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STUDY OF THE THERMAL DECOMPOSITION OF SOME NEW CYANINE DISPERSED DYES

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Abstract

The structure of the studied compounds was confirmed by elemental analysis, IR and NMR. TG and DTG data were used to study the kinetics of the thermal decomposition process of some new cyanine dispersed dyes derived from 2-[(*p*-chloro)-styryl]-6-[5-(3-aryl-rhodanine)]-1,2-dihydropyridine. The reaction was found to follow first order mechanism. The activation energy E_a was calculated and used to calculate the thermodynamic parameters enthalpy change (ΔH^*), entropy change (ΔS^*), and free energy change (ΔG^*), related to the thermal decomposition process. Two different calculation methods including Coats–Redfern and Chatterjee were applied to evaluate the kinetic and thermodynamic parameters. Quantum study was performed to support both the structure and the thermal data.

Keywords: cyanine dispersed dyes, thermal analysis, thermodynamics

Introduction

Cyanine dispersed dyes which contain a styryl group constitute an interesting class of dye stuff in the textile industry, since they could be used as starting materials for the preparation of rhodanine dyes, which are used on a large scale for dyeing polyester, polyacrylic and cotton fibers [1].

The importance of these dyes arises from their following properties [2, 3]:

- They proved to give a wide range of colour shades with a reasonably good levelness and depth.
- Their (*K*/*S*) values are high at short wavelength but low at long wavelength.
- They are readily fixed on the fibers.

In spite of the large number of studies reported on the thermal analysis of coordination compounds, and the calculation of the kinetic and thermodynamic parameters of the thermal decomposition process [4–8], yet there are relatively few reports on the thermal analysis of organic compounds.

The aim of the present work was to study the thermochemical behaviour of some cyanine dispersed dyes as well as to calculate some kinetic and thermodynamic parameters related to the thermal decomposition process from their TG and DTA curves.

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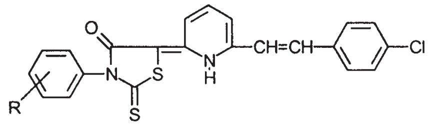
Experimental

Cyanine dyes were synthesised as described before [3]; by the addition of 2-(*p*-chloro)-styryl-pyridine on 3-aryl-rhodanine in presence of acetic anhydride and refluxed for 1–2 h at 90°C. After cooling, the precipitated crystals were filtered and recrystallized from ethanol. The structure of the obtained compounds was confirmed by elemental analysis, IR and NMR.

The thermal studies were carried out by using DTA-50, TG-50, Shimadzu thermogravimetric analyser (Japan), with the rate of heating 10°C min^{-1} using Pt crucible of the instrument fitted with Pt–Pt,Rh (10%) thermocouple. The mass of the sample varied from 0.63–2.29 mg.

Results and discussion

The structure of the compounds under investigation can be generally represented by:



R= H(I), *o*-CH_3(II), *o*-OCH_3(III), *p*-OCH_3(IV), *p*-OH(V)

Table 1 includes the results of the elemental analysis and some physical properties of 2-[(*p*-chloro)-styryl]-6-[5-(3-aryl-rhodanine)]-1,2-dihydropyridine and its derivatives.

Table 1 Characterization data of 2-[(*p*-chloro)styryl)]-6-[5-(3-aryl rhodanine)]-1,2-dihydropyridines and its derivatives

Compd. No.	*R*	*M.p.*/ °C	Colour of crystals	Molecular formula	Analysis; calcd. (found)/%			
					C	H	N	S
I	H	225	reddish brown	$C_{22}H_{15}N_2S_2OCl$	62.5 (62.1)	3.6 (3.5)	6.6 (6.5)	15.2 (15.1)
II	*o*-CH_3	>300	brown	$C_{23}H_{17}N_2S_2OCl$	63.2 (63.0)	3.9 (3.8)	6.4 (6.5)	14.5 (14.6)
III	*o*-OCH_3	>300	brown	$C_{23}H_{17}N_2S_2O_2Cl$	61.5 (60.8)	3.8 (3.6)	6.2 (6.1)	14.2 (14.3)
IV	*p*-OCH_3	>300	reddish brown	$C_{23}H_{17}N_2S_2O_2Cl$	61.0 (60.6)	3.8 (3.7)	6.2 (6.3)	14.2 (14.1)
V	*p*-OH	>300	reddish brown	$C_{22}H_{15}N_2S_2O_2Cl$	60.2 (60.0)	3.4 (3.4)	6.4 (6.4)	14.6 (14.5)

