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Cyanation of water-soluble disperse dyes

Honglin Wang, Zhenfu Han, Xin Pan *

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Zhongshan Road 158, Dalian, Liaoning Province, 116012, People's Republic of China

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Abstract

Dyes containing the SO_2CH_2COOH group (SMC) are water soluble and, in the dyeing process these dyes decarboxylate to give disperse dyes which can be absorbed by polyester fibres. Some *ortho*-bromo azo dyes of this type are treated with a cyanating agent to give the corresponding *ortho*-cyano dyes. The cyanation reaction takes place in aqueous solution preferably of pH 7–9 at room temperature. Various factors affecting this reaction are considered. The dyes colour polyester fibres in red to blue shades with good fastness. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Dyes containing ionizable groups cannot be used to dye hydrophobic fibres. Disperse dyes for colouring polyester fibres are virtually water-insoluble. However, most textile fibres are conventionally dyed in aqueous solution. The press cake of a disperse dye is not suitable for such a dyeing purpose, and must be processed as follows: ground with dispersants in aq. medium for many hours to give a dispersion which has a particle size of approximately 1 μm.; the dispersion is then dried on a spray-drying equipment to obtain a so-called ultradisperse powder and the powder can then be dispersed in water to dye polyester.

To avoid these inconvenient processes, many researchers have introduced solubilizing groups into disperse dyes. These solubilizing groups are cleaved off in the dyeing process to give dyes which can then be absorbed by hydrophobic fibres; these dyes are called water-soluble disperse dyes.

Dyes containing the SMC (carboxymethylsulfonyl) group can be dissolved in water at pH 7–9. (In basic medium, the dyes are converted to their water-soluble salts.) In the dyeing process, these dyes undergo decarboxylation [Eq. (1)] [1]:

$$\mathrm{Dye} - SO_2CH_2COOH \rightarrow \mathrm{Dye} - SO_2CH_3 + CO_2 \uparrow \qquad (1)$$

Dyes containing methylsulfonyl group can readily be absorbed by polyester fibres.

After the pretreat process, some base is left on the polyester fibres, which can affect the dyeing process because many conventional disperse dyes are applied in acidic medium and are sensitive to the base. However, dyes containing the SMC

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[*] Corresponding author. Fax: +86-411-3633080.

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group are relatively stable and not sensitive to the base. These dyes can be used in basic solution and can be applied with reactive dyes in the same bath to dye cotton–polyester blend fibres.

Yellow, orange and red dyes of this type were obtained in this present work. To achieve shades of bluish-red, violet and blue, we tried to convert *ortho*-bromo azo dyes of this type to *ortho*-cyano dyes. We found the reaction could take place easily at room temperature if the dyes were dissolved in basic aq. solution.

The reaction of *ortho*-bromo azo disperse dyes with cuprous cyanide usually takes place in aprotic polar solvents such as DMF or DMSO. However, cyanation of reactive-disperse dyes containing $SO_2CH_2CH_2OSO_3Na$ group can take place in aqueous solution [2]. The dye forms a complex with Cu (I), which helps the nucleophilic substitution of Br by CN.

The reaction of aromatic halides with CuCN in DMF was originally studied by Friedman [3]. The mechanism of copper assisted nucleophilic substitution reaction has also been explored by Lindley [4].

Most copper catalyzed nucleophilic substitions take place in relatively severe conditions. However, if the reactant has an appropriate structure and can provide ligand for the formation of the cuprous complexes, the reaction can take place in a mild condition [5]. Explanation of the high cyanation activity of water-soluble disperse dyes containing the SO_2CH_2COOH group in aqueous medium is that the $–COO^-$group helps to form a cuprous complex.

2. Experimental

2.1. Intermediates

p-Carboxymethylsulfonylacetanilide was prepared by condensation of *p*-acetamido-benzenesulfinic acid with chloroacetic acid in basic aq. solution. *p*-Carboxymethylsulfonylacetanilide was hydrolized in sulphuric acid to give *p*-carboxymethylsulphonylaniline. *p*-Carboxymethylsulphonylaniline was treated with (1) HBr and H_2O_2 to give 2-bromo-4-carboxymethylsulphonylaniline and with (2) Br_2 and H_2O_2 to give 2,6-dibromo-4-carboxymethylsulphonylaniline [6].

3-Carboxymethylsulfonamide-*N*,*N*-diethylaniline was prepared through the following process: CH_3COOH, $POCl_3$ and $ClSO_3H$ were heated to give ClO_2SCH_2COCl [7]. ClO_2SCH_2COCl was partly hydrolized in benzene to give ClO_2SCH_2COOH [8]. 3-Amino-*N*,*N*-diethylaniline, which was prepared by acid hydrolysis of 3-acetamido-*N*,*N*-diethylaniline, reacted with ClO_2SCH_2COOH in benzene to give 3-carboxymethylsulfonamide-*N*,*N*-diethylaniline.

