·83	4 011·46	5 531·72	7 216·28	8 003·32	9 807·56	10 596·47
A_{M2}	0	421·23	822·12	1 301·52	1 685·14	2 001·23	2 451·78	2 841·89	3 223·91
A_{D1}	0	1 012·34	1 898·93	3 135·61	4 309·55	5 274·58	6 671·02	7 219·53	8 670·45

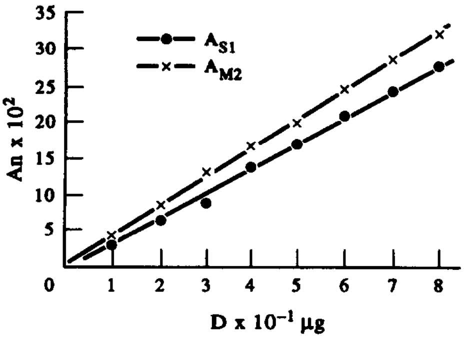


Fig. 1. Standard curves of S_1 and M_2.

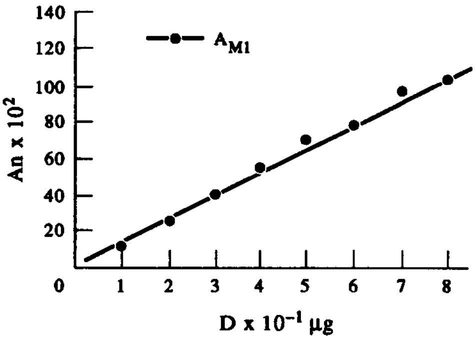


Fig. 2. Standard curve of M_1.

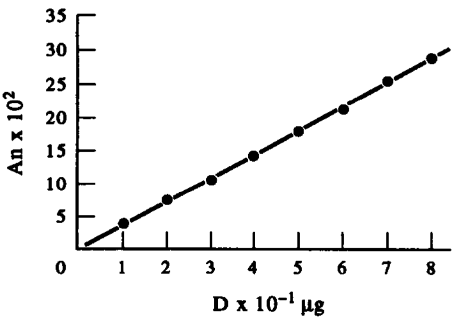


Fig. 3. Standard curve of D_1.

The regression equations are:

$$
\begin{aligned}
A_{S1} &= -27{\cdot}396 + 3591{\cdot}573W, & r &= 0{\cdot}9996\\
A_{M2} &= 53{\cdot}720 + 3980{\cdot}295W, & r &= 0{\cdot}9994\\
A_{M1} &= 7{\cdot}078 + 13\,627{\cdot}118W, & r &= 0{\cdot}9976\\
A_{D1} &= -85{\cdot}552 + 3637{\cdot}918W, & r &= 0{\cdot}9983
\end{aligned}
$$

2.2 Kinetic determination

2.2.1 Preliminary study

A sample (0·2400 g) of M_1 (0·5 × 10^{-3} mol) was added to 5 ml of acetic anhydride and 0·0125 g anhydrous sodium acetate and the mixture heated to 135°C. It was then added at 135°C to 0·326 g S_1 (1·0 × 10^{-3} mol) in 5 ml of acetic anhydride, maintaining a temperature of 135°C throughout. Aliquot portions (0·01 ml) were taken every minute, and added to 5 ml cold acetic anhydride to stop the reaction. A sample, 0·01 ml of solution, was applied to a chromatographic plate (silica Gel G + 0·2% CMC), which was dried, developed and the peak areas of the spots measured (CS-930). From the respective standard curves, the weight changes, or concentration changes of S_1, M_1, M_2 and D_1 were obtained. On plotting the changes in concentrations against time of reaction in minutes, the curves shown in Fig. 4 were obtained.

From Fig. 4, it can be seen that the formation of D_1 is a complicated reaction; the concentration of the intermediate M_2 gradually increases

