

THERMAL ANALYSIS OF AMIDE DERIVATIVES OF *N,N*-DIALKYLAMINOAZOBENZENE

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Thermal analysis was performed on amide derivatives of *N,N*-dialkylaminoazobenzene. A correlation was found between the stability of the investigated dyes and the nature of the amide residue. The intermolecular interaction and the mechanism of thermal decomposition are discussed.

Thermal stability is an important factor determining the applicability of some dyes for special use. The resistance to heat at elevated temperature is one of the main properties required from disperse dyes considered for use in high-temperature processes of dyeing and printing [1].

In previous work [2] on the synthesis, and the physical, chemical and performance properties of amide derivatives of *N,N*-dialkylaminoazobenzene, it was found that these compounds are stable disperse dyes. Their particular advantage is a good fastness to sublimation, which is probably connected with a possible association of the dye molecules by means of the amide groups [3]. The tendency of disperse dyes to form intermolecular hydrogen-bonds is considered useful, due to their thermal stability, but at the same time this leads to difficulties in diffusion of the dye associates into fibres and consequently causes problems in the use of the dyes in bath processes of dyeing.

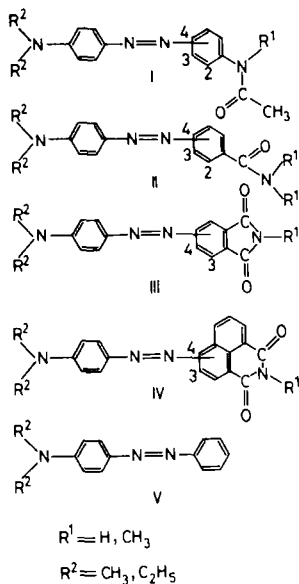
The presence of hydrogen-bonds between dye molecules can be found by IR spectrum analysis, using a KBr mixture or, even better, solutions in non-polar solvents [4], and also by intricate UV-vis spectrophotometric studies [5]. The need to use non-polar solvents restricts the application of these methods to the simplest compounds.

Most of the previous studies on the physical and chemical properties of dyes and model compounds were carried out in solution, i.e. under conditions different from those met during the dyeing or weaving of textile fabrics.

The understanding of the phenomena taking place in the crystalline state of a compound during heating would allow a faster and simpler evaluation of the

intermolecular interactions in crystalline structures and would make it possible to foresee some performance properties of the dyes under investigation. Thermal analysis reveals the existence of such interactions and changes in the crystalline structure and in the dyes themselves at elevated temperature.

For a better understanding of the phenomena taking place in monoazo dyes with amide groups during heating, the thermal analysis was carried out of four derivatives of *N,N*-dialkylaminoazobenzene, containing acetylamine (I), carbamide (II) and five-member (III) and six-member (IV) imide groups. Unsubstituted *N,N*-dialkylaminoazobenzene (V) was used a standard.



Experimental

Dyes I—V were prepared and purified by the methods described previously [2]. Thermal analysis was carried out with an OD—102 derivatograph, using 200 mg samples which were heated in air at a rate of 5 deg/min from 20° to 500°. Al_2O_3 was used as a reference substance. DSC analysis was performed with a 990 Thermal Analyser (Du Pont Instruments), using 3 mg specimens heated at a rate of 10 deg/min from 20° to 500°. The reference was an empty measurement vessel.

Results and discussion

The results of melting point and decomposition point determinations, as well as the calculated value $\Delta t = \text{decomp. p.} - \text{melt. p.}$, are given in the Table.