IR and NMR studies

The infrared measurements of the compounds under investigation showed stretching frequencies at (1300–1100 cm^{-1}) characteristic of the thione group, 1600 cm^{-1} (C=N), and 1555 cm^{-1} (C=C), grouping of the styryl moiety. NH absorption was recorded at 3250 cm^{-1} besides 1,4-disubstituted benzene ring at 815 cm^{-1}.

The NMR spectra of the compounds showed mainly two characteristic doublets at δ 5.32 and 5–6 attributable to the CH=CH protons besides the other normal protons as expected.

Thermal study

The thermal decomposition of 2-[(*p*-chloro)-styryl]-6-[5-(3-aryl-rhodanine)]-1,2-dihydropyridine and its derivatives is represented in Fig. 1. It appears that during heating of the compounds the corresponding TG and DTA curves undergo a series of

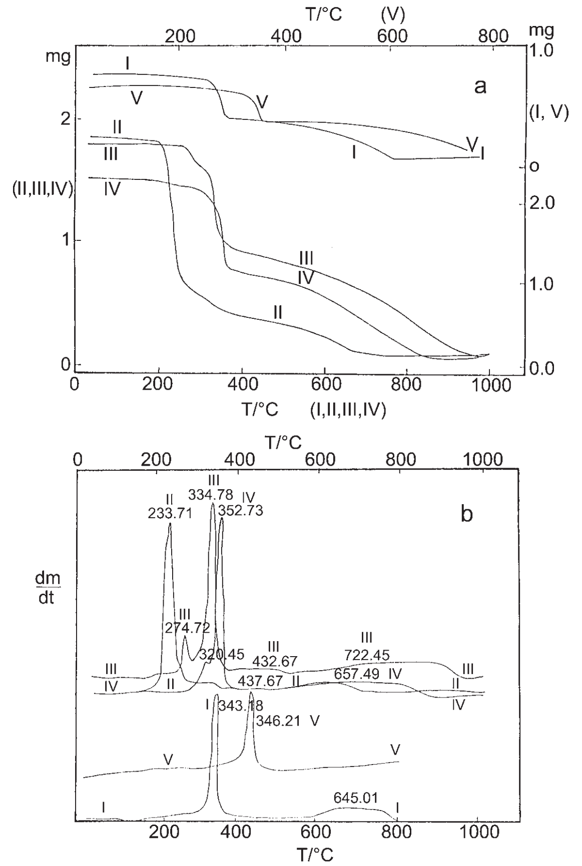


Fig. 1 TG (a) and DTG (b) curves of the thermal decomposition of the cyanine dispersed dyes

Table 2 Analysis of TG curves of thermal decomposition of 2-[(*p*-chloro)styryl]-6-(5(3-aryl rhodanine) 1,2-dihydropyridine and its derivatives

Compd. No.	Stage (1)			Stage (2)			Stage (3)		
	Range/°C	Mid point/ °C	Mass loss/ %	Range/°C	Mid point/ °C	Mass loss/ %	Range/°C	Mid point/ °C	Mass loss/ %
I	304.1–379.6	343.2	45.68	381.7–781.8	645.0	45.06	–	–	–
II	188.8–276.2	233.7	65.80	276.2–294.6	432.7	28.30	–	–	–
III	259.3–294.9	274.7	7.30	293.9–375.5	334.7	38.77	379.7–949.1	722.5	46.58
IV	281.8–334.9	320.5	9.46	333.4–390.5	352.7	37.11	393.9–867.5	657.2	45.20
V	298.8–385.4	346.2	40.98	–	–	–	–	–	–

