ELSEVIER

Dyes and Pigments, Vol. 37, No. 3, pp. 265–272, 1998

Printed in Great Britain
PII: S0143-7208(97)00066-1 0143-7208/98 $19.00+0.00

Synthesis of Phthalimide-based Alkali-dischargeable Azo Disperse Dyes and Analysis of their Alkali–Hydrolysis Mechanism

J. S. Koh & J. P. Kim

Department of Fiber and Polymer Science, College of Engineering, Seoul National University, Seoul 151-742, Korea

(Received 12 May 1997; accepted 16 June 1997)

ABSTRACT

Three alkali-dischargeable azo disperse dyes containing phthalimide moieties were synthesized. 4-Aminophthalimide which was used as a diazo component was prepared from phthalimide and coupled with three coupling components. Some physico-chemical properties of the synthesized dyes were also measured. The alkali dischargeable properties of the synthesized dyes were verified through analysis of the dye hydrolysis under alkali discharge conditions by IR, mass and UV–Visible spectrophotometry. These phthalimide based dyes could thus obviate the need for the use of hydrosulfite, which places a very high BOD on the effluent system, but they liberate no carcinogenic amine and thus should significantly reduce the cost of effluent treatment. © *1998 Elsevier Science Ltd*

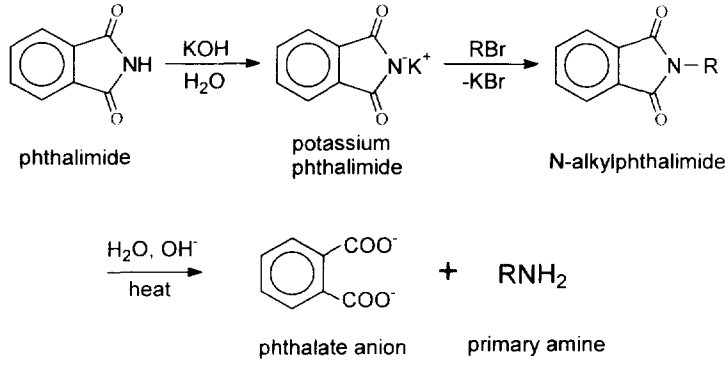
Keywords: Azo disperse dye, phthalimide, alkali-clearability, physico-chemical property, alkali-hydrolysis mechanism, wet fastness.

1 INTRODUCTION

In disperse dyeing of polyester fibers, reduction clearing is generally performed for the improvement of wet fastness of the dyed material. However, when the

conventional reduction clearing process is applied to azo disperse dyes, the azo linkage can be broken and carcinogenic aromatic amines liberated into the effluent, which already has high BOD values due to the presence of sodium hydrosulphide [1].

The Gabriel phthalimide synthesis is a reaction that yields primary amines without secondary and tertiary amines [2]. In this reaction, alkaline hydrolysis of the substituted phthalimide yields the primary amine and the water-soluble phthalate anion (Scheme 1).



Scheme 1

Therefore, by the introduction of phthalimide moiety, azo disperse dyes can have an alkali-dischargeable property. This is desirable in the dyeing of polyester, where the selection of a readily dischargeable dye means that the costly and environmentally damaging reduction clearing process can usually be omitted. This alkali-clearability is also of particular interest in the dyeing of polyester/cotton blends since it enables these dyes to be applied in the same bath with cotton reactive dyes for a one-bath two-step dyeing process.

The aim of this study was the synthesis of alkali-dischargeable azo disperse dyes containing phthalimide moieties and evaluation of their alkali–hydrolysis by IR, mass and UV–Visible spectrophotometry.

2 EXPERIMENTAL

2.1 Materials

All the chemicals used were of laboratory-reagent grade.