Table 1 Thermal decomposition data of N₁N-dialkylaminoazobenzene derivatives

$R^2 = \text{CH}_3$										$R^2 = \text{C}_2\text{H}_5$				
Dye	azo group position	R ¹	melt. p. °C	decomp. p. °C	Δt	% mass loss	Dye	azo group position	R ¹	melt. p. °C	decomp. p. °C	Δt	% mass loss	
Ia	2	H	163	304	141	65	I'a	2	H	147	292	145	63	
Ib	3	H	179	314	135	48	I'b	3	H	157	303	146	37	
Ic	3	CH ₃	85	315	230	45	I'c	3	CH ₃	56	310	254	52	
Id	4	H	217	281	63	36	I'd	4	H	180	324	164	60	
Ie	4	CH ₃	154	326	172	55	I'e	4	CH ₃	95	290	195	56	
IIa	2	H	205	—	0	56	II'a	2	H	—	—	—	—	
IIb	2	CH ₃	104	288	184	52	II'b	2	CH ₃	66	292	226	53	
IIc	3	H	176	298	122	38	II'c	3	H	145	300	155	42	
IId	3	H, CH ₃	180	317	137	49	II'd	3	H, CH ₃	161	320	159	52	
IIf	3	CH ₃	126	330	204	58	II'e	3	CH ₃	63	333	270	64	
IIg	4	H	245	286	39	38	II'f	4	H	211	290	79	42	
IIh	4	H, CH ₃	225	305	80	43	II'g	4	H, CH ₃	171	313	142	53	
IIIa	3	CH ₃	173	327	154	67	II'h	4	CH ₃	134	330	196	60	
IIIb	3	H	256	269	13	19	III'a	3	H	224	276	52	34	
IIIc	3	CH ₃	216	317	101	51	III'b	3	CH ₃	164	324	160	57	
IIId	4	H	290	310	20	17	III'c	4	H	259	304	45	26	
IVa	3	CH ₃	218	337	115	58	III'd	4	CH ₃	190	339	149	33	
IVb	3	H	284	305	21	22	IV'a	3	H	265	298	33	26	
IVc	4	CH ₃	254	301	47	21	IV'b	3	CH ₃	192	308	116	27	
IVd	4	H	280**	297	17	24	IV'c	4	H	269**	282	13	21	
V	—	CH ₃	(261)	279	(18)	14	IV'd	4	CH ₃	217	269	52	13	
V'	—	—	112	255*	143	80	V'	—	—	84	257*	173	83	

*, ** see text

Exothermic and endothermic changes are observed in the investigated substances during heating. The melting process is usually accompanied by an endothermic change and the decomposition by an exothermic change. In all but four (IVc, IV'c, V and V') cases, the beginning of the exothermic decomposition is observed immediately after the endothermic phase change. In the four cases mentioned above, a reversed order of changes occurred, in which the endothermic decomposition succeeded the exothermic melting process.

The weight loss during heating ranges from 13% to 83%, depending on the substituents and on the interactions which take place between dye molecules.

Phase changes are not observed during heating. Typical curves for selected dyes are shown in Fig. 1.

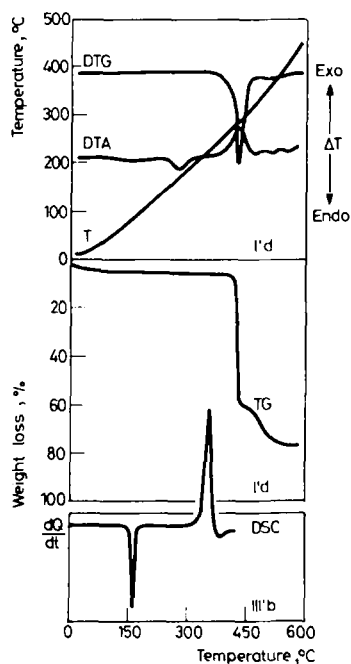


Fig. 1 Examples of typical thermal curves

The investigated disperse dyes, derivatives of acetanilide (I), benzamide (II), phthalimide (III), and naphthalimide (IV), show considerable differences in melting points (from 63° to 280°), while the decomposition points of all the dyes are similar, being about 300°. The most significant feature of the dyes is the difference between the decomposition and melting points, $\Delta t = \text{decomp.p.} - \text{melt.p.}$ This is a value closely associated with the dye structure and intermolecular interactions taking place in the crystalline state.

It follows from the data in the Table that all the *N,N*-dimethylaniline derivative dyes (I—V) have higher melting points than those of their *N,N*-diethyl analogues (I'—V'). The decomposition points of the respective compounds exhibit low and random differences, and hence are of rather low informative value. It is very likely that the lower melting points of the *N,N*-diethyl derivatives as compared with those of the *N,N*-dimethyl derivatives is brought about by the attenuation of the intermolecular interactions in the crystals of dyes I'—V', due to the steric hindrance caused by the longer alkyl chain. It may be concluded that the mutual interactions in the dye crystals lead to hydrogen-bonds yielding not only flat dimeric structures, but also "sandwich" systems. The latter are made difficult by the steric hindrance. The dyes containing the *N,N*-dimethyl group have melting points higher by about 15—60° than those of their diethyl analogues. The differences depend on the other substituents and on their position in the dye molecule.