Table 3 The kinetic parameters of the compounds under investigation by two different methods; Coats-Redfern and Chatterjee

No.	Stage (1)					Stage (2)					Stage (3)				
	$k\cdot10^2$	$t_{1/2}$	n	E_a/kJ mol^{-1}		$k\cdot10^2$	$t_{1/2}$	n	E_a/kJ mol^{-1}		$k\cdot10^2$	$t_{1/2}$	n	E_a/kJ mol^{-1}	
				Coats	Chatterjee				Coats	Chatterjee				Coats	Chatterjee
I	27.33	2.52	1.0	89.10	87.57	–	–	1.0	24.02	22.15	–	–	–	–	–
II	21.85	3.16	1.0	51.93	49.03	2.93	23.55	1.0	15.37	14.89	–	–	–	–	–
III	57.35	1.20	1.0	148.82	147.19	27.11	2.55	1.0	86.12	84.63	2.63	26.23	1.0	18.50	17.33
IV	34.81	1.98	1.0	112.7	110.48	37.43	1.84	1.0	129.0	127.16	2.20	31.36	1.0	21.35	19.58
V	24.73	2.79	1.0	79.20	77.02	–	–	–	–	–	–	–	–	–	–

thermal changes associated with the mass loss. The TG curves show two or three thermal decomposition stages starting at 188.8 and ending at 949.1°C. The analysis of the TG curves of the compounds under investigation is given in Table 2.

Determination of the kinetic parameters

Two calculation methods were used:

1. Coats–Redfern [9] proposed a method for the determination of the order of the reaction on the basis of thermogravimetric data, based on a plot of $-\log\{[1-(1-\alpha)^{1-n}]/[T^3(1-n)]\}$, in this case $n\neq1$, if $n=1$ the equation will be modified to $[-\log(-\log(1-\alpha)/T^2$ *vs.* $(1/T)\cdot10^3$, where α is the degree of the thermal decomposition of the sample calculated from TG curves. A number of such relationships are plotted for a number of assumed values of n. The correct value of n for a given thermal decomposition reaction gives a straight line. The activation energy of the decomposition process E_a, kJ mol^{-1} is calculated from the equation

$$E_a=2.303\ RS$$

where R and S are gas constants and the slope of the obtained straight line, Table 3.

2. Chatterjee's method [10]. This method is based on the general equation for rate of the heterogeneous kinetics (V),

$$V=-\frac{\mathrm{d}m}{\mathrm{d}t}=km^{\mathrm{n}}$$

where k, m and t are the rate constants of the reaction, the active mass of the reacting material (mg) and the time (min) elapsed from the start of the experiment. Substituting $\sim k$ from the Arrhenius equation into the last one gives,

$$\log V=\log A-n\log m-\frac{E_a}{2.303RT}$$

This equation gives the relationship of the reaction rate and the temperature. The activation energy E_a may be determined from the slope of the straight line (S); plot of $\log V$ *vs.* $1/T$, where $E_a=2.303\ RS$ (Fig. 2).

The evaluated values of the specific rate constant and the activation energy are given in Table 3 and Fig. 3. It is clear that the order of the decomposition reaction for all cases is unity, this indicate that the decomposition reactions follow the same mechanism [7]. It is also obvious that the values of the activation energy given by both calculation methods are in good agreement with each other (Table 3).

Calculation of the thermodynamic parameters

By using the values of the specific rate constant of the thermal decomposition process in each stage according to the rate theory [11] and Arrhenius equation [12], as well as the normal thermodynamic equations given before [7]. The thermodynamic parameters ΔS^*, ΔH^* and ΔG^* were evaluated and listed in Table 4.