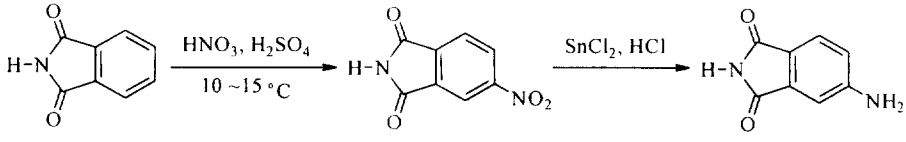
2.2 Synthesis of dye intermediates

2.2.1 4-Nitrophthalimide

Fuming nitric acid (48 ml; d. 1.50) was added to 280 ml of concentrated sulfuric acid and phthalimide (**1**) (40 g) was then stirred into the liquor rapidly, maintaining a temperature of 10–15°C. The reaction mixture was then allowed to warm slowly to room temperature. After 16 h, the crude product (**2**) which precipitated was filtered, washed four times with ice water, and purified by crystallization from ethanol, giving buff-coloured plates (Scheme 2) [3], 26.9 g (51.5%). ^{1}H-NMR (d_6-DMSO): $\delta = 8.0$–8.7 (m, 3H, aromatic protons), 11.81 (s, lH, C–NH_2) ppm. Calculated for $C_8H_4N_2O_4$: C, 50.00; H, 2.10; N, 14.58; found: C, 50.09; H, 2.03; N, 14.65.

2.2.2 4-Aminophthalimide

4-Nitrophthalimide (**2**) (20 g) was stirred into a solution of stannous chloride (84 g) in 450 ml of hydrochloric acid (sp. gr. 1.14) and 150 ml of water. After 90 min, the precipitate was collected at 0°C and washed with hot water until free from acid, the hydrochloride thus being completely hydrolyzed and the base was obtained as golden-yellow needles. This aminated product (**3**) was purified by crystallization from acetic acid, giving golden-yellow needles (Scheme 2) [4], 10.1 g (48.0%). ^{1}H-NMR (d_6-DMSO): $\delta = 6.36$ (s, 2H, C–NH_2), 6.7–7.5 (m, 3H, aromatic protons) 10.68 (s, lH, C–NH–C) ppm. Calculated for $C_8H_6N_2O_2$: C, 59.25; H, 3.73; N, 17.28; found: C, 59.45; H, 3.45; N, 17.07.



1 **2** **3**

Scheme 2

2.3 Synthesis of dyes

4-Aminophthalimide (**3**) (0.025 mol) was diazotized in 8.6 ml of 35% HCl and 90 ml of water by adding 0.025 mol of $NaNO_2$ at a temperature of 0–5°C. After 5–6 h, completion of diazotization was checked using a solution of

4-dimethylaminobenzaldehyde and the pH value of the diazo liquor was then adjusted to pH 5–6 by adding sodium acetate. The diazonium liquor was filtered and then added to a solution containing 0.025 mol of the appropriate coupling component, 50 ml of water, and 4.3 ml of 35% HCl. After 5–6 h, completion of coupling was checked by 10% H-acid solution, and the precipitated dye (**4**) was filtered, washed with water and dried. The dyes were purified by crystallization from methanol and washing with cyclohexane [5].

Dyes 1–3 (Table 1) were obtained as red powders:

Dye-1: 4.20 g (57.1 %), ^{1}H-NMR (d_6-DMSO): $\delta = 3.10$ (e, 6H, N–CH_3), 6.8–8.2 (m, 7H, aromatic protons) 11.41 (s, lH, C–NH–C) ppm. Calculated for $C_{16}H_{14}N_4O_2$: C, 65.29; H, 4.80; N, 19.04; found: C, 65.58; H, 4.94; N, 18.36.

Dye-2: 5.10 g (66.2%). ^{1}H-NMR (d_6-DMSO): $\delta = 1.13$ (t, 3H, C–CH_3), 3.05 (d, 3H, N–CH_3) 3.54 (q, 2H, N–CH_2–C) ppm. Calculated for $C_{17}H_{16}N_4O_2$: C, 66.22; H, 5.23; N, 18.17; found: C, 66.12; H, 4.90; N, 18.61.