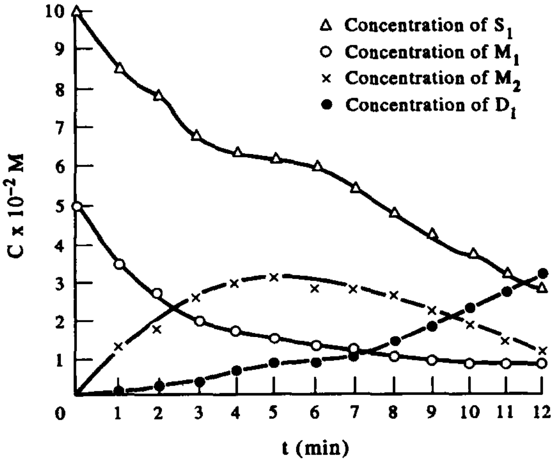
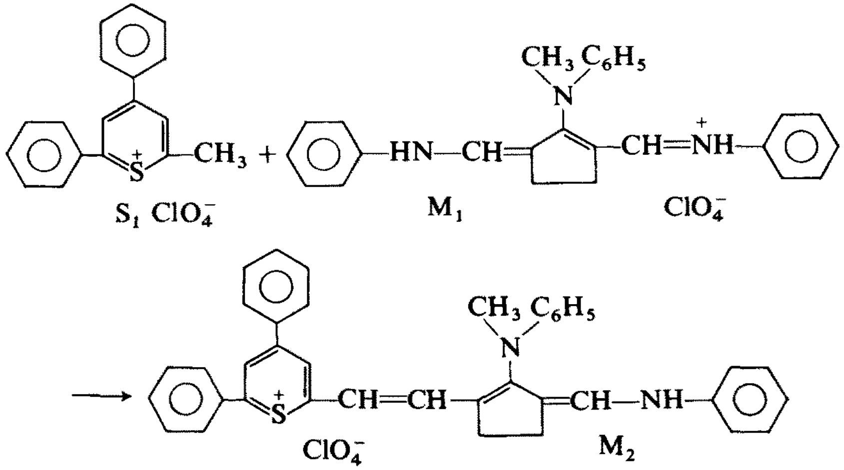


Fig. 4. Changes of concentration of S_1, M_1, M_2 and D_1 against time of reaction *t*.

initially, and then decreases as the reaction proceeds. This suggests that the overall reaction consists of two consecutive steps.

2.2.2 *Preparation of hemicyanine M_2*

In order to confirm this hypothesis, M_2 was prepared and a kinetic study of the reaction (eqn (5)) carried out.



(7)

A portion (0·326 g) of S_1 (0·001 mol) and 0·47 g (0·001 mol) of M_1 were added to 10 ml acetic anhydride and the mixture heated to 125°C and maintained at this temperature for 10 min. After cooling and filtering, the precipitation obtained was recrystallized from acetic anhydride, giving pure M_2 with m.p. 198–199°C (calculated: C 69·51%, H 4·95%, N 4·06%; found: C 69·69%, H 4·66%, N 4·11%).

2.2.3 *Study of kinetics of reactions (5) and (6)*

A sample (0·2400 g) (0·0005 mol) of M_1 in 5 ml acetic anhydride was heated to 125°C, and maintained at this temperature for 30 min before adding to 0·1815 g (0·0005 mol) S_1 in 5 ml acetic anhydride at 125°C. Samples (0·01 ml) were taken every 2 min, applied to a chromatographic plate, and the peak areas after development were measured by using the CS-930 double scanner.

From the standard curves of S_1, M_1 and M_2, the related peak areas and dosage weights of S_1, M_1 and M_2 were obtained (Table 2).

If the reaction is second-order bimolecular, the following equations should be obeyed.

$$1/C_{M1} - 1/C_{M10} = k_5 t \qquad \text{and} \qquad k_5 = (C_{M10} - C_M)/t$$

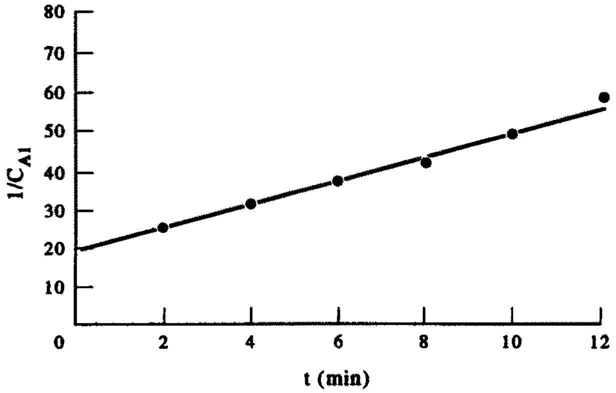
and on plotting $1/C_{M10}$ against time t, a straight line should be obtained.

TABLE 2
Peak Areas of Spots for S_1, M_1 and M_2 and Dosage Weights

Time (min)	*0*	*2*	*4*	*6*	*8*	*10*	*12*	*16*
A_{S1}	1260·84	931·25	214·79	577·28	495·63	392 67	321·17	262·96
$W_{S1}(\mu g)$	0·3701	0·2795	0·2200	0·1822	0·1597	0·1314	0·1118	0·0958
$C_{S1}(\times 10^{-2}$ M)	5·10	3·85	3·03	2·51	2·20	1·81	1·54	1·32
A_{M1}	6548·10	5214·00	4141·55	3539·23	3120·88	2649·38	2231·03	1969·39
$W_{M1}(\mu g)$	0·4800	0·3821	0·3434	0·2592	0 2285	0·1939	0·1632	0·1440
$C_{M1}(\times 10^{-2}$ M)	5·00	3·98	3·16	2·70	2·38	2·02	1·70	1·50
AM_2	0	609·37	1038·45	1208·80	1440·06	1632·31	1808·63	1918·49
$W_{M2}(\mu g)$	0	0·1396	0·2474	0 2402	0·3483	0·3966	0·4409	0·4685
$C_{M2}(\times 10^{-2}$ M)	0	1·01	1·79	2·21	2·52	2·87	3·19	3·39

