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Thermal Investigation of Sulphonylazide Dyes

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ABSTRACT

The thermal behaviour of sulphonylazide dyes was studied using differential thermal analysis. The temperatures at which thermolysis of the sulphonylazide group takes place were determined. The dyes studied showed a difference of decomposition temperature within a range of 25°C, without any noticeable correlation between structure and decomposition temperature.

1 INTRODUCTION

Dyes containing a sulphonylazide group can dye materials of natural and synthetic origin binding covalently to the substrate. By thermolysis of the sulphonylazide group a sulphonylnitrene is formed, which reacts chemically with the fibre:[1]

$$D{-}SO_2N_3 \xrightarrow{T^\circ C} D{-}SO_2N: \xrightarrow{>CH{-}F} D{-}SO_2{-}NH{-}F$$
$$D = \text{dye};\ F = \text{fibre}$$

The thermofixation at an optimal temperature requires knowledge of the temperature at which the thermolysis of the sulphonylazide group occurs. The literature describes a wide temperature range over which the thermolysis of sulphonylazides to sulphonylnitrenes takes place. Thus, L'Abbé reports decomposition in the range of 120–150°C.[2] Horner & Christmann state that the thermolysis begins at 120–140°C and the highest

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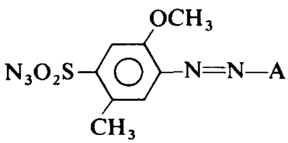
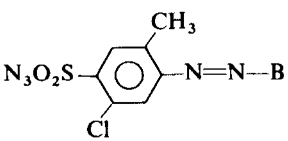
speed of the process is in the range 150–180°C, independent of the nature of R in RSO_2N_3.[3] Fagbule reports that the introduction of electron-donating groups into the molecule of sulphonylazide can decrease the fixation temperature.[4] Most studies on the thermolysis of sulphonylazides have been carried out in solution.[5]

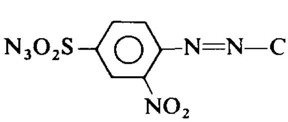
The thermofixation of the sulphonylazide dyes on the fibre is carried out in the solid phase and in air. Under these conditions thermal analysis is especially suitable for a study of the thermal behaviour of the sulphonylazide dyes. It allows the determination of the temperature at which thermolysis takes place with great precision and is a relatively rapid method. The following dyes were studied:



1 A = 2-hydroxy-1-naphthyl
2 A = 1-phenyl-3-methyl-5-hydroxy-4-pyrazolyl
3 A = 4[N-ethyl-N-(2-hydroxyethyl)-amino]-phenyl
4 A = *N*-[3-(2-cyanoethyl)-*N*-(2-hydroxyethyl)amino]-2-acetylamino-5-methoxyphenyl



5 B = 2-hydroxy-1-naphthyl
6 B = 1-phenyl-3-methyl-5-hydroxy-4-pyrazolyl
7 B = 4[*N*-ethyl-*N*-(2-hydroxyethyl)-amino]-phenyl
8 B = *N*-[3-(2-cyanoethyl)-*N*-(2-hydroxyethyl)-amino]-2-acetylamino-5-methoxyphenyl



9 C = 2-hydroxy-1-naphthyl
10 C = 1-phenyl-3-methyl-5-hydroxy-4-pyrazolyl
11 C = 4[*N*-ethyl-*N*-(2-hydroxyethyl)-amino]-phenyl
12 C = *N*-[3-(2-cyanoethyl)-*N*-(2-hydroxyethyl)-amino]-2-acetylamino-5-methoxyphenyl

2 EXPERIMENTAL

The dyes were prepared by conventional methods through diazotization of 2-methyl-4-amino-5-methoxyphenylsulphonylazide,[6] 2-chloro-4-amino-5-methylphenylsulphonylazide,[7] 3-nitro-4-aminophenylsulphonylazide[8] and coupling, depending on the azo-compound, in weakly alkaline or acid medium. They were purified by recrystallization from aqueous–organic solvent and all dyes used in further studies were chromatographically pure.