The melting points of phthalimide (III and III') and naphthalimide (IV—IV') dyes are always higher than those of the corresponding acetanilide (I and I') and benzamide (II—II') dyes. Almost all the dyes with an unsubstituted amide group melt at a higher temperature than that of the *N*-methyl analogue. This suggests that the -CO-NH- group takes part in the formation of intermolecular hydrogen-bonds in the crystalline state. A measure of these interactions can be found in the Δt values. It is characteristic that the compounds with unsubstituted amide groups have considerably lower Δt values than those containing the -NCH₃ group. Absolute values of Δt oscillate between several (IVc and IV'c) and 200° (Ic, I'c, IIc, II'c). The Δt value is the lowest for compounds in which dimeric structures via hydrogen-bonds were found by another method [6]. Strong hydrogen-bonding needs higher energy to bring about cleavage of the molecule, and the melting point therefore rises almost to the level of the decomposition point. In acetanilide and benzamide dyes (I and II), these interactions are of a weak nature, which is confirmed by the high values of Δt , from 60° to 150°. In similar dyes containing phthalimide and naphthalimide groups (III and IV), Δt varies merely up to 30°, which suggests the existence of strong intermolecular interactions.

The weight losses observed during thermal decomposition of the dyes are given in the Table. In acetamide (I and I') and carbamide (II and II') dyes, this loss is about 50%. Deviations from this value are quite high particularly for compounds containing the unsubstituted NH group. Despite the considerable scatter of the results showing the variations of the thermal decomposition, it is very likely that a major part is played here by heterolytic splitting of the bond between the aryl ring and the azo nitrogen. Similar thermal decomposition has been observed by other authors [7] in the thermal analysis of other monoazo dyes.

The dyes containing phthalimide (III and III') and naphthalimide (IV and IV') groups probably decompose by a different scheme. In phthalimide dyes with a

substituted imide group =NCH₃ (IIIb,d and III'b,d), the weight loss is about 50%. This suggests a decomposition similar to that observed for other monoazo dyes. On the other hand, the most associated phthalimide dyes with an unsubstituted NH group (III a,c and III'a,c) and all the naphthalimide dyes (IV and IV') give weight losses of 13—34%, suggesting a different type of decomposition. It may be assumed that there is a decomposition of imide groups (CO)₂NR¹ or the splitting-off of alkylamine group-NR₂². The latter possibility would reveal a protective part by the strongly associating imide system in relation to the whole azo dye molecule.

Conclusions

The thermal studies of monoazo disperse dyes, derivatives of acetanilide, benzamide, phthalimide and naphthalimide, demonstrated that the stability of the dyes depends on the nature of the amide substituents and their ability for intermolecular interactions. One measure of these interactions is the difference between the decomposition and melting points of a compound, the value being inversely proportional to the strength of the interactions. In addition, it was found that in a crystal the dye molecules form not only typical flat or almost flat hydrogen-bonded associates, but also sandwich systems in various planes, which are quite stable under the measurement conditions.

The thermal decomposition mechanism of the dyes under investigation is complex. Basically, as for most azo compounds, it consists of a heterolytic splitting of azo bonds, while in stable imide compounds, the decomposition proceeds through the elimination of imide or alkylimide groups.

The use of thermal analysis allowed simple evaluation of the properties of disperse azo dyes acetamide, benzamide, phthalimide and naphthalimide derivatives and elucidation of the significance of intermolecular interactions, which would be impossible to examine by other methods.

References

- 1 C. H. Giles, D. G. Duff, R. S. Sinclair, "The Chemistry of Synthetic Dyes" (Ed. K. Venkataraman) Vol. VIII, Acad. Press, New York,
- 2 J. Szadowski, K. Wojciechowski, W. Malinowski, *J. Soc. Dyers Colour.*, 101 (1985) 105.
- 3 J. Szadowski, W. Malinowski, *Textilveredlung*, 18 (1983) 360.
- 4 H. E. Affsprung, S. D. Christian, J. D. Worley, *Spectrochim. Acta*, 20 (1964) 1415.
- 5 W. E. Forbes, A. R. Knight, *Can. J. Chem.*, 37 (1959) 334.
- 6 J. Szadowski, *J. Soc. Dyers Colour.*, 97 (1981) 358.
- 7 M. Nečas, M. Horák, *J. Thermal Anal.*, 23 (1981) 153.

Zusammenfassung — Die thermische Analyse von Amidderivaten von *N,N*-Dialkylamino-azobenzol wurde ausgeführt. Es besteht eine Korrelation zwischen der Stabilität der untersuchten Farbstoffe und der Natur der Amidgruppe. Die intermolekulare Wechselwirkung und der Mechanismus der thermischen Zersetzung wurden diskutiert.

Резюме — Проведен термический анализ амидпроизводных *N, N*-диалкиламиноазобензола. Установлена корреляция между устойчивостью исследованных красителей и природой амидного остатка. Обсуждены межмолекулярные взаимодействия и механизм термического разложения.