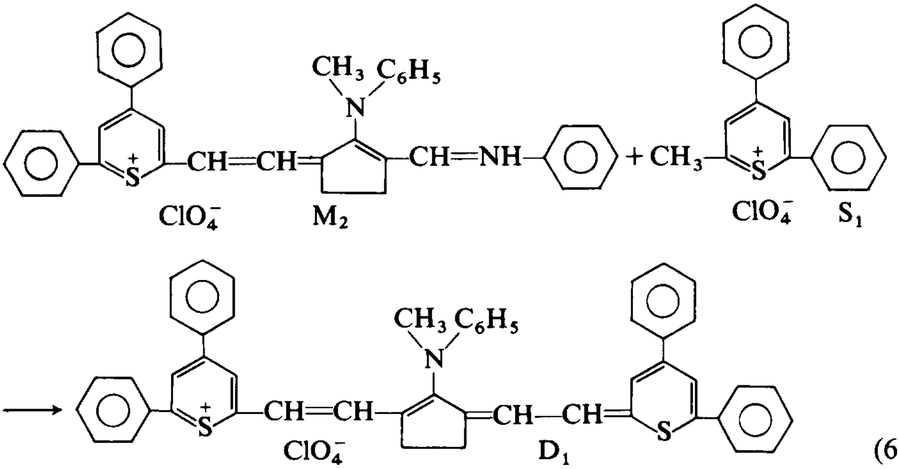
Figure 5 confirms this and therefore reaction 5 is shown to be a second order bimolecular reaction; the rate constant of the reaction at 125°C is $2{\cdot}88\text{M}^{-1}\ \text{min}^{-1}$.

The kinetics of reaction 6 were similarly studied. Solutions of 0·3257 g (0·0005 M) M_2 in 5 ml acetic anhydride and of 0·1815 g (0·0005 M) S_1 in 5 ml acetic anhydride were heated to 135°C for 30 min. The two solutions were then mixed, the temperature being maintained at 135°C, with stirring. At 3 min intervals, 0·01 ml samples were added to cold 5 ml acetic anhydride to stop the reaction. Following the usual chromatography and scanning, the peak areas of spots S_1, M_2 and D_1, and hence the corresponding weights, were determined (Table 3).



$1/C_{M1} - 19.75 = 2.88t$, r = 0.986

Fig. 5. Plot of $1/C_{M_1}$ against time *t*.



(6)

For a second-order bimolecular reaction:

$$1/C_{M2} - 1/C_{M20} = k_6 t \qquad \text{and} \qquad k_6 = (C_{M20} - C_{M2})/t$$

On plotting $1/C_{M2}$ against time t, a straight line $1/C_{M2} - 19{\cdot}37 = 0{\cdot}42t$ ($r = 0{\cdot}979$) was obtained (Fig. 6). From the slope of the plot, the rate constant of the reaction at 135°C, without addition of catalyst, was 0·42 M^{-1} min^{-1}; the rate constant of reaction (5) is thus greater than that of reaction (6).

2.2.4 Kinetics of reactions (5) and (6) in the presence of catalyst

The kinetics of reactions (5) and (6) were similarly studied in the pres-

TABLE 3

Change of Peak Areas of D_1 and Corresponding Weights of Spot S_1, M_2 and D_1 During the Reaction

Time (min)	*0*	*3*	*6*	*9*	*12*	*15*	*18*	*21*	*24*
A_{S1}	1 240·47	1 150·60	1079·31	1 018·56	968·36	918·15	826·49	804·65	788·64
W_{S1}(μg)	0·3645	0·3398	0·3202	0·3035	0·2879	0 2759	0·2606	0·2447	0·2403
C_{S1}($\times 10^{-2}$ M)	5·02	4·68	4·41	4·18	3·99	3·80	3·59	3·37	3·31
A_{M2}	2 804·08	2 655·64	2501·60	2 363·89	2 265·17	2 154·92	2 033·92	1 929·14	1 981·03
W_{M2}(μg)	0·6910	0·6573	0·6150	0·5804	0·5556	0·5279	0·4925	0·4713	0·4616
C_{M2}($\times 10^{-2}$ M)	5·00	4·73	4·45	4·20	4·02	3·82	3·60	3·41	3·34
A_{D1}	0	137·08	307·67	448·46	554·40	675 59	812·62	953·76	—
W_{D1}(μg)	0	0·0258	0·0933	0·1325	0·1620	0·1963	0·2339	0·2732	—
C_{D1}($\times 10^{-2}$ M)	0	0·28	0·57	0·81	0·99	1·20	1·43	1·67	—