The DTA curves (enthalpy change) were recorded on a model Q-Derivatograph (MOM, Hungary) under the following conditions: temperature interval 20–250°C, heating rate 2·5°C min^{-1}, sensitivity of DTA 1/20, air medium, platinum crucible with $d = 10$ mm, inert substance Al_2O_3, and sample weight 100 mg. The temperature of the crucible was measured with the inert substance because thermolysis of the sulphonylazide group is a strongly exothermal process and when the temperature of the crucible is measured with the substance under study a distortion of the *D*-curve (temperature curve) is observed. Because of the less precise determination of the inflexion point, temperatures of the extremes are given.

3 RESULTS AND DISCUSSION

The DTA curves of the dyes showed an endothermal process which corresponds to the melting point, and a strongly exothermal process, corresponding to the thermolysis of the sulphonylazide group (Figs 1, 2 and 3).

In the literature the fact that high-melting compounds melt with decomposition is often ignored and there is occasional confusion between melting point and decomposition temperature.[5] The DTA curves distinguish between these, since melting is an endothermal process, whilst decomposition is an exothermal process. For comparison, the melting temperatures of the dyes were determined with a Koffler type of apparatus, model Boetius PHMK 5. The precision of this method is ±0·2°C. The temperatures of melting thus obtained are shown in Table 1.

Dyes **1**, **2**, **9** and **10** do not melt up to 300°C and an endothermic effect is not observed in the DTA curves of these dyes. Dyes **3**, **4**, **7**, **8** and **12** melt at a temperature lower than the temperature of decomposition of the sulphonylazide group. An endothermic effect in the DTA curves is observed at the respective melting temperatures. Comparison between the melting temperatures measured with the Koffler type of apparatus, and the melting

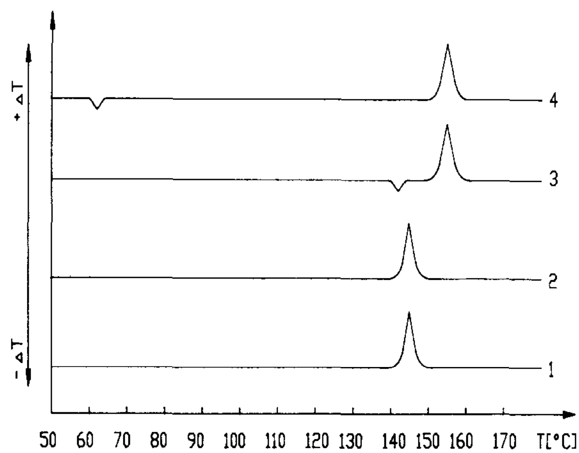


Fig. 1. DTA curves of dyes, derivatives of 2-methyl-4-amino-5-methoxyphenylsulphonylazide (dyes **1**, **2**, **3** and **4**).

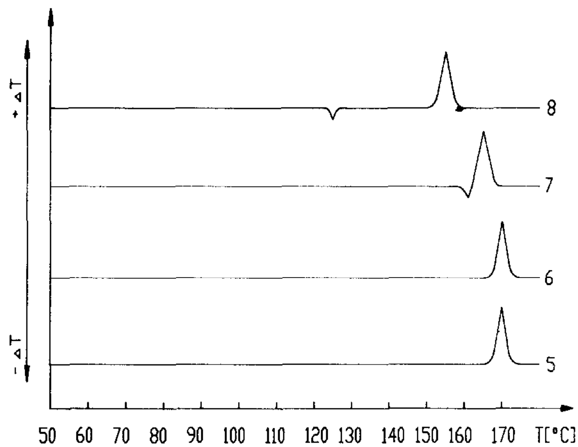


Fig. 2. DTA curves of dyes, derivatives of 2chloro-4-amino-5-methylphenylsulphonylazide (dyes **5**, **6**, **7** and **8**).

temperatures determined through the DTA curves, shows that the precision of determination through the DTA curves is $\pm 2°C$.

