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The Dyeing of Cellulose with Reactive Dyes Containing Phosphonic Acid Groups

Gaetano Alberghina, Maria E. Amato and Salvatore Fisichella†

Department of Chemistry of the University, Viale A. Doria 6,
95125 Catania, Italy

and

Ian D. Rattee‡

Department of Colour Chemistry and Dyeing, University of Leeds,
Leeds LS2 9JT, Great Britain

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SUMMARY

The fixation of some Procion T phosphonated reactive dyes on cotton in the presence of dicyandiamide in different conditions of dyeing is reported, in order to clarify the role of the carbodiimide in the fixation process.

Paper chromatographic studies on Procion Red T-2B show that the reaction mechanism between the phosphonic dye and cellulose in the presence of dicyandiamide is an initial condensation of the phosphonic dye with dicyandiamide to produce a phosphonic acid anhydride, followed by subsequent reaction with cellulose to give a dye covalently bonded to the cellulose. The phosphonic acid anhydride, isolated by means of column chromatography, shows the characteristic adsorption bands of the P—O—P linkage.

1. INTRODUCTION

Dyes can be attached to the fibre by means of physical adsorption, mechanical retention or chemical reaction. Reactive dyes are covalently

† To whom all correspondence should be addressed.
‡ Present address: Textech UK Ltd, Suite 3, Concourse House, 78 Wellington Street, Leeds 1, Great Britain.

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bonded to the fibre and they give dyeings that are fast to washing by virtue of the dye–fibre covalent linkage. In theory, any group that is capable of reacting with sites in the fibre is a potential reactive system to be incorporated in a reactive dye. In practice, there are many restrictions on the type of reactive group employed, such as level of reactivity, stability to hydrolysis, stability of the dye–fibre bond and ease of manufacture.[1–6]

Reactive groups commercially available in reactive dyes for cellulose can be divided into types that react under alkaline dyeing conditions (by means of nucleophilic substitution or addition) or under acidic dyeing conditions.

The dichlorotriazinyl reactive dyes constitute a range of reactive dyes that react with cellulose under alkaline dyeing conditions and have been studied extensively, in particular with respect to the physical chemistry of their hydrolysis.[7–9] Simultaneously with its reaction with the fibre, the reactive dye molecule undergoes hydrolysis by the water of the dyebath. The efficiency of the dyeing process has been defined as the ratio between the rate of fixation and the rate of hydrolysis.

The fact that reactive dyes react with water is important not only for the colour yield during the dyeing process, but also for the storage stability of the dyestuffs, the stability of pad liquors and print pastes, and the changes in reactive dye content. Consequently, the consideration of hydrolysis kinetics is of primary importance. During the dyeing of a fibre, a certain amount of unfixed hydrolysed dye is retained due to the competitive hydrolysis reaction. In order to achieve high wet-fastness it is necessary to remove the unfixed dye. An important problem in reactive-dye chemistry is that involving dyes of improved fixation characteristics in order to minimize, or even eliminate, washing-off processes.

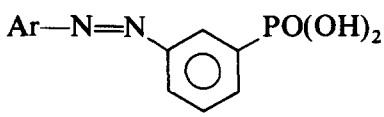
In the past few years there have been several publications relating to phosphonated or carboxylated dyes for use on cellulose, wool and polyamide under acidic dyeing conditions in the presence of a carbodiimide, to give reactive dyeings with significant fixation and dyeings fast to washing under severe conditions.[10–17] Whilst these dyes did not lead to a fully successful conclusion, they gave some valuable indications on the possible use of fibre-reactive dye systems not subject to the limitation caused by hydrolysis. In fact, the phosphonated reactive dyes do not hydrolyse and all the unfixed dye at the end of the dyeing process is still reactive.