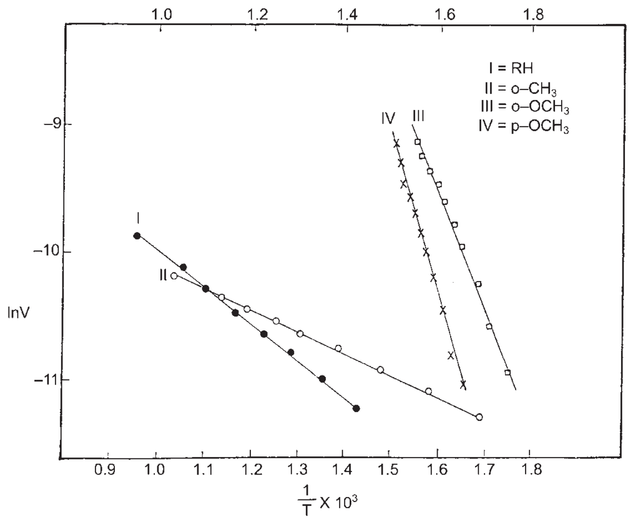


Fig. 2 Graphical determination of activation energies of the 2^{nd} step of the thermal decomposition process of the dye stuff by Chatterjee's method

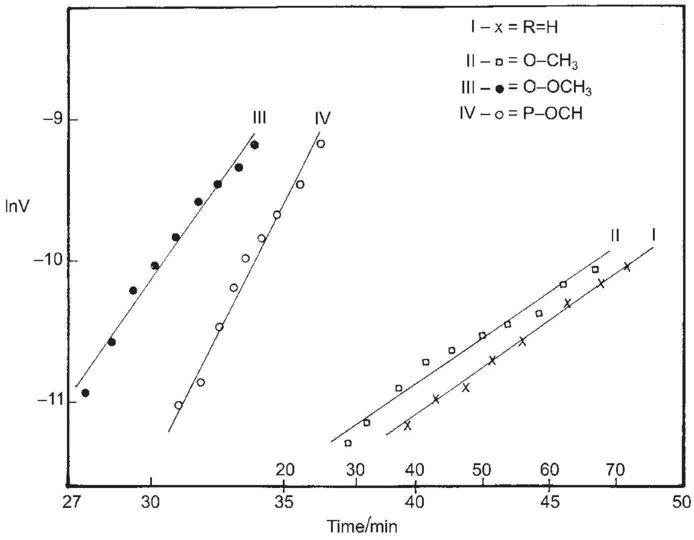


Fig. 3 Graphical determination of specific rate constant of the 2^{nd} step of the thermal decomposition process related to the dispersed dye stuff

Again the plot of log(dm/dt), rate of the decomposition process *vs*. time t gives a straight line for all cases. Figure 3 shows the variation of logarithmic value of rate of reaction with time of the second step as an example of the thermal decomposition steps. This linear relationship confirms that the reaction follows a first order. The slope of the straight line gives the specific rate constant (k) (Table 2) and $t_{1/2}$ can be calculated from the equation:

$$t_{1/2}=\frac{0.693}{k}$$

From Table 4 it is clear that the values of ΔH^* and ΔS^* for all cases are positive, this means that the decomposition process is an endothermic one and is accompanied by the increases of the disorder of the system since the number of the decomposed fragments increases. On the other hand, the negative values of ΔG^* in all cases indicates that the decomposition process is a spontaneous reaction. The observed difference in the values of E_a and ΔH^* of the thermal decomposition process of the studied compounds is strongly related to the nature of the substituted (R) group and its position in the aryl ring.