The melting temperature of dyes **5**, **6** and **11** measured by the Koffler type of apparatus is higher than the decomposition temperature of the sulphonylazide group. No endothermic process is observed in the DTA curves of these dyes due to the masking effect of the preceding strong exothermal process. The melting temperature observed on the Koffler type of apparatus is not of the initial sulphonylazide but of the products from the thermolysis of the sulphonylazide group. This shows that in order to avoid

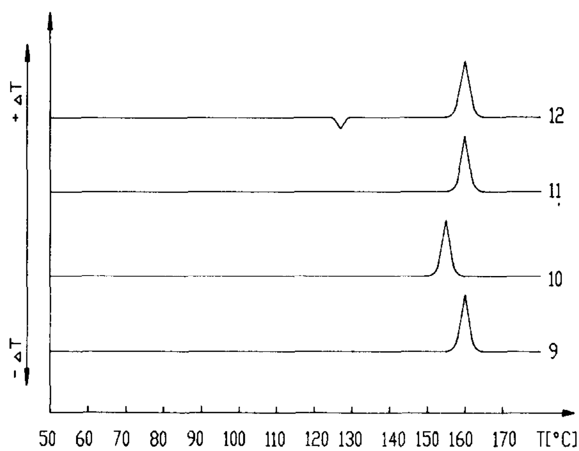


Fig. 3. DTA curves of dyes, derivatives of 3-nitro-4-aminophenylsulphonylazide (dyes **9**, **10**, **11** and **12**).

TABLE 1
Melting Temperatures of the Dyes, Measured with the Koffler Type of Apparatus

Dye	*M.p.* (°*C*)	*Dye*	*M.p.* (°*C*)	*Dye*	*M.p.* (°*C*)
1	—	**5**	189–191	**9**	—
2	—	**6**	191–193	**10**	—
3	142–144	**7**	161–163	**11**	167–169
4	63–64	**8**	123–125	**12**	126–128

errors in determining the melting temperatures of the sulphonylazides it is preferable to use both methods simultaneously.

Proof that the exothermal effect is due to the thermolysis of the sulphonylazide groups is as follows:

(1) Comparion of the IR spectrum of the reaction mixture in the crucible before and after the exothermal effect showed that in the IR, the azide group has an absorption band in the range 2120–2140 cm^{-1}. This absorption band is observed in the spectra of all the dyes studied before the exothermal effect, while in the spectra of the products it disappears.

(2) The DTA curves of analogous dyes containing a sulphonamide group in place of the sulphonylazide group were investigated. In the DTA curves of the corresponding sulphonamide derivatives over the temperature range 20–250°C no exothermal process was observed.

(3) The exothermal effect is observed in the DTA curves of the sulphonylazide dyes both in an air medium and in inert medium (argon and nitrogen). If the exothermal effect is due to combustion, it should disappear in inert medium.

The recording of the DTA curves under isothermal conditions at the beginning of the exothermal process and with a heating rate of 0·6°C min^{-1} showed that complete reaction takes place in an interval of 10°C.

In comparing the temperatures of thermolysis of the sulphonylazide group in the dyes there were observed differences of up to 25°C. A considerable influence on the decomposition temperature is exercised by the nature of the diazo compound containing the sulphonylazide group. The thermolysis of the initial diazo compounds takes place at the following temperatures:

2-Methyl-4-amino-5-methoxyphenylsulphonylazide	145°C
2-Chloro-4-amino-5-methylphenylsulphonylazide	170°C
3-Nitro-4-aminophenylsulphonylazide	145°C

These data show that the introduction of electron donating as well as electron accepting groups can decrease the decomposition temperature of the sulphonylazide.

The nature of the azo compound has a much lower influence on the temperature of decomposition of the sulphonylazide group and no specific correlation is observed. Probably the general structure of the molecule, the crystal modification and other factors are of significance. These results show that it is possible to synthesize dyes with different decomposition temperatures by changing the substituents in the molecule of the sulphonylazide dye, but this has to be evaluated empirically.

It is preferable to carry out the thermofixation of the sulphonylazide dyes on the fibres at temperatures, near the decomposition temperature of the sulphonylazide group. At lower temperatures thermolysis of the sulphonylazide group takes place very slowly and incompletely.[1] At higher temperatures there is a danger of the parallel occurrence of decomposition of the sulphonylnitrene and the evolution of sulphur dioxide.[9]

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