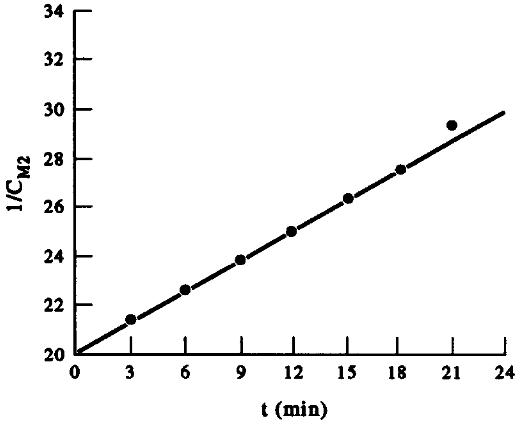
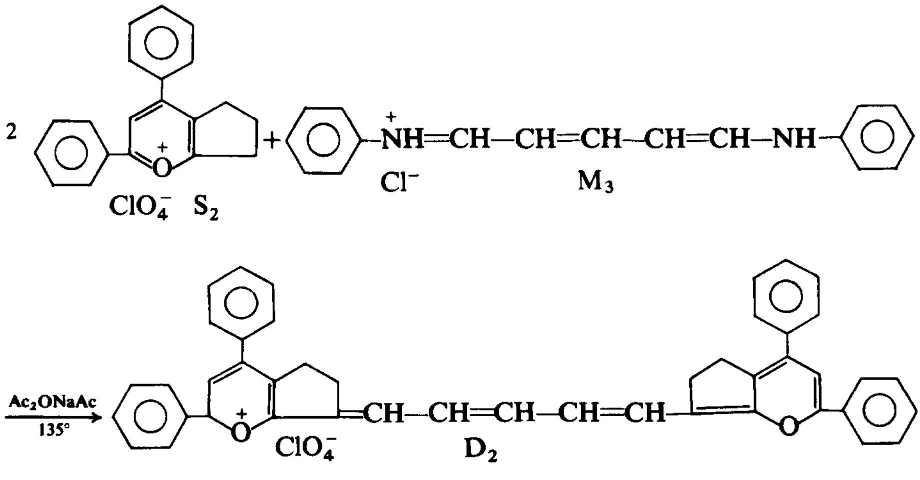


Fig. 6. A plot of $1/C_{M2}$ against time *t*.

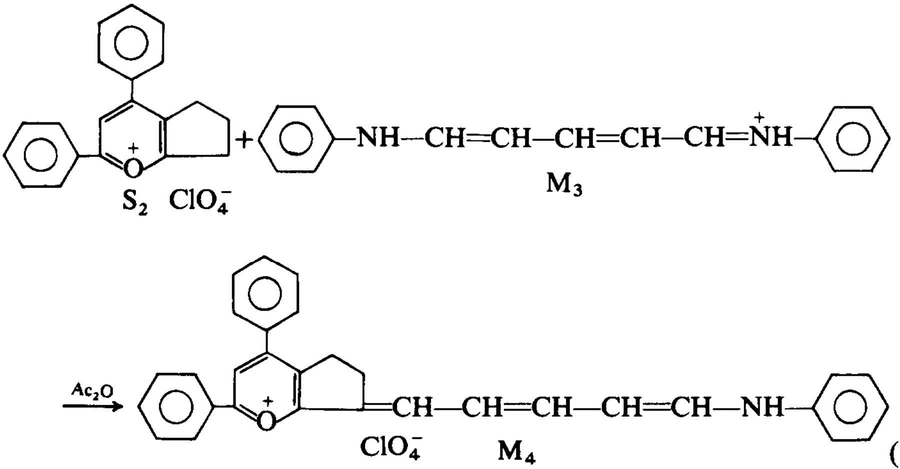
ence of sodium acetate; two linear plots were obtained, giving, from their slopes, k'_5, the rate constant of reaction (5) at 75°C in the presence of sodium acetate, as 4·33 M^{-1} min^{-1}, and k'_6, the rate constant of reaction (6) at 85°C in the presence of sodium acetate, as 1·99 M^{-1} min^{-1}.