In 1977 ICI introduced the Procion T dyes, a new range of liquid reactive dyes, based on a phosphonic acid reactive group.[18] Fixation

takes place under acidic dyeing conditions in the presence of a carbodiimide at about 200 °C. The development of the Procion T reactive dyes is related to the flame-retardant investigations carried out at SRI International[19] with respect to the addition of phosphorus to cellulose during finishing to prevent the loss of the flame-retardant finish during laundering. The use of carbodiimides in the fixation of dyes containing phosphonic or carboxylic groups has been described in a patent.[20] Van Beek and Heertjes described the use of carbodiimides in the fixation of dyes containing COOH, NH_2 or OH groups on protein and polyamide fibres.[21] Recent work on the stability of the dye–fibre bond of Procion T dyes demonstrated that this class of reactive dyes have dye–fibre stabilities in the same range as those of the other major classes of reactive dyes[22] and reflected the high wet-fastness properties of these dyeings. However the mechanism of fixation of Procion T on cellulose is complicated and the role of the carbodiimide present is not fully understood.[10,23]

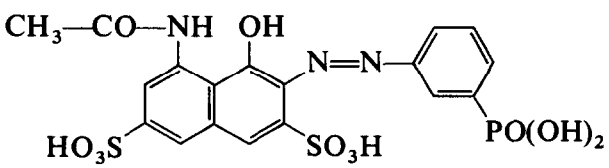
The aim of this present work is to study the fixation of some Procion T phosphonated reactive dyes on cotton in the presence of dicyandiamide under different conditions of dyeing, in order to clarify the role of the carbodiimide in the fixation mechanism.

The dyes used in this study were the following commercial Procion T dyes: Procion Red T-2B, Procion Yellow T-4G, Procion Scarlet T-G, Procion Blue T-G, and Procion Blue T-3GD, which are derived from *m*-aminophenyl phosphonic acid of general structure **I**. The structure of



I

these dyes are not known except for Procion Red T-2B (**II**), which was prepared by diazotizing *m*-aminophenyl phosphonic acid and coupling to *N*-acetyl-H-acid.



Procion Red T-2B

II

2. RESULTS AND DISCUSSION

In order to study the role of dicyandiamide on the fixation mechanism of Procion T dyes on cotton, the latter was padded at 25 °C in a pad liquor containing a variable amount of reactive dye (1%, 2% or 4%) at approximately 75% expression and $NH_4H_2PO_4$ (15 g litre^{-1}); the material was dried for 2 min at 110 °C and thermofixed for 1 min at 210 °C (run 1).

From the results of the dye content, listed in Table 1, it can be seen that in the absence of dicyandiamide the amount of reactive dye fixed on the fibre is very low at all concentrations of dye.

It is known that the dyeing properties of textile materials such as cellulose can be improved by the incorporation therein of a product obtained by reaction of carbodiimide and formaldehyde under acid or

TABLE 1
Dye Content of Dyeings

Dye	*Run*	*Content (g dye/g cotton × 10^3)*		
		Dye in the pad bath		
		1%	*2%*	*4%*
Procion Red T-2B (λ_{max} 526 nm)	1	0·162	0·315	0·521
	2	1·26	3·85	4·97
	3	4·54	5·92	12·9
	4	4·98	6·32	14·3
Procion Yellow T-4G (λ_{max} 430 nm)	1	0·132	0·291	0·493
	2	1·97	3·05	4·50
	3	3·21	5·70	10·9
	4	3·41	6·02	11·5
Procion Scarlet T-G (λ_{max} 504 nm)	1	0·181	0·385	0·790
	2	1·57	3·94	6·02
	3	5·61	7·82	18·2
	4	6·12	8·51	19·1
Procion Blue T-G (λ_{max} 650 nm)	1	6·52	12·8	7·94
	2	9·71	20·0	30·7
	3	12·1	24·4	47·5
	4	12·9	25·7	50·1
Procion Blue T-3GD (λ_{max} 610 nm)	1	0·310	0·742	1·82
	2	3·23	6·13	8·42
	3	6·24	17·3	34·4
	4	6·81	18·5	36·3

neutral conditions.[24] The material is impregnated with a solution containing the carbodiimide and formaldehyde maintained slightly acid and then subsequently dried and heated to cause condensation. This process increases the affinity of the fibre for substantive, sulphur, vat and azoic dyes. Cotton padded in a bath containing dicyandiamide (3%) and formaldehyde (4%) at 25 °C was then dried for 2 min at 110 °C and baked for 1 min at 210 °C. The fibre was then padded again in the pad bath used in run 1 (run 2). The results listed in Table 1 indicate that the amounts of reactive dye fixed on the fibre are higher than those of run 1.