Dye-3: 4.35 g (54.0%). ^{1}H-NMR (d_6-DMSO): $\delta = 1.17$ (t, 6H, C–CH_3), 3.50 (q, 4H, N–CH_2–C) 6.8–8.2 (m, 7H, aromatic protons), 11.39(s, lH, C–NH–C) ppm. Calculated for $C_{18}H_{18}N_4O_2$: C, 67.06; H, 5.63; N, 17.38; found: C, 67.25; H, 5.26; N, 17.37.

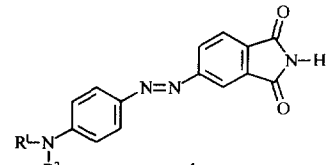
2.4 Physico-chemical properties of the synthesized dyes

λ_{max} and ε_{max} values of the dyes were measured in DMF on a Hewlett Packard 8452A UV–Visible spectrophotometer. Melting points of the dyes were measured using a DSC7 (Perkin-Elmer).

2.5 Analysis of alkali-hydrolysis mechanism

Dye-3 was used to evaluate the hydrolysis mechanism under alkaline conditions. Dye-3 (0.02 g) was treated with a solution of sodium carbonate (20 g litre^{-1}) in 100 ml of water for 20 min at 80°C. After the alkali treatment,

TABLE 1
Dyes Synthesized in the Present Study

Dye	R^1	R^2	*Structure*
Dye-1	CH_3	CH_3	
Dye-2	CH_3	C_2H_5	
Dye-3	C_2H_5	C_2H_5	**4**

Dye-3 was filtered to remove unhydrolyzed dye, DMF was added to precipitate residual sodium carbonate and this was removed by filtering. The filtrate was evaporated under vacuum and the dried dye analyzed by IR spectroscopy (Prospect-IR, MIDAC) and mass spectrometry (JMS AX505WA, JEOL).

The UV–Visible spectra of Dye-3 treated by the reducing agent and alkali were measured every 5 min while the temperature of the dispersions was raised 40 to 80°C using a laboratory dyeing machine (Turbo Color, Ahiba) coupled with a UV–Visible spectrophotometer (Perkin-Elmer Lambda 16).

3 RESULTS AND DISCUSSION

3.1 Physico-chemical properties of the synthesized dyes

The physico-chemical properties of the dyes are given in Table 2. The increasing alkyl chain length tends to give a bathochromic effect, due to the increased electron donating power of the coupling components, which decrease the energy difference between the ground and excited state of the dyes [6].

The melting points of the dyes were relatively high compared with those of other general disperse dyes. This can be attributed to the self-association of dyes in the crystalline state [5].

3.2 Analysis of alkali-hydrolysis mechanism

Figure 1 shows the IR spectrum of the alkali-treated Dye-3. Characteristic peaks were observed at 1605 and 1397 due to the asymmetric and symmetric stretching vibration of C=O, and which were not apparent in the case of the untreated Dye-3.

Figure 2 shows the mass spectrum of alkali-hydrolyzed Dye-3. Peaks for carboxylate salts were observed at m/z 385 ($C_{18}H_{17}N_3O_4Na_2$), 363 ($C_{18}H_{18}N_3O_4Na$), and 341 ($C_{18}H_{18}N_3O_4$).

