

THERMAL STABILITY OF SOME TEXTILE DYES

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Abstract

The effect of thermal treatment at 25–800°C on the structure of some textile dyes (rhodanine's derivatives) has been investigated. The general formula of these dyes are; [(R)-C₆H₄-C₃NS₂O-C₅H₄N-CH=CH-C₆H₄N(CH₃)₂]; 2-[*p*-dimethylamino-styryl]-6-[5-(3-aryl)-rhodanine]-1,2-dihydropyridine and its derivatives, *R*=H (I), *o*-OCH₃ (II), *p*-OCH₃ (III) and *p*-OH (IV). The techniques employed were TG, IR, UV, NMR and elemental analysis. The results showed that the thermal stability of these dyes depends on the nature of the substituent (*R*) alkyl radical present and its position in the benzene ring.

On the basis of the application of a non-isothermal kinetic equation, it was found to be a first order reaction. Some kinetic and thermodynamic parameters for the thermal decomposition process in each stage have been evaluated by the application of two different calculation methods.

To support the above results a simple quantum study was reported.

Keywords: kinetic parameters, rhodanine dyes, thermal stability

Introduction

In the last two decades a great interest could be observed in the cyanine dyes, the interest arises not only from their applications as textile dyes but also from their unrivalled ability to impart high sensitivity to silver halide in a region of the spectrum to which it's not ordinarily sensitive [1].

Cyanine dyes could be used as a starting material for the preparation of rhodanine dyes which are used in a large scale for dyeing polyester, polyacrylic and cotton.

The importance of these dyes comes from their following properties [2–3].

1. They proved to give wide range of color shades with a reasonably good levels and depth of shade.
2. Their (*K/S*) values are high at short wavelength.
3. They are fixed readily on the synthetic fibers.

Thermogravimetric analysis (TG) is widely used as a method to investigate the thermal decomposition of the compounds, to determine the mechanism of the thermal decomposition process and to calculate the related kinetic and thermodynamic parameters; (*n*, *E_a*, ΔH , ΔS and ΔG) which are, the order, activation energy the

enthalpy-, entropy- and the free energy change of the thermal decomposition process, respectively.

There is a large number of studies that described the thermal decomposition process and the calculation of the kinetic parameters of complexes and inorganic compounds [4–7], but there are few studies that described the thermal decomposition of organic compounds and their derivatives [8–9].

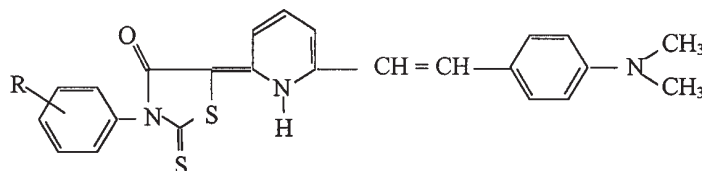
The aim of the present work was to investigate the effect of temperature on the decomposition of some rhodanine dyes, to calculate some kinetic and thermodynamic parameters related to the thermal decomposition process and to discuss the effect of substituent (*R*) in the aryl ring on the values of the evaluated parameters.

Experimental

Rhodanine dyes were synthesized as described by Fadda [3], by the addition of 2-[*p*-(dimethylamino)-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, UV and NMR.

The thermal studies were carried out 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 0.409–3.696 mg.



where *R*=H for compound I; *R*=*o*-OCH₃ for compound II; *R*=*p*-OCH₃ for compound III and *R*=*p*-OH for compound IV

Results and discussion

The structure of the investigated compounds may be represented as follows:

Table 1 shows the characterization data of 2-[*p*-dimethylamino-styryl]-6-[5-(3-aryl)-rhodanine]-1,2-dihydropyridine and its derivatives.

The stoichiometries of the isolated rhodanine dyes, together with some analytical and physical data are given in Table 1, which includes the percentage of the elements as calculated on the basis of the suggested formula. Comparison of both calculated and found percentages of the elements determined indicates that the composition of the prepared compounds coincide with the suggested formula.

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

Comp.	<i>R</i>	Yield/%	<i>m.p.</i> /°C	Color of crystals	Molecular formula	Analysis; calc. (found)	
						C	H
I	H	70	>300	brown	C ₂₄ H ₂₁ N ₃ S ₂ O	66.8 (66.6)	4.9 (4.8)
II	<i>o</i> -OCH ₃	60	300	yellow	C ₂₅ H ₂₃ N ₃ S ₂ O ₂	65.0 (64.8)	5.0 (4.8)
III	<i>p</i> -OCH ₃	76	>300	brown	C ₂₅ H ₂₃ N ₃ S ₂ O ₂	65.0 (64.7)	5.0 (5.0)
IV	<i>p</i> -OH	67	>300	reddish brown	C ₂₄ H ₂₁ N ₃ S ₂ O ₂	64.4 (64.1)	4.7 (4.5)

The infrared measurements of the investigated compounds showed stretching frequencies at about (1300–1100 cm⁻¹) characteristic of the thione group, 1600 cm⁻¹ for (C=N), 1555 cm⁻¹ for ν(C=C), grouping of styryl moiety and ν(NH) absorption was recorded at 3250 cm⁻¹ [10].