Table 4 Values of the thermodynamic parameters of the thermal decomposition of the studied compounds

R	1st Step	2nd Step	3rd Step	Total
		ΔS^*/J mol^{-1} K^{-1}		
H	142.12	24.15	–	166.27
o-CH_3	96.76	21.15	–	177.91
o-OCH_3	268.73	139.25	17.41	425.39
p-OCH_3	186.17	203.22	21.05	410.22
p-OH	124.31	–	–	124.31
		ΔH^*/J mol^{-1}		
H	82.45	14.52	–	96.97
o-CH_3	44.82	9.02	–	53.84
o-OCH_3	142.62	79.58	9.05	231.25
p-OCH_3	105.55	121.96	11.85	239.36
p-OH	71.87	–	–	71.87
		ΔG^*/J mol^{-1}		
H	–5.12	–7.62	–	–12.77
o-CH_3	–4.21	–5.91	–	–10.12
o-OCH_3	–4.57	–5.05	–8.28	–17.90
p-OCH_3	–4.93	–5.20	–7.73	–17.86
p-OH	–5.10	–	–	–5.10

This effect may be due to both the inductive (I) and mesomeric (M) (resonance) effects of the substituent group (R) in the molecule of dye. In the case of methyl which has a relatively high $+I$ effect due to the donating nature of the methyl group this effect leads to a relative increase of the electron density in the rhodanine dye molecules. The latter effect may be supported by the effect of this group in dyeing process. Rhodanine moiety usually offered a deepening in colour with a good affinity to polyester fibers. For *p*-OCH_3, *o*-OCH_3 and *p*-OH substituents on the dye molecule, the mesomeric effect will has major effect in comparison with the inductive ($-I$) effect. The summation of the overall ($+M$) and ($+I$) effects may be arranged in the following decreasing order *p*-OCH_3≥*o*-OCH_3>*p*-OH>*o*-CH_3. Because of this trend of substituent groups, the electron density will increase and consequently the vibrational energy and wavenumber of the bonds between different atoms in the dye molecule will also increase. This observation is in good agreement with the (K/S) values of these dye stuff given in literature [2].

A study of the quantum mechanics of the compounds

To support the experimental data given in the present work together with a correlation with the obtained thermal data, simple quantum-mechanical calculations were performed by using omega-self constituent field molecular orbital theory, FMOT [13, 15]. The thermal stability of the cyanine dispersed dyes under investigation may be affected by their quantum chemical properties such as bond order (*BO*), π-delocalization energy (*DE*) and energy of formation of the molecular orbital including high occupied molecular orbital (*HOMO*) and low unoccupied molecular orbital *(LUMO*). The values of these parameters were evaluated and are listed in Table 5.

Table 5 Quantum mechanical values of the compounds

Compound	*BO*	*DE*, β	*HOMO*	*LUMO*
I	2.0126	9.7702	–0.0945250	–0.339393
II	2.4088	9.7694	–0.0945830	–0.339460
III	2.4129	11.9732	–0.0948065	–0.3396347
IV	2.4135	11.9735	–0.0948091	–0.3396663
V	2.4126	12.0645	–0.0947955	–0.3396561

Increase in the bond order leads to an increase in the strength of the bonds and consequently increases the stability of the compounds. Values of *BO* of the studied dyes increase in this order of substituents and/or compounds respectively: (IV)>(III)>(V)>(II)>(I).

This arrangement is in good agreement with that given for the increase of the activation energy of these compounds except in the case of compounds (II) and (I). This observation may be explained as due to the decrease in the delocalization energy of the methyl compound which means the decrease in the resonance energy and consequently to the decrease in the stability of the *o*-CH_3 substituted compound with respect to the unsubstituted compound (*R*=H). The increase in the values of the *HOMO* of the compounds is in good agreement with the order given for the activation energy.

Conclusions

The large industrial use of cyanine dispersed dyes as starting materials for the preparation of rhodanine dyes which are used successfully on a large scale for dyeing of polyester, polyacrylic and cotton fibers let us study in details the thermal stability and thermodynamic parameters of such dyes. The values of ΔH^* and ΔS^* for all cases are positive, which means that the decomposition processes of such dyes are endothermic ones and are accompanied by the increase of the disorder of the system. The observed difference in the values of E_a and ΔH^* of the thermal decomposition process of the investigated dyes is strongly related to the nature of the substituted group, its position and the electron density on the aryl ring. Increasing the electron density on the rhodanine moiety increases the colour density, stability and good levelness and depth of colour shades.

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