Figure 3 shows the change in the absorption spectra of Dye-3 resultant from (a) reduction clearing and (b) alkali clearing. In the case of reduction

TABLE 2
Physico–Chemical Properties of the Synthesized Dyes

Dye	*Mol. wt.*	λ_{max} *(nm)*	ε_{max} *(mol cm^{-1})*	*m.p. (°C)*
Dye-1	294.3	478	29 726	289
Dye-2	308.3	486	32 221	247
Dye-3	322.4	490	33 107	262

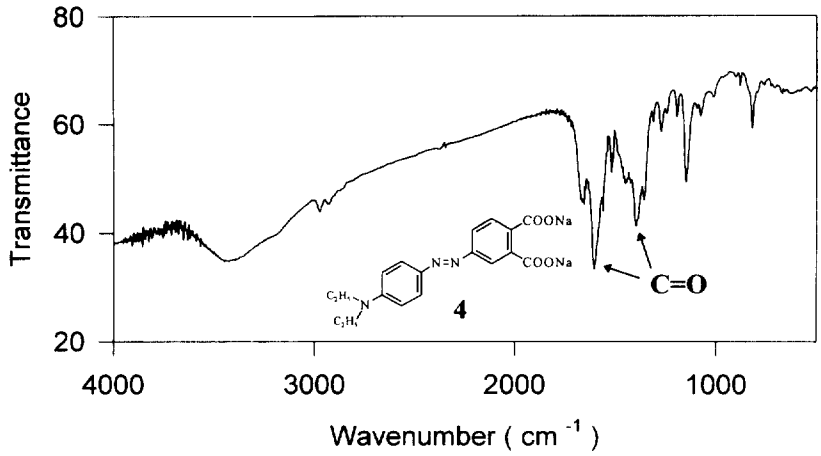


Fig. 1. I.R. spectrum of alkali-hydrolyzed Dye-3.

clearing, with increase in time, the absorbance at λ_{max} tends to decrease, since the azo link of the dye is broken by the action of the reducing agent and the dye becomes colorless. However, in the case of alkali clearing, the absorption spectrum shows a tendency for gradual increase of the absorbance at λ_{max}. This result implies that the amount of water-soluble phthalate salt increases due to hydrolysis of dye.

All the results (Figs 1–3) indicate that the phthalimide ring in the structure of these synthesized dyes undergoes ring opening and converts to a water-soluble carboxylate salt (**5**) by hydrolysis under relatively mild alkaline conditions (Scheme 3).

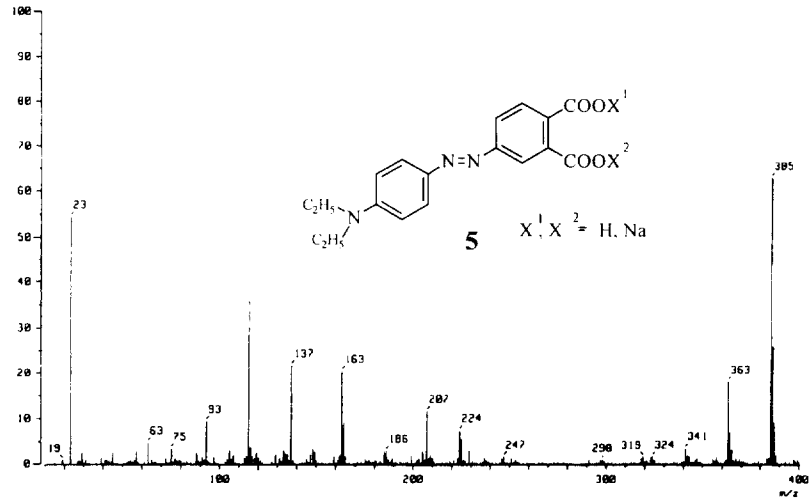


Fig. 2. Mass spectrum of alkali-hydrolyzed Dye-3.

