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Short communication

THERMAL CHARACTERIZATION OF SOME AZO DYES CONTAINING INTRAMOLECULAR HYDROGEN BONDS AND NON-BONDS

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Abstract

Thermal behaviour of substituted monoazo dyes I–XVI, have been investigated by means of differential thermal analysis (DTA) and thermogravimetry (TG). The thermal stabilities of these dyes have been determined using the DTA and TG curves and the influence of the substituents and intramolecular hydrogen bonds on the DTA and TG curves of the dyes together with the melting points were also examined.

Keywords: azo dyes, intramolecular hydrogen bonds, thermal analysis

Introduction

Azo dyes are the most versatile class of dyes [1] and thermal analysis plays an important role in studing their structure [2]. The applicability of same the dyes for special uses and determining thermal stabilities of them are also very important [2]. The resistance to heat at elevated temperatures is one of the main properties required from dyes used in high temperature processes such as dyeing, printing and photo-copying and in high technology areas as lasers, electro optical devices [3].

Most of the previous studies on the physical and chemical properties studies of monoazo dyes were carried out in solution. Very few literature are reported showing the relationship between thermal stabilities and structures of azo dyes [4]. Literature reported

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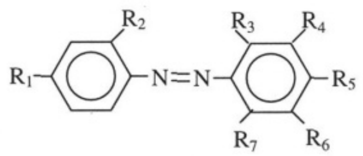
for azo dyes containing sterically hindered groups such as tert-butyl, sec-butyl and isopropyl is also scarce [5]. The thermal behaviour of some azo dyes containing sterically hindered and water-soluble group have been reported in previously [6].

We report here the thermal stabilities in solid state of the monoazo dyes synthesized having groups like tert-butyl, sec-butyl, iso-propyl, methoxy, nitro, chloro and so on. The influence of the substituents and intramolecular hydrogen bonds on the DTA and TG curves of the azo dyes synthesized has also been described and melting points.

Experimental

Preparation of dyes

Substituted monoazo dyes I–XVI, were synthesized and purified by the methods described previously [6]. The structures of all these compounds containing intramolecular hydrogen bonds and non-bonds are shown in Scheme 1.



	R_1	R_2	R_3	R_4	R_5	R_6	R_7
I	NO_2	H	H	H	OH	H	H
II	NO_2	H	H	CH_3	OH	CH_3	H
III	NO_2	H	H	i-pro	OH	H	CH_3
IV	NO_2	H	H	Bu^t	OH	H	H
V	NO_2	H	OH	H	H	Bu^t	H
VI	NO_2	H	OH	H	H	s-Bu	H
VII	NO_2	H	OH	Bu^t	H	CH_3	H
VIII	NO_2	H	OH	Bu^t	H	OCH_3	H
IX	NO_2	Cl	H	H	OH	H	H
X	NO_2	Cl	H	CH_3	OH	CH_3	H
XI	NO_2	Cl	H	i-pro	OH	H	CH_3
XII	NO_2	Cl	H	Bu^t	OH	H	H
XIII	NO_2	Cl	OH	H	H	Bu^t	H
XIV	NO_2	Cl	OH	H	H	s-Bu	H
XV	NO_2	Cl	OH	Bu^t	H	CH_3	H
XVI	NO_2	Cl	OH	Bu^t	H	OCH_3	H

i-pro : iso-propyl s-Bu : sec-butyl Bu^t : tert- butyl

Scheme 1 The structures of the dyes I–XVI

Instrumentation

Thermal analysis was carried out with a Rigaku TG 8110 simultaneous thermal analyser combined with a TAS 100 thermogravimetric analyser using 3–5 mg samples which were heated at a rate of 10°C min^{-1} from 20 to 800°C. The measurement were obtained using a flowing nitrogen atmosphere. Al_2O_3 was used as a reference material.

Results and discussion

The thermoanalytical results obtained from DTA and TG curves of all the monoazo dyes containing intramolecular hydrogen bonds and non-bonds, are given in Table 1.

Table 1 Thermoanalytical results of the dyes I–XVI

Monoazo dye	Melt point[1]/°C	Melt point[2]/°C	Mass loss temp./°C	Max. mass loss/%	DTA_{max}/°C
I	211	214	220–230	63	280 exo
II	174–176	182	215–311	57	277 exo
III	166–168	175	209–310	65	270 exo
IV	151–153	158	220–375	65	285 exo
V	192–194	198	210–314	96	290 endo
VI	130–132	141	204–300	91	291 endo
VII	178–180	185	213–300	96	287 endo
VIII	171	176	204–325	99	292 endo
IX	199–202	210	187–320	48	274 exo
X	212–214	226	218–300	47	268 exo
XI	166–167	177	213–300	43	258 exo
XII	156–157	167	216–317	43	268 exo
XIII	175–178	190	191–332	48	279 exo
XIV	135–138	151	216–310	49	277 exo
XV	201–203	216	230–300	54	264 exo
XVI	192–193	196	205–326	36	266 exo

[1]interval values under normal condition
[2]minimum values in nitrogen atmosphere (from DTA curves) exo: exothermic, endo: endothermic

It is clearly seen considering DTA and TG curves of all the dyes from Table 1, that the mass loss of all the compounds which contain intramolecular hydrogen bonds and non-bonds, are similar to each other by exothermic change but the dyes V–VIII, endothermic process. When these dyes V–VIII, having only nitro groups, nearly lose all mass% 91–99, in the other dyes XIII–XVI, with intramolecular hydrogen bonds containing chloro groups also, mass loss are about 50%. Similar thermal process in the thermal behaviour of monoazo dyes has been observed [7] related to mass loss.