2.3 Kinetic study of the formation of the pyrylium heptamethine dye D_2

The pyrylium heptamethine dye D_2 is prepared according to the following equation.[3]



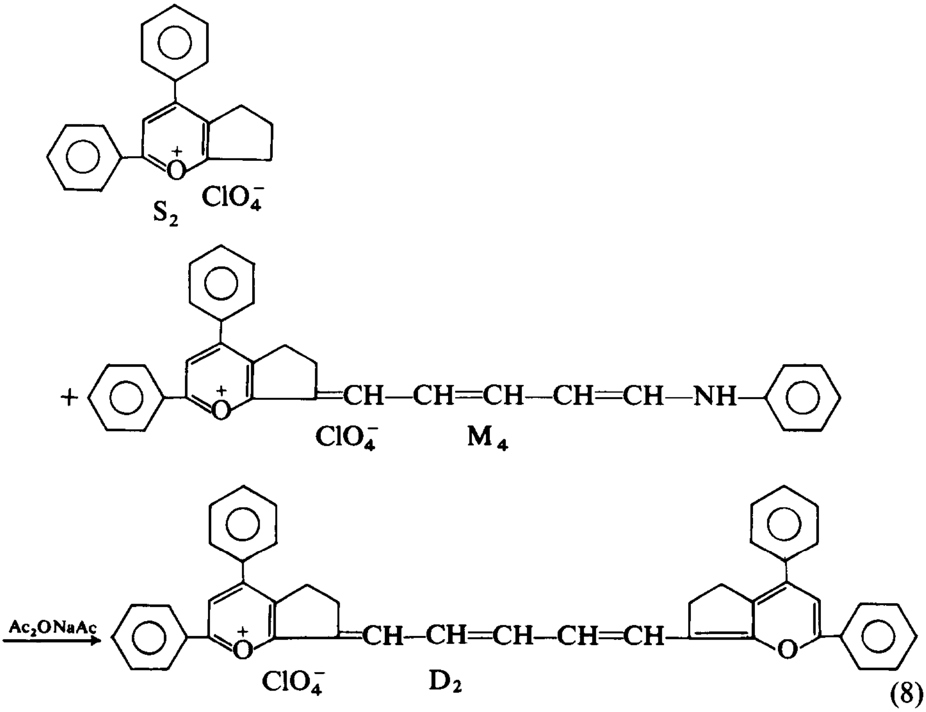
This reaction may also be assumed to be a consecutive reaction comprising two bimolecular reactions, (7) and (8):



(7)

Samples of S_2, M_3, M_4 and D_2 were prepared and purified. For M_4 m.p. 202–203°C (calculated: C 69·53%, H 4·98%, N 2·46%; found: C 69·34%, H 5·46%, N 2·08%). Standard curves of S_2, M_3, M_4 and D_2 were obtained in the usual way.

Solutions of 0·1865 g (0·0005 M) of S_2 in 5 ml acetic anhydride and of 0·1423 g (0·0005 M) of M_3 in 5 ml acetic anhydride were heated to 125°C



(8)

TABLE 4

Change of Peak Areas, Concentrations of M_4 During the Reaction

Time (min)	*0*	*2*	*4*	*6*	*8*	*10*	*12*	*14*
A_{M4}	0	2099·90	3111·02	3632·97	4133·08	4502·73	4687·55	4892·40
W_{M4}(μg)	0	0·203	0·296	0·344	0·390	0·424	0·441	0·450
C_{M4}($\times 10^{-2}$ M)	0	1·78	2·60	3·02	3·42	3·72	3·87	3·95

and M_3 then added to S_2, maintaining a temperature of 125°C. Samples (0·01 ml) were taken every 2 min and added to cold acetic anhydride to stop the reaction. Following the usual procedure as described above, the data in Table 4 were obtained.

Since $C_{M3} = C_{M30} - C_{M4}$, the change of C_{M4} during the reaction can be obtained, and on plotting $1/C_{M_3}$ against time t in minutes at 125°C, a straight line resulted ($1/C_{M3} - 19{\cdot}88 = 5{\cdot}50t$; $r = 0{\cdot}993$).

The rate constant of reaction (7) at 125°C is thus 5·50 M^{-1} min^{-1}. The reaction (8) between S_2 and M_4 in the presence of sodium acetate was carried out at 120°C (see also Table 5).

Plotting $1/C_{M4}$ against time t in minutes at 120°C gave a straight line, from the slope of which the rate constant k_5' of reaction (8) in the presence of sodium acetate at 120°C was found to be 14·97 M^{-1} min^{-1}.