The NMR spectra of the above rhodanine dyes showed mainly two characteristic doublets at δ 5.32 and 5–6 attributed to the (CH=CH) protons besides the other normal protons as normally expected.

Thermal decomposition of textile dye compounds

The thermochemical behavior of the isolated rhodanine dyes was investigated by means of thermogravimetry. The TG curves of the thermal decomposition of the compounds showed two to four decomposition steps. It appears that during heating of these compounds the corresponding TG curves exhibited a series of thermal changes associated with mass loss. The analysis of the TG curves of the thermal decomposition of the isolated rhodanine dyes are given in Table 2. It is clear that the quantitative treatment of the mass loss in each decomposition step is in a good agreement with the proposed products produced in each step (Table 2).

Determination of the kinetic parameters

Two calculation methods were used:

1. Coats–Redfern [11] proposed a method for the determination of the order of the decomposition reaction on the basis of the thermogravimetric data, based on a plot of $A = \log \{ [1 - (1 - \alpha)^{1-n}] / [T^3(1-n)] \}$, $n \neq 1$ if $n = 1$, $A = -\log \{ [1 - (1 - \alpha)] / T^2 \}$ vs. $1/T \cdot 10^3$, where α and n are the degree of thermal decomposition of the sample calculated from TG curves and the order of the reaction, respectively. 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. Figure 1 shows the plots of the above relationship. The activation energy, E_a of the decomposition pro-

Table 2 Analysis of the TG curves of the thermal decomposition process of some rhodanine dyes

Comp.	Step	Range/°C	Mid. point/°C	Mass loss/mg	Mass loss/%		Probable composition of expelled group	At higher temperature
					found	calc.		
I	1	104.2–291.9	228.5	1.904	51.53	52.38	N(CH ₃) ₂ +CS+aryl+CO	1/2SO ₂ (≈7.2%)
	2	295.1–396.0	342.6	0.702	19.14	19.54	pyr.	
	3	518.4–585.9	545.0	0.111	3.30	3.24	1/2CO	
	4	576.4–928.6	720.5	0.725	19.64	18.08	aryl	
II	1	271.6–390.5	346.0	0.409	50.33	50.72	N(CH ₃) ₂ +CS ₂ +aryl+CO	1/2NO (≈3.2%)
	2	556.7–768.5	639.9	0.250	30.57	30.94	pyr.+2CO	
III	1	97.4–176.6	143.0	0.061	15.74	16.15	N(CH ₃)+CO	1/2NO ₂ (≈5.0%)
	2	311.2–394.3	356.1	0.173	42.83	43.02	2aryl+1/2CS ₂	
IV	3	394.3–687.4	572.2	0.143	35.39	36.09	pyr.+1/2CS ₂ +3/2CO	aryl+1/2NO ₂ (≈22.3%)
	1	313.2–388.6	350.0	0.222	47.39	47.27	N(CH ₃) ₂ +CS ₂ +aryl+1/2CO	
	2	546.7–762.6	639.8	0.152	32.23	30.38	pyr.+2CO	

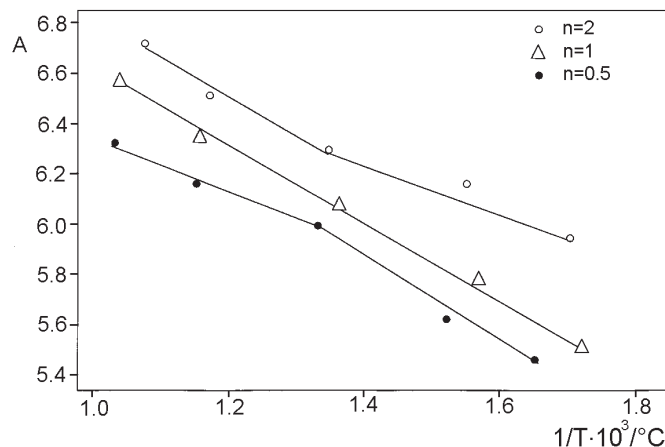


Fig. 1 Graphical determination of the order of the reaction

cess is calculated from the equation $E_a = -2.303 RS$, where R and S are respectively gas constant and the slope of the obtained straight line found in the previous plot.

2. Chatterjee's method [12]

This method is based on the general equation for the rate of the heterogeneous kinetics, $v = -dm/dt = Km^n$, where K , m and t are the specific rate constant of the reaction, the active mass of the reacting material and time elapsed from the start of the experiment.

Substituting K from the Arrhenius equation into the last one gives $\log v = \log A - n \log m - E_a / (2.303RT)$ 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 $\log v$ vs. $1/T$; $E_a = 2.2030RS$. The evaluated values of the kinetic parameters K , $t_{1/2}$ and E_a using the above two different methods are summarized in Table 3. It was found that the order of the decomposition process for all cases is unity, this means that the decomposition reactions have the same mechanism [7].