In run 3 the method recommended by Graham was used:[10] cotton was padded at 25 °C in a pad liquor containing a variable amount of reactive dye (1%, 2% or 4%) at approximately 75% expression, dicyandiamide (30 g litre^{-1}) and $NH_4H_2PO_4$ (15 g litre^{-1}); the material was dried for 2 min at 110 °C and thermofixed for 1 min at 210 °C. The results reported in Table 1 indicate that the amounts of reactive dye fixed on the fibre are higher than those obtained in runs 1 and 2, demonstrating that the dicyandiamide is necessary in the dyebath for high fixation of dye on the fibre.

It has been reported that the concentration of dicyandiamide required in the pad bath for effective dye fixation is 30 g litre^{-1}.[10] This represents a very high concentration of carbodiimide relative to dye in the bath and in the fibre, but there is some evidence of loss of dicyandiamide under high temperature conditions. Some carbodiimides are known to either decompose or polymerize on heating.[25] Sugino[26] has reported the mechanism of the reaction between dicyandiamide and ammonium salts. A monoacid salt of biguanidine was formed when dicyandiamide was melted with an ammonium salt that is decomposed slowly at low temperatures, rapidly at high temperatures and instantaneously at about 200 °C. Kobayashi[27] studied the reaction of dicyandiamide with $NH_4H_2PO_4$. It was found that most of the phosphate was converted into condensed phosphates and 70–80% of the dicyandiamide was converted into guanidine. Then, after the normal process of thermofixation, a significant amount of the dye in the fibre can be still capable of reacting with the fibre if additional dicyandiamide is present. Cotton was then padded using a pad liquor as in run 3. The baked fibre was padded again in a solution containing dicyandiamide (30 g litre^{-1}) and $NH_4H_2PO_4$ (15 g litre^{-1}), dried for 2 min at 110 °C and baked again for 1 min at 210 °C (run 4). The results shown in Table 1 indicate that the amount of fixed dye is about 10% higher than that of run 3, demonstrating that unfixed dye in the fibre is

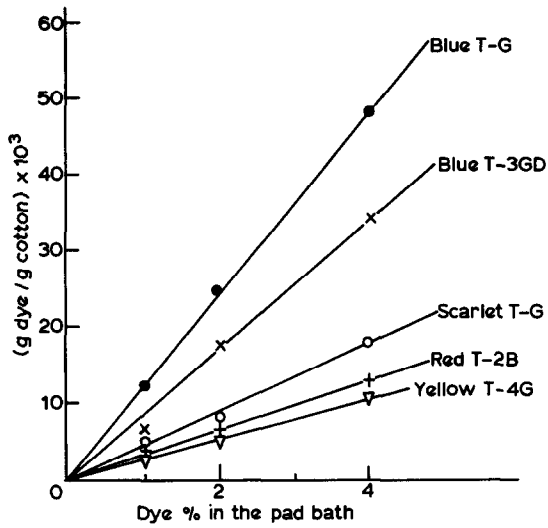
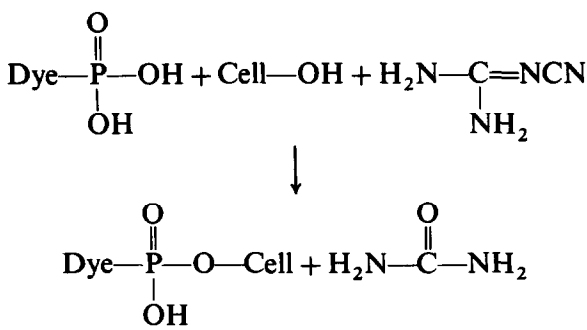


Fig. 1. Dye content of dyeings against percentage of dye in the pad bath.

still capable of reacting with the fibre in the presence of additional dicyandiamide.