2.4 Kinetic study of the formation of the thiopyrylium heptamethine dye D_3

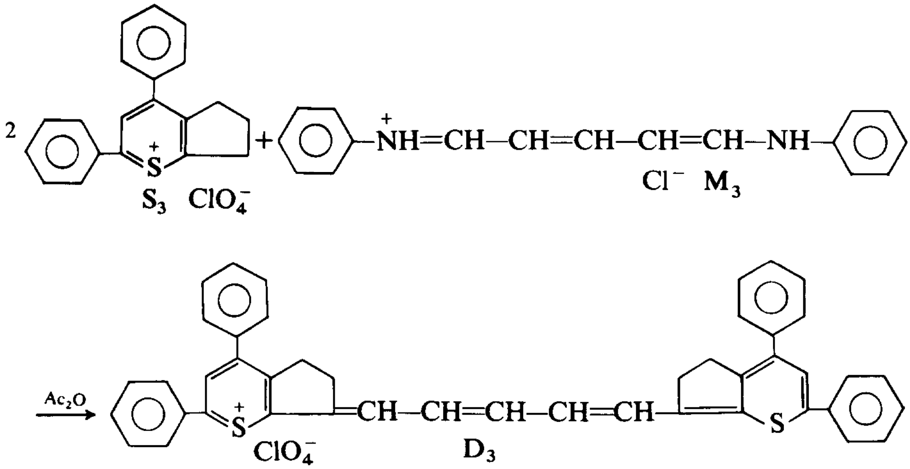
The thiopyrylium heptamethine dye D_3 is prepared using the following reaction[3]. This reaction may also be assumed to involve the two bimolecular reactions (9) and (10).

Reactant M_5 was prepared by reaction of equimolar amounts of S_3 and M_3 in acetic anhydride at 125°C. After 10 min the reaction solution

TABLE 5

Change of Peak Areas of M_2 in Reaction (8)

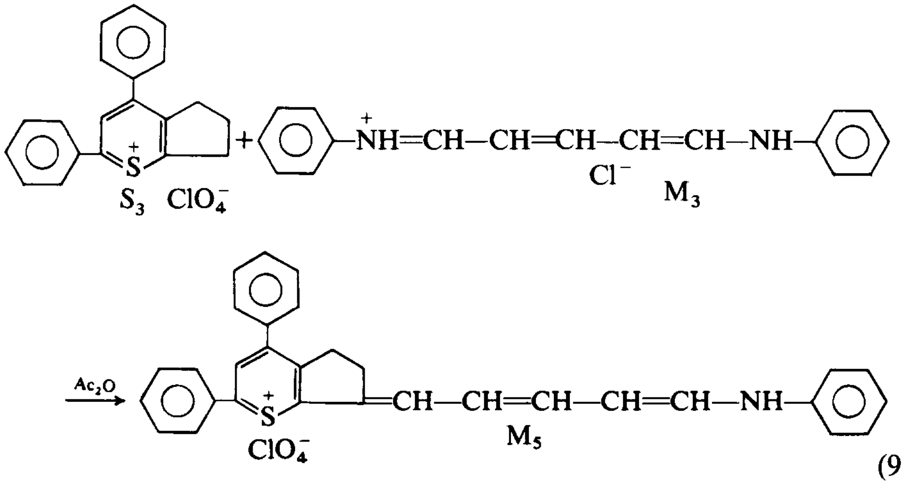
Time (min)	*0*	*0·5*	*1*	*1·5*	*2*	*2·5*	*3*	*3·5*	*4·0*
A_{M4}	6209·63	4426·56	3469·98	2839·22	2436·94	2002·05	1741·11	1588·90	1404·08
W_{M4}(μg)	0·581	0·470	0·329	0·271	0·234	0·194	0·170	0·156	0·139
C_{M4}($\times 10^{-4}$ M)	5·10	3·66	2·89	2·38	2·05	1·70	1·49	1·37	1·22



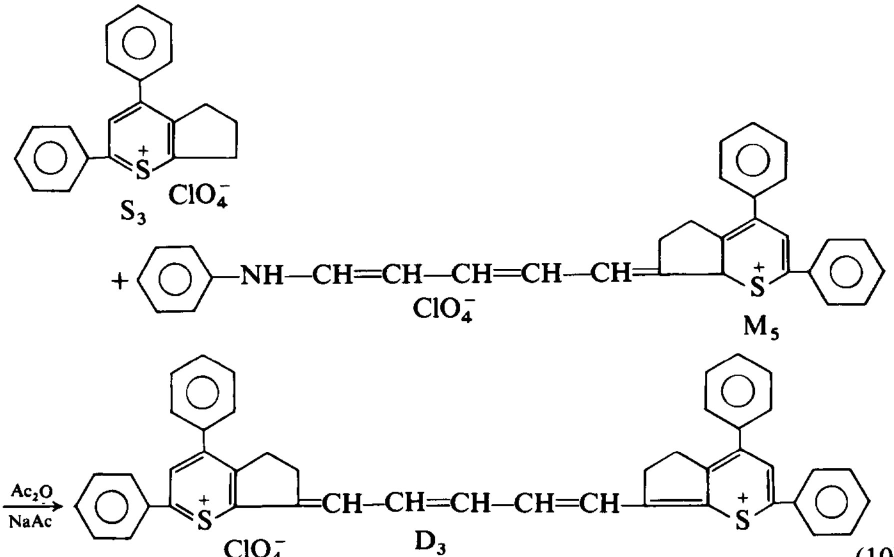
was cooled, and filtered and the resultant M_5 recrystallized from acetic anhydride, m.p. 213–215°C (analysis: C, found 67·65%, calc. 67·60%; H, found 4·78%, calc. 4·33%; N, found 2·39%, calc. 2·09%).