Some dyestuff companies provided the other intermediates. Traditional methods were used to prepare the *o*-bromo azo dyes.

2.2. Cyanation of the dyes

4.65 g (9 mmol) of dye I was added to 20 ml of an aq. solution of 1 g Na_2CO_3; the solution was stirred until the dye was dissolved; 0.5 g (5.6 mmol) CuCN, 0.27 g (5.5 mmol) NaCN and 0.5 ml 36% HCHO (6.5 mmol) were dissolved in 10 ml water. The solution of cyanides was added to the solution of the dye and the mixture stirred at 40°C for 3 h, whilst monitoring the reaction with TLC. When the cyanation was complete, 2 g NaCl was added to salt out the product. The product was treated with ammonia solution to wash off impurities. After purification the yield of dye I was 80%, 3.3 g.

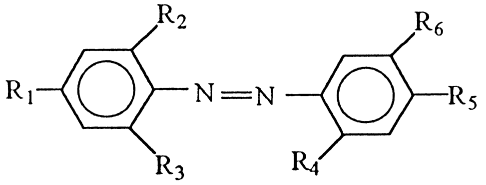
2.3. Application of the dyes

0.05–0.1 g dye I was dissolved in 10 g printing paste of pH 7–8 then the paste was printed on polyester fabric. The coloured piece was dried at 100°C and heated in an oven at 200°C for 1–2 min. After being soap-boiled and dried, the coloured fabric was tested for light and sublimation fastness.

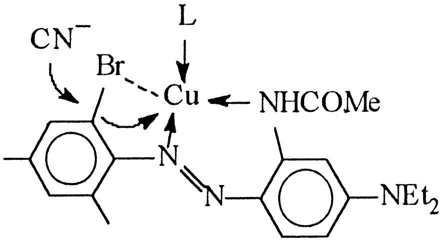
3. Results and discussion

3.1. Cyanation reaction in water

Several azo dyes were prepared, as illustrated in Scheme 1 and Table 1.



Scheme 1.



Scheme 2.

When the *ortho*-bromo azo dye I is treated with CuCN in polar aprotic solvents such as DMF, DMSO and NMP, cyanation occurs at relatively high temperature, and is not complete before the dye decarboxylates. Once ammonia is added to the reaction mixture we found that cyanation took place easily even at room temperature. Further experiments showed that if dye I was dissolved in a basic aq. solution preferably of pH 7–9, the cyanation reaction was complete after 2–3 hours at 30–40°C and the dye did not decarboxylate. This phenomenon is interesting. It is presumed that cyanation of aromatic halides with CuCN is depressed in the presence of water and other protic solvents and can be accelerated by using some polar aprotic solvents such as DMF.

But, in this present investigation of water-soluble disperse dyes containing the SMC group, the cyanation rate is the highest in aq. medium. This may be explained below.

It is well established that for halogenated azo disperse dyes, forming the cuprous complex (as shown in Scheme 2) is the crucial step for the cyanation reaction [9]. In aq. medium of pH 7–9, the *ortho*-bromo azo water-soluble disperse dye containing the SO_2CH_2COOH group is dissolved, and therefore SO_2CH_2COOH is in the form of $SO_2CH_2COO^-$, which helps the dye to form the cuprous complex and makes the cyanation reaction easier.

3.2. Cyanating agent

3.2.1. CuCN–NaCN

As is well known, cyanation is catalyzed by copper, which also causes some by-reactions and a trace residual amount of copper in the products can make the dyes have a poor colour when applied on polyester. With CuCN–NaCN as the cyanation agent and by controlling its composition, the amount of copper used is reduced and the rate of cyanation is increased. Some experimental results are shown in Table 2.

CuCN is almost insoluble in water. NaCN can react with CuCN to form $Na_xCu(CN)_{x+1}$ ($x = 1$–3) which is soluble in water. So some NaCN–CuCN mixtures are more reactive than CuCN alone. If the concentration of CN^- in the solution is relatively high ($[CN^-]/[Cu^+] > 6$), practically all copper exists in the form of $Cu\ (CN)_4^{3-}$ which is

Table 1
ortho-Cyano dyes and their *ortho*-bromo dyes precursor

Dyes	R_1	R_2	R_3	R_4	R_5	R_6	Colour	λ_{max} (nm)	Bromo analogues
I	SMC	CN	H	NHAc	NEt_2	H	Red	533	I
II	SMC	CN	CN	NHAc	NEt_2	OCH_3	Blue	621	ii
III	SMC	CN	Br	NHAc	NEt_2	OCH_3	Blue	592	ii
IV	SMC	CN	CN	NHAc	NEt_2	H	Blue	605	iv
V	SMC	CN	CN	H	NEt_2	H	Purple	573	v
VI	CH_3	CN	CN	NH (SMC)	NEt_2	H	Red	521	vi
VII	NO_2	CN	CN	NH (SMC)	NEt_2	H	Blue	–	vii

[a] λ_{max} Values in 95% ethanol; Br substitutes all CN in Table 1 when the dyes are bromo analogues.