In the dyes I–IV and IX–XII the mass loss in one stage during heating changes from 43 to 65% depending on the substituted groups as can be seen from Table 1. When the dyes, V–VIII, with intramolecular hydrogen bonds changes from 91 to 99%, the other compounds, XIII–XVI, containing intramolecular hydrogen bonds with chlorine group from 36 to 65%. The thermal mass loss temperatures of these dyes starts between 187 and 230°C and ends in the interval 300–375°C.

The typical DTA and TG curves of these dyes V, XI, are shown in Figs 1 and 2, respectively. In TG curve the dye V, one of the compounds V–VIII, having endothermic thermal behaviour, when the initial mass loss of this compound takes place slowly, its end step becomes sharp and one stage mass loss. However, examining TG curve of the dyes XI, one of the dyes I–IV, IX–XVI, with exothermic thermal behaviour, although initial-end mass loss is similar, the end mass loss continue slowly from 300 to 800°C as can be seen from Fig. 2.

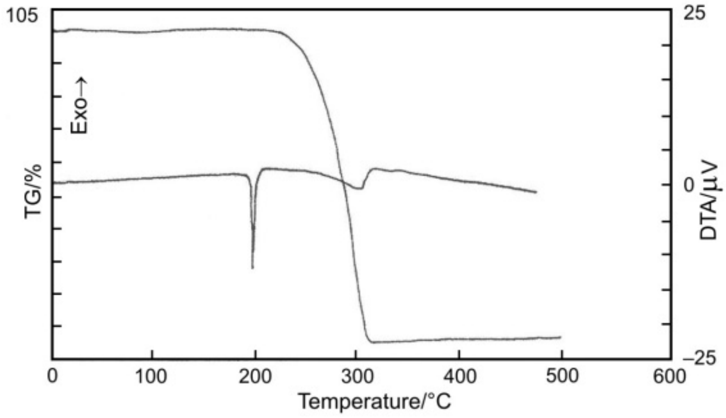


Fig. 1 DTA and TG curves of the dye V

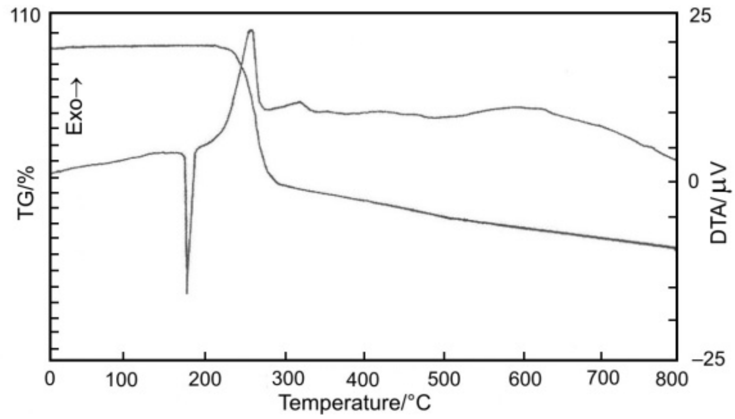


Fig. 2 DTA and TG curves of the dye XI

The melting process is accompanied by an endothermic change in all these dyes. Exothermic phase change is observed at 163°C for only dye II. The investigated dyes show considerable differences from 141 to 226°C in melting points depending on substituted groups. While the maximal mass loss of all the dyes are similar which is about 270°C from the present DTA results, it is observed that the melting points of the related dyes are higher than the normal values which may be the result of nitrogen atmosphere. From the data in Table 1, all 2-chloro-4-nitroaniline derivatives dyes IX–XVI, have higher melting points than those of their 4-nitroaniline anologues I–VIII, e.g. between II and X; III and XI; IV and XII.

Conclusions

The thermal behaviour of the azo dyes with intramolecular hydrogen bondings and non-bondings was determined by means of DTA and TG. The thermal analysis of the dyes demonstratd that the stability up to 187–230°C and decomposition of the dyes depend on the substituted groups as well as intramolecular hydrogen bonds in the structures. The maximal mass loss of all the dyes are similar which is about 270°C. The present TG and DTA data of the dyes, I–XVI showed that they could be used for versatile applications in various fields such as textile fibers.

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