A sample (0·1945 g) (0·0005 M) of S_3 in 5 ml acetic anhydride and 0·1423 g (0·0005 M) M_3 in 5 ml acetic anhydride were both heated to 125°C, and the M_3 solution added to S_3. Samples (0·01 ml) were taken every 2 min and added to cold acetic anhydride (5 ml) to stop the reaction. After applying (0·01 ml) onto TLC plates, drying and developing, a chromatogram of three spots (S_3, M_3 and M_5) was obtained; the peak areas were measured by double-scanning (Table 6).

On plotting $1/C_{M3}$ against time t, a straight line was obtained ($1/C_{M3} - 19{\cdot}77 = 6{\cdot}17t$; $r = 0{\cdot}993$).



(9)



(10)

The k'_{M3} for reaction (9) at 125°C was found to be 6·17 M^{-1} min^{-1}.

The kinetic study of the reaction in the presence of sodium acetate was carried out similarly (Table 7) and a straight line obtained on plotting $1/C_{M5}$ against time t ($1/C_{M5} - 19{\cdot}65 = 17{\cdot}55t$, $r = 0{\cdot}987$); the rate constant k_{M5} of reaction (7) at 125°C with catalyst was thus 17·55 M^{-1} min^{-1}.

TABLE 6
Changes of Peak Areas of M_5 in Reaction (9)

Time (min)	*0*	*2*	*4*	*6*	*8*	*10*	*12*	*14*
A_{M5}	0	2117·85	2979·51	3473·17	3805·26	4020·68	4254·04	4370·73
$W_{M5}(\mu g)$	0	0·226	0·322	0·377	0·414	0·438	0·464	0·477
$C_{M5}(\times 10^{-2}\ \mathrm{M})$	0	1·93	2·75	3·22	3·53	3·74	3·96	4·07

TABLE 7
Changes of Peak Areas of M_5 in Reaction (10)

Time (min)	*0*	*0·5*	*1·0*	*1·5*	*2 0*	*2·5*	*3·0*	*3·5*	*4·0*
A_{M5}	5384·97	3760·39	2925·66	2378·15	1983·22	1758 83	1 534 44	1 359·93	1 247·22
$W_{M5}(\mu g)$	0·590	0·409	0·316	0·255	0·211	0·186	0·161	0·141	0·129
$C_{M5}(\times 10^{-2}\ \mathrm{M})$	5·03	3·49	2 70	2·18	1·80	1·59	1·37	1·20	1 10

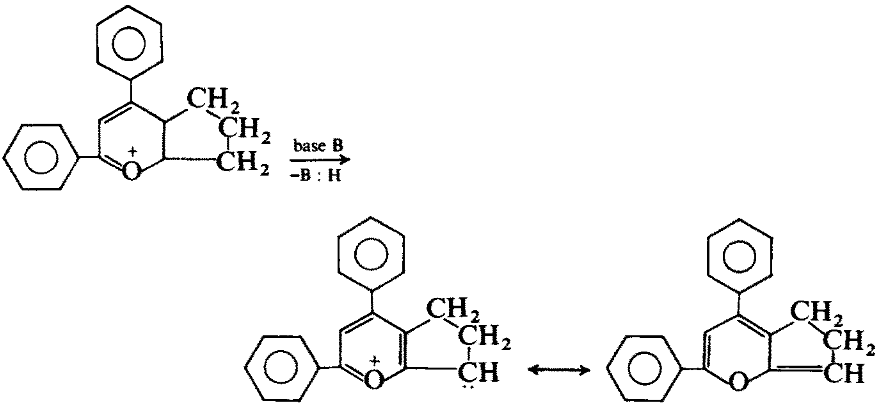
TABLE 8
Rate Constants of the Consecutive Reactions

Reaction type	*Reaction temp. (°C)*	*Catalyst*	*k (M^{-1} min^{-1})*	*Reaction time (min)*
$S_1 + M_1 \rightarrow M_2$	125	No	2·88	12
$S_1 + M_2 \rightarrow D_1$	135	No	0·42	24
$S_1 + M_1 \rightarrow M_2$	75	Yes	4·33	7
$S_1 + M_2 \rightarrow D_1$	85	Yes	1·99	8
$S_2 + M_3 \rightarrow M_4$	125	No	5·50	14
$S_2 + M_4 \rightarrow D_2$	120	Yes	14·97	4·0
$S_3 + M_3 \rightarrow M_5$	125	No	6·17	14
$S_3 + M_5 \rightarrow D_3$	120	Yes	17·55	4·0