[b] Dye VII was not obtained, so its λ_{max} value is not given.

Table 2
Influence of different composition of CuCN–NaCN on the rate of cyanation [a]

	CuCN:NaCN (mol)				
	1:0	1:1	1:2	1:3	1:5 or more
Reaction time	4–5 h	30 min	40 min	2 h	No reactions occur

[a] Dye II is tested under the condition:temperature, 25°C; pH, 7–9; CN/dye = 2.5 (mol).

co-ordinately saturated and cannot form complexes with dyes, so no reaction occurs.

3.2.2. CuCN–NaCN–HCHO

It has been reported that *ortho*-bromo azo disperse dyes can react with $HOCH_2CN$ or NaCN–HCHO in the presence of very small amounts of a cuprous salt [10,11]. Formaldehyde is used to regulate the concentration of CN^- in the solution. The concentration of CN^- is regulated through the following equilibrium:

$$H_2O+CN^-+HCHO \rightleftarrows HOCH_2CN+OH^- \quad (2)$$

Even when the quantity of cuprous salt is decreased to a catalytic amount, cuprous ions cannot be saturated by CN^- in the solution in the presence of HCHO, which ranges the CN^- concentration according to the equilibrium shown in Eq. (2). Thus the unsaturated cuprous ions can form complexes with the dyes and have catalytic activity. As the cyanation proceeds and CN^- becomes exhausted, $HOCH_2CN$ converts to CN^- and HCHO reversely, and provides further CN^- for the cyanation reaction. The effects of formaldehyde on the cyanation reaction of dye II are shown in Table 3.

Introduction of formaldehyde makes the cyanation reaction occur even when the concentration of cuprous ion is lower. So, some by-reactions caused by relatively excessive cuprous ion are hindered and the by-products are drastically reduced.

3.2.3. $CuSO_4$–NaCN–HCHO

Cupric salt was also used to catalyze the cyanation reaction. A $CuSO_4$–NaCN mixture was added to an aq. solution (pH = 8) of dye II. The cyanation reaction took place, but with a lot of by-products.

Table 3
Reactivity of CuCN–NaCN–HCHO mixtures [a]

	CuCN:NaCN:HCHO (mol)				
	1:1:1	1:2:2	1:3:3	1:5:5	1:10:10
Reaction time	30 min	45 min	1.5 h	6 h	24 h

[a] Reaction condition:temperature, 25°C; pH 7–9; CN/dye II = 2.5 (mol)

When a $CuSO_4$–NaCN–HCHO (mole ratio, 1:3:4) mixture was used to treat dye II, cyanation took place easily and the produced *ortho*-cyano dye (II) was free from the unwanted by-products. However, in this system, cupric ion is reduced to cuprous ion by formaldehyde and it is the cuprous ion that results in the final effect.

3.3. Reactivity of the dyes

For the water-soluble disperse dyes containing the SMC group, the influence of the dye structures on the rate of the cyanation reaction is shown in Table 4.

Substitution of the first bromine in the *ortho*-dibromo azo dye is easier than substitution of the second one. When dye II is treated with a solution containing stoichiometric amount of CN^-, it is partly substituted to give dye III.

4. Application of the dyes

It is convenient to use the water-soluble disperse dyes containing the SMC group to colour

Table 4
Influence of dye structure on the cyanation reaction [a]

Reactant	Reaction time	Reaction temperature (°C)	Product
vii	5 min	25	VII[b]
vi	20 min	25	VI
ii	40 min	25	II
i	3 h	40	I
v	10 h	30	V

[a] Reaction condition: CuCN:NaCN:HCHO = 1:2:2 (mol), bromo (in dye) /CN = 1:1.2 (mol) pH = 7–9.

[b] The resulted dye (VII) contains lots of by-product.

Table 5
Fastness and visible absorption [a] of the dyes

	λ_{max} (nm)	$\epsilon_{max}\times10^4$	Light fastness	Sublimation fastness
Dye (I)	533	4.45	5	4–5
Dye (II)	618	6.84	5	4–5
Dye (VI)	521	5.56	4–5	4–5

[a] Visible spectra of the dyes were measured in 95% ethanol.

polyester fibres and cotton–polyester blended fibres. These dyes dissolve in neutral or basic aq. solution and can be applied just like other kinds of disperse dyes. In a standard process, polyester fibres and the solution of the dyes were held in a sealed bath at 130°C for 30 min and most of the dyes were absorbed by the fabric. In the thermofixing process at 200°C for 1–2 min, most of the dyes were fixed on the polyester.

To dye polyester–cotton blended fibres, reactive dyes containing a monochloro-s-triazinyl active group were chosen for application with the water-soluble disperse dyes containing the SMC group. Two kinds of dyes of identical colour were mixed and dissolved in an alkaline solution. The solution was applied in a one-bath process, and coloured the blended fabrics evenly.

The fastness of several dyes on polyester fibres are shown in Table 5.

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