As previously found by Graham,[10] the results reported in Table 1 at different dyebath concentrations show that the fixation of phosphonated reactive dyes on cotton is proportional to dyebath concentration. The structure of reactive dye also influences the efficiency of fixation, as has been reported by Zollinger.[22] In Fig. 1 the dye content on the fibre obtained in run 3 against the concentration of dyebath for the different Procion T dyes studied here is shown.

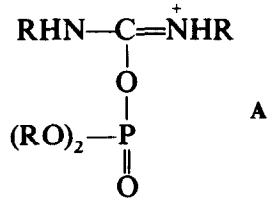
The reaction between a phosphonic dye and cellulose in the presence of dicyandiamide may be described in an overall equation[10,23] (**Scheme 1**).



Scheme 1

The reaction is considered to be an initial condensation of the phosphonic dye with dicyandiamide to produce a phosphonic acid anhydride, followed by subsequent reaction with cellulose to give a dye covalently bonded to the cellulose chain.

In the reaction of carbodiimides with phosphonic acids it was observed that the first step is almost certainly the formation of a cation of type **A**,



A

which is further attacked by a second phosphate anion to yield urea and pyrophosphate.[25,28] The rate of formation of the cation is a function of the strength of the acid employed.[25,29] Isolation of the intermediate **A** was not possible.[30]

The exact role of the carbodiimide in the process of dye fixation into the fibre, as well as the exact nature of the reaction products, has not been explained. It is not essential to assume anhydride formation to explain the end result. Graham[10] supposed the formation of an adduct of type **A** between the carbodiimide and the phosphonic dye that then reacted with cellulose to give the dye covalently bonded to the cellulose.

In order to study the reaction mechanism of phosphonated dyes on cotton (cellulose), chromatographic studies on paper (cellulose) were carried out on Red T-2B. Ascending chromatography on Whatman No. 1 paper with an eluent consisting of isoamyl alcohol, pyridine, acetic acid and water (4:8:1:4, v/v) was used. Various solutions of Red T-2B were prepared and the corresponding R_f values were measured (Table 2). All four solutions showed the same R_f values. The possible formation of the

TABLE 2
Paper Chromatographic Studies on Procion Red T-2B

	Solution	R_f
1	Dye (4 g litre^{-1})	0·36
2	Dye (4 g litre^{-1}) + $NH_4H_2PO_4$ (15 g litre^{-1})	0·36
3	Dye (4 g litre^{-1}) + dicyandiamide (30 g litre^{-1})	0·36
4	Dye (4 g litre^{-1}) + dicyandiamide (30 g litre^{-1}) + $NH_4H_2PO_4$ (15 g litre^{-1})	0·36

adduct between the phosphonic dye and dicyandiamide is thus not evident by means of such paper chromatography tests.

Spots of the four solutions on paper were heated at 210 °C for 1 min. The chromatogram of these spots showed that at 210 °C the phosphonic dye reacts with cellulose. In fact the spots of the solutions remained on the starting line, indicating that the dye had reacted with cellulose. Only a very small part of dye was fixed on the cellulose with solutions 1 and 2, as was found in the fixation studies. With solutions 3 and 4 almost all the dye reacted with cellulose and only a small amount of unreacted dye was still present. The amount of fixed dye with solutions 3 and 4 was almost the same, indicating that the presence of the dicyandiamide is necessary to fix the phosphonic dye on cellulose. The solution 4 was then evaporated under reduced pressure and the residue heated at 110 °C for 2 min; part of the residue was treated with water and the chromatogram of the spot showed an R_f value of 0·36, indicating that all the dye was unchanged up to this temperature. A further part of the residue was heated at 210 °C for 1 min. The chromatogram of the aqueous solution showed the presence of unreacted dye ($R_f = 0{\cdot}36$), one main component with R_f 0·20 and a trace of another component with R_f 0·13, indicating that at temperatures between 110 ° and 210 °C products of condensation of the reactive dye are formed. The spot of the aqueous solution of the compound obtained at 210 °C was baked again at 210 °C for 1 min and the chromatogram showed that the intensity of the spots diminished and only one spot remained on the baseline, indicating that at 210 °C reaction between phosphonic dye and cellulose occurs. The spot of the aqueous solution of the compound obtained at 210 °C to which additional dicyandiamide had been added was baked at 210 °C and the chromatogram then showed only a spot on the baseline, indicating that all the phosphonic dye had reacted with the cellulose.