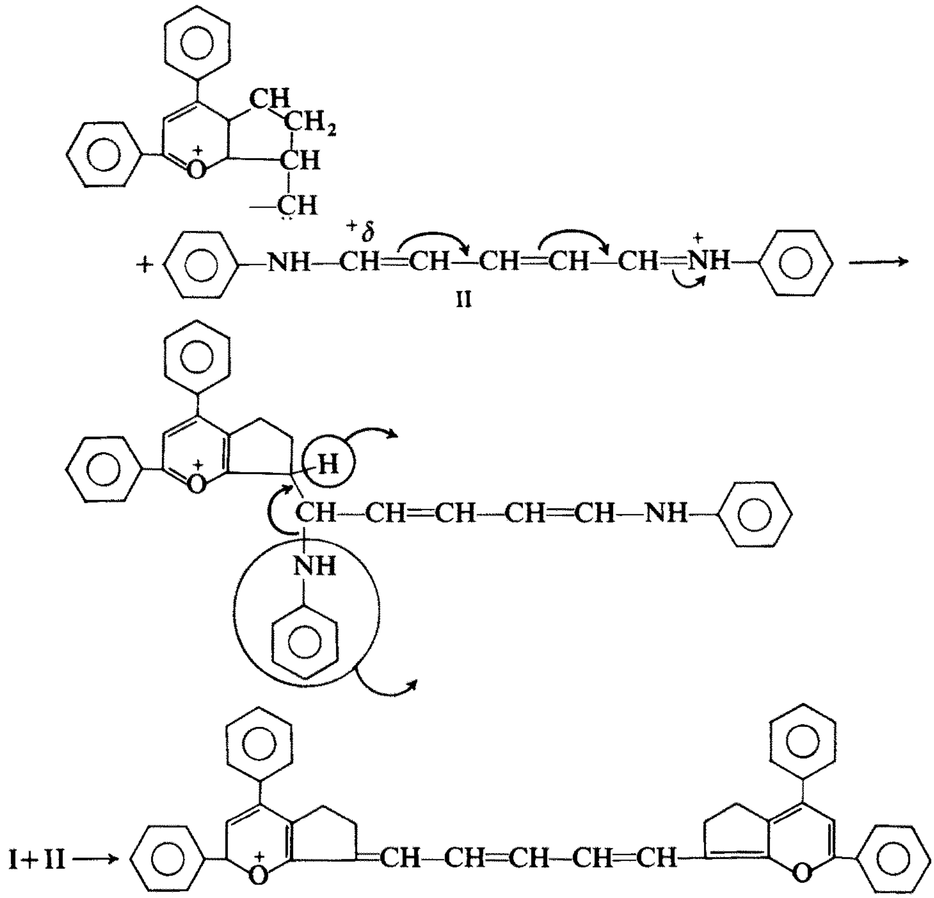
3 RESULTS AND DISCUSSION

The rate constants of the reactions are summarized in Table 8. From Table 8, the formation of heptamethine pyrylium and thiopyrylium cyanine dyes, is shown to proceed through two steps, i.e. the initial formation of a hemicyanine dye, and then the formation of a heptamethine pyrylium or thiopyrylium cyanine dye. The rate of formation of the hemicyanine intermediate is greater than that of the pyrylium or thiopyrylium dyes. There is therefore an accumulation of the intermediate in the course of the reaction, and this is the reason why unsymmetrical pyrylium or thiopyrylium cyanine dyes may be prepared.

The function of sodium acetate in the reaction is to accelerate the formation of both the hemicyanine dye and the final dye; its effect is even greater in the formation of the final dye. It is therefore reasonable to assume the mechanism of the reaction is as follows:



Methylene base (I)



When the rates of formation of pyrylium and thiopyrylium dyes are compared, it is evident that k_9 is greater than k_7 and that k_{10} is greater than k_8. This is due to the different basicities of S_2 and S_3, the basicity of S_3 being higher than that of S_2.

4 CONCLUSIONS

The formation of some pyrylium or thiopyrylium dyes has been kinetically studied by a TLC double-scanning method. The reaction consists of consecutive parts, with initial formation of an intermediate, hemicyanine dye. The standard curves of reactants, intermediates and product were determined. Changes of concentrations of reactants, intermediates and products could then be indirectly determined, and the rates of reaction thus measured. The mechanism of the reaction can therefore be established on the basis of this kinetic study.

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