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Hasan KOCAOKUTGEN

Zerrin HEREN

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Thermal Behaviour of Some Azo Dyes Containing Sterically Hindered and Water-Soluble Groups

Hasan KOCAOKUTGEN, Zerrin HEREN
*Ondokuz Mayıs University, Department of Chemistry,
55139, Samsun-TURKEY*

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Thermal behaviour of six azo dyes containing steric hindered groups such as tert-butyl, sec-butyl and isopropyl, were investigated by means of thermogravimetry (TG), differential thermal analysis (DTA) and differential thermogravimetry (DTG). The thermal decomposition points and amount of volatile pyrolysis products, were determined in nitrogen atmosphere using TG, DTA and DTG curves.

Introduction

Thermal analysis plays an important role in the study of the structure and stability of dyes. The applicability of some dyes for special uses and determining the thermal stabilities of them are also very important¹. The resistance to heat at elevated temperatures is one of the main properties required of dyes used in high temperature processes such as dyeing, printing and photocopying and in high technology areas such as lasers and electro optical devices².

Literature on azo dyes with sterically hindered groups such as tert-butyl, sec-butyl and isopropyl is scarce^{3,4}. Previously Akhtar reported that two azo dyes with the tert-butyl group were synthesized⁵. Nagai and Matsuo have shown that azo dyes containing tert-butyl groups are very suitable for the direct dyeing of polypropylene fibre⁶. The synthesis of some azo dyes containing these groups has been reported in our previous studies^{7,8}. Azo dyes containing both these types of group and sulphanilic acid groups have not been described previously. The results of the thermal analysis of these dyes can be used to obtain useful information about their thermal stability and also to determine the temperature range in which they can be used without changes in their composition, colour and properties⁹.

Here we report the thermal behaviour and the amount of volatile pyrolysis products of some new water-soluble azo dyes which have sterically hindered and sulphanilic acid groups.

Experimental

Preparation of dyes

The diazotization of sulphanilic acid was carried out as described in the literature¹⁰. The cooled sodium salt of diazotized sulphanilic acid was added gradually to the solution of cooled phenol dissolved in

10% sodium hydroxyde and the resulting mixture was continuously stirred at 0-5°C for 60 min. The desired product was precipitated out by adding con. 2ml HCl. The solid was filtered and washed with acidified water, respectively and then dried in vacuo.

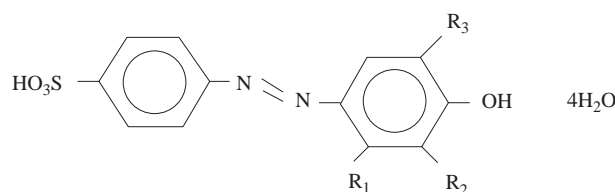
The other dyes, II-VI, were synthesized similarly.

Instrumental

TG, DTG and DTA curves were obtained simultaneously by using a Rigaku TG 8110 thermal analyser combined with a TAS 100 thermogravimetric analyser. The measurements were carried out in flowing nitrogen atmosphere within the temperature range of 20-900°C in a platinum crucible. The heating rate was 10 deg/min and the sample masses were in the range of 3-5 mg. Highly sintered α -Al₂O₃ was used as the reference material.

Results and Discussion

The structures of the water-soluble azo dyes which were synthesized by azo-coupling diazonium salts of sulphanilic acid and substituted phenol derivatives, are shown in Scheme 1. The TG, DTA and DTG curves of dyes I and V are illustrated in Figs. 1 and 2. The amount of volatile pyrolysis products for dyes I-VI and the thermoanalytical results obtained from TG, DTA and DTG curves are also given in Tables 1 and 2 respectively.



Dye	R ₁	R ₂	R ₃
I	H	H	H
II	H	CH ₃	CH ₃
III	H	i-pro	i-pro
IV	H	H	Bu ^t
V	CH ₃	H	i-pro
VI	H	H	s-Bu

i-pro: iso-propyl s-Bu:Sec-butyl

Scheme 1. The structures of the water-soluble azo dyes

From the TG and DTA curves, the weight losses at the first stage take place at 150°C by a slow process, depending on four moles water in the structures. Furthermore, all the anhydrous dyes are stable from 221°C to 245°C but dye I, is stable to 317°C because of not having the substituted groups. There are no colour differences between the hydrous and anhydrous dyes. According to these values, the decomposition points of dyes II-VI which contain substituted groups such as tert-butyl sec-butyl, isopropyl and methyl show considerable differences from 82°C to 121°C relative to dye I which does not have substituted phenol derivatives. In addition, exothermic changes just before the decomposition are observed in all dyes between 237°C and 245°C although that process is observed in parallel with the decomposition of dye I.