Thin-layer chromatography on silica gel of the aqueous solution of the dye, using the same eluent as above, showed only one compound with R_f 0·33. The chromatogram on silica gel of the residue of solution 4 (Table 2) heated at 210 °C for 1 min showed the presence of unreacted dye (R_f 0·33), one component with R_f 0·18 and a trace of another component with R_f 0·12. The compound with R_f 0·18 was isolated by means of column chromatography on silica gel (70–230 mesh ASTM) with the same eluent as above. The IR spectrum (KBr disc) of the compound so isolated was different from that of Procion Red T-2B in the spectral region 950–750 cm^{-1}, showing absorption bands at 922 and 756 cm^{-1} characteristic of the P—O—P linkage (Fig. 2). It is known that the organic esters

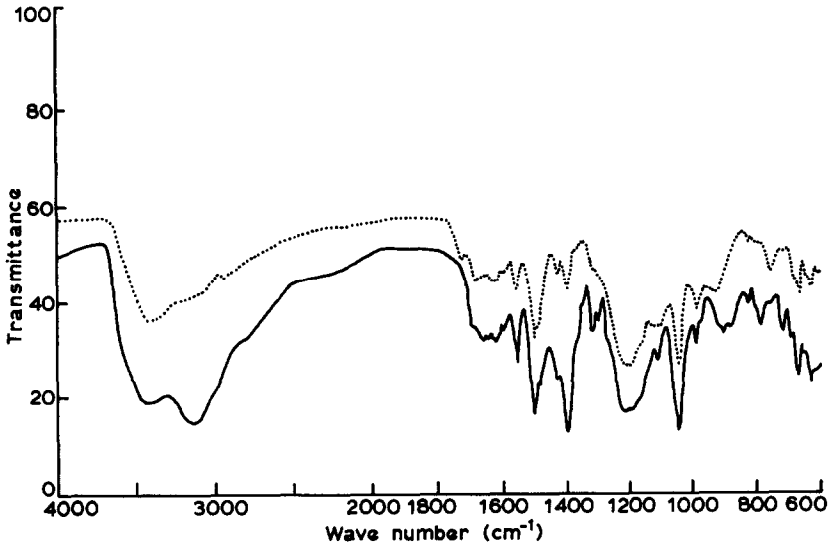
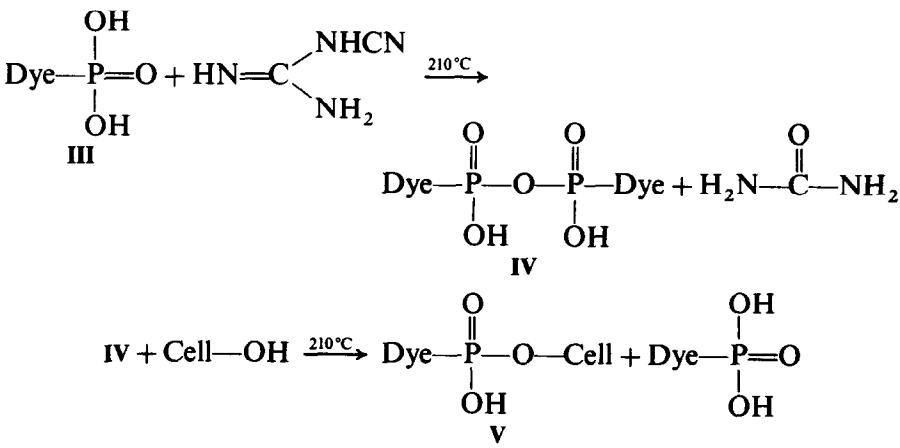


Fig. 2. Infrared spectrum of Procion T Red-2B (———) and of product of condensation (IV) (·····) in KBr pellets.

of phosphorus containing compounds with a P—