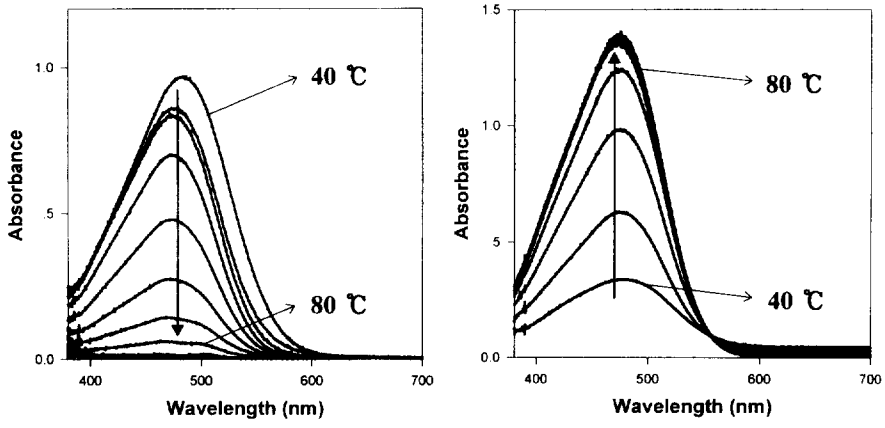
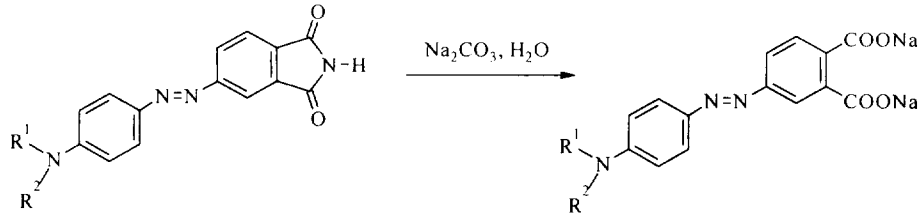


Fig. 3. UV–Visible spectra of Dye-3 under (a) a reduction clearing condition and (b) an alkali clearing condition, measured every 5 min while the temperatures of the dispersions were raised 40 to 80°C.



4 **5**

$R^1/R^2 = CH_3/CH_3, CH_3/C_2H_5, C_2H_5/C_2H_5$

Scheme 3

4 CONCLUSION

Alkali-dischargeable azo disperse dyes containing a phthalimide moiety were synthesized and the alkali-hydrolysis mechanism was investigated by IR, mass and UV–Visible spectrophotometry. From the results of the hydrolysis mechanism, it can be concluded that azo disperse dyes containing the phthalimide moiety undergo ring opening and convert to water-soluble products without fission of the azo bonds under relatively mild alkaline conditions. Therefore, it can be presumed that phthalimide-based azo disperse

dyes have an alkali-clearable property which enables an alkaline treatment to substitute for the reduction clearing process, thus preventing the generation of potentially carcinogenic amines. These alkali-dischargeable dyes will thus be able to obviate the need for the use of hydrosulfite, which places a very high BOD on any effluent system, thus liberating no carcinogenic amine and significantly reducing the cost of effluent treatment.

In addition, it is thought that polyester/cotton blends can be dyed using a one-bath two-step dyeing method, as alkali clearability enables these dyes to be applied in the same bath with cotton reactive dyes. Therefore, by incorporation of an alkali clearing stage, in addition to the improved productivity, we can anticipate high levels of wash fastness even in heavy depths [7].

REFERENCES

1. Aspland, J. R., *Textile Chemists Colorists* 1992, **24**, 18.
2. Fessenden, R. J. and Fessenden, J. S., *Organic Chemistry*, 4th edn. Brooks/Cole, CA, 1990, pp. 746–747.
3. Huntress, E. H. and Shriner, R. L., *Organic Syntheses*, Collective Vol. 2. Wiley and Sons, New York, p. 459.
4. Levy, L. F. and Stephen, H., *J. Chem. Soc.*, 1931, **I**, 79.
5. Szadowski, J. and Malinowski, W., *J. Soc. Dyers Colorists*, 1981, **72**, 97.
6. Gordon, P. F. and Gregory, P., *Organic Chemistry in Colour*. Springer-Verlag, Berlin, Heidelberg, New York, London, Paris, Tokyo; 1987, p. 126.
7. Leadbetter, P. W. and Leaver, A. T., *Rev. Prog. Col.*, 1989, **19**, 33.