Table 1. The amount of volatile pyrolysis product (%) at different temperatures, °C

Dye	50	100	150	200	250	300	350	400	450	500	550	600	650	700	750
I	7.93	17.53	21.15	23.00	24.32	26.87	40.44	45.90	49.78	53.92	63.70	69.60	76.30	86.84	100 (745)
II	10.04	17.73	21.14	22.97	26.03	38.78	47.07	50.83	55.37	59.56	64.45	70.66	77.55	85.33	97.47
III	8.59	14.58	18.99	20.22	25.25	37.76	47.58	55.16	58.92	61.23	64.00	65.63	68.45	73.43	85.20
IV	7.69	15.27	18.64	21.18	24.85	32.84	38.58	43.25	47.93	50.89	52.60	55.38	59.05	64.14	71.83
V	8.55	17.73	22.67	25.57	31.74	50.58	59.71	64.65	69.42	74.30	79.36	85.41	91.51	98.43	99.88 (706)
VI	6.81	10.59	14.01	16.32	21.78	37.04	44.21	48.16	52.70	55.39	57.70	60.20	63.03	67.76	74.54

() the max. temperature of weight loss °C

Table 2. The thermoanalytical results obtained from TG, DTA and DTG curves

Dye	Stage	Temperature range/ $^{\circ}\text{C}$	DTG _{max} / $^{\circ}\text{C}$	Exothermic change/ $^{\circ}\text{C}$	Max water loss/ $^{\circ}\text{C}$
I	1	140	63		
	2	317-364	341	-	140
	3	484-569	540		
II	1	117	64		
	2	238-331	292	240	117
	3	680-760	750		
III	1	134	-		
	2	237-410	308	237	134
	3	652-820	720		
IV	1	128	65		
	2	245-435	290	245	128
I	3	700-850	790		
V	1	126	45		
	2	237-362	288	237	126
VI	1	140	105		
	2	221-381	266	237	140
	3	706-860	858		