It is also obvious that the values of the activation energy given by both calculation methods are in a good agreement with each other.

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 [13, 14] and to the normal thermodynamic equations given before [5–8], the thermodynamic parameters ΔS , ΔH and ΔG of the thermal decomposition process were evaluated and are listed in Table 4.

The observed difference in E_a and ΔH values of the thermal decomposition process of the studied compounds is strongly related to the nature of the substituent (R) in the aryl ring and its position. This relation may be due to the $+I$ (inductive effect) and $+M$ (mesomeric) effect of the substituent (R), for example, in the case of p -methoxy group, which has low $+I$ effect due to the high electronegativity of the ox-

Table 3 Values of the kinetic parameters of the thermal decomposition of some rhodanine dyes

Comp.	First stage				Second stage				Third stage				Fourth stage		
	$k \cdot 10^2$	$t_{1/2}/\text{min}$	$E_a/\text{kJ mol}^{-1}$		$k \cdot 10^2$	$t_{1/2}/\text{min}$	$E_a/\text{kJ mol}^{-1}$		$k \cdot 10^2$	$t_{1/2}/\text{min}$	$E_a/\text{kJ mol}^{-1}$		$k \cdot 10^2$	$t_{1/2}/\text{min}$	E_a
			(a)	(b)			(a)	(b)			(a)	(b)			
I	9.70	7.14	118.93	117.43	5.21	13.33	82.18	81.65	2.40	29.22	192.28	191.87	1.99	34.27	55.9
II	9.24	7.52	57.02	56.83	3.29	21.60	73.31	72.45	–	–	–	–	–	–	–
III	10.93	6.32	37.92	36.90	9.95	6.96	103.28	102.77	3.45	20.18	35.49	34.13	–	–	–
IV	11.78	5.88	104.07	103.20	3.40	20.26	66.08	65.76	–	–	–	–	–	–	–

(a) Coats–Redfern method

(b) Chatterjee’s method

Table 4 Values of thermodynamic parameters of the thermal decomposition of some rhodanine dyes

Compd.	First stage			Second stage			Third stage			Fourth stage		
	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG^*	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG
I	38.83	114.76	-4.36	134.29	77.06	-5.61	242.14	184.99	-13.29	85.61	77.34	-7.62
II	98.17	57.87	-2.89	80.15	65.72	-7.45	-	-	-	-	-	-
III	93.00	34.46	-4.23	165.79	98.05	-6.25	45.72	28.46	-8.51	-	-	-
IV	167.06	98.89	-5.19	73.66	58.49	-8.75	-	-	-	-	-	-

ΔS in $\text{J mol}^{-1} \text{K}^{-1}$; ΔH and ΔG in kJ mol^{-1}

xygen atom which decreases the electron density all over the molecule and consequently decreases the vibration energy and stability of the dye molecule and leads to hypsochromic effect. This conclusion is in a good agreement with the law (K/S) values of the methoxy derivatives as given in the literature [2].

The $+I$ effect of the substituent group (R) in the aryl ring decreases in the following order [15]. $R=H < o\text{-OCH}_3 > p\text{-OCH}_3 > p\text{-OH}$.

The $+M$ effect leads to the increase in the thermal stability of the compounds, so the values of the total activation energy of the thermal decomposition of these compounds decreases in the direction: $I > III > IV > II$.

The higher molecular stability of the $p\text{-OH}$ derivative with the comparison with the $o\text{-OH}_3$ may be due to the $+M$ effect of the $p\text{-OH}$ on the molecule which increases its stability and increases E_a of this compound.

A quantum study

To support the experimental data given in this work a simple quantum mechanics calculation was performed using Omega SCF MO method [16]. It is based on drawing a molecule model, then calculation of the bond energy, bond length, bond order and other parameters by the application of the corresponding mathematical quantum equations. Some important factors, which effect the stability of these dyes such as delocalisation energy (DE), the bond order (BO) and the highest unoccupied molecular orbital (HOMO) were calculated and are listed in Table 5.

Table 5 Results of quantum mechanics calculation

Compound	DE (B)	BO	HOMO
I	8.9380	2.0126	-0.094525
II	11.1409	2.4135	-0.094806
III	11.1413	2.4129	-0.094809
IV	11.2322	2.4126	-0.094795

Table 5 indicates that the increase in the delocalisation energy, the bond order and the (HOMO) values increase in this order:

$$I < II < III < IV$$

The increase in the delocalisation energy leads to the decrease in the resonance energy and consequently decrease in the stability of the compound. This means that the activation energy decreases in the same direction.

The HOMO energy values correspond to the ionisation potential; lower values of HOMO indicate enhanced electron releasing character.

Conclusions

This study proved that the thermal stability of the investigated rhodanine dye and its derivatives is a junction of the nature and position of the substituent (*R*) in the aryl ring present; the *+I* and *+M* effect of the (*R*) group plays a very important role in increasing the delocalisation of electrons all over the molecules, this hence decreasing the resonance energy and leads to the increase in the thermal stability of the compounds in the following order:



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