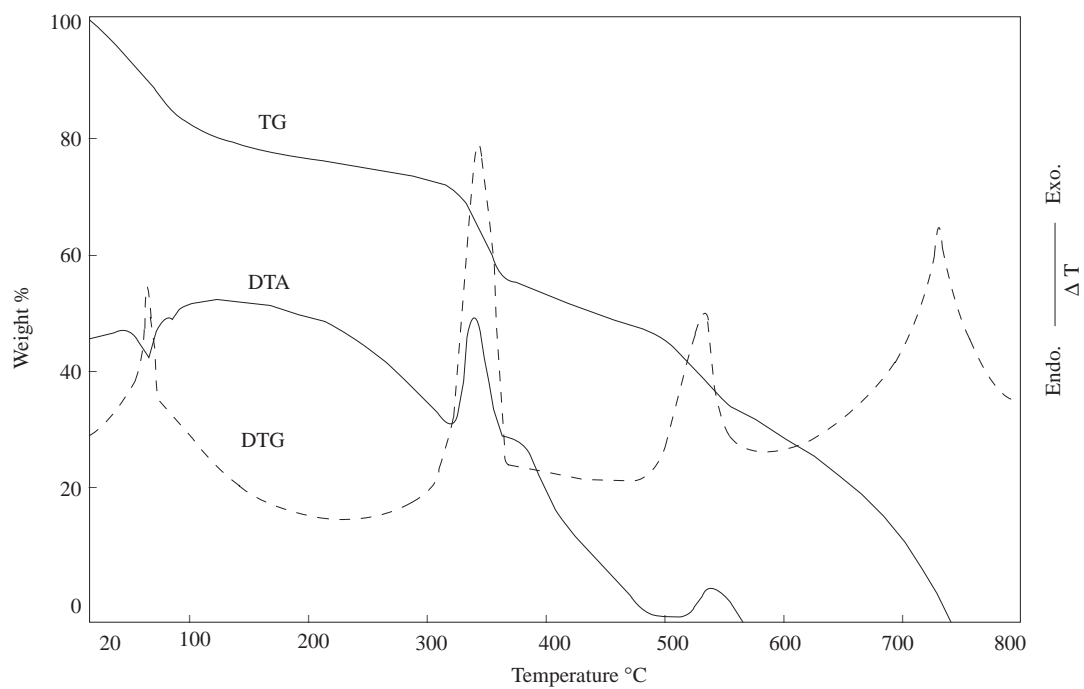


Figure 1. The TG, DTA and DTG curves of dye I

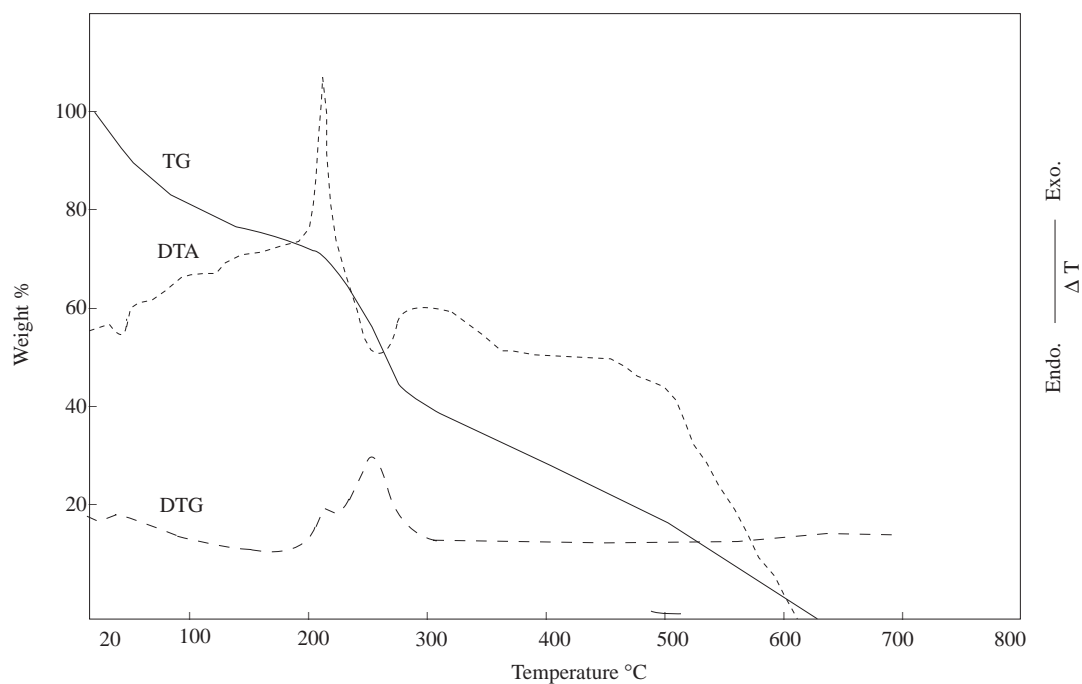


Figure 2. The TG, DTA and DTG curves of dye V

It was observed that the dyes investigated do not have the same thermal decomposition stages. For example, all the dyes decompose in at least two stages, whereas the decomposition of dye V takes place in a single stage. Although the thermal decomposition mechanism of dyes is complex, it basically consists of a heterolytic splitting of azo bonds in most of the azo dyes¹¹.

From the TG curve of dye I [Figure 1] without substituted groups, it is shown that the weight losses occurred between 50-140°C, 317-364°C and 484-569°C. The temperature range 50-140°C corresponds to the loss of water in the structure, and the other values are the decomposition stages. While the DTA curve of dye I gives exothermic decomposition peaks at 341°C and 540°C, the endothermic dehydration peak is at 63°C.

The TG curve of dye, V which is a 2-isopropyl-5-methylphenol derivative, shown in Figure 2, illustrates that the removal of four moles of water and the formation of the anhydrous dye V took place during the first stage simultaneously. The decomposition of dye V occurred at 237-362°C in the second part. In the DTA curve of the dye, the exothermic change was observed near decomposition at 237°C like dyes II-VI.

The thermal analysis of azo dyes demonstrated that the stability of the dyes depends on the substituted groups and their position in the dye structures. As a result, the TG and DTA studies on dyes I-VI showed that they can be used for versatile applications in various fields such as textile fibres, which require thermal stability up to 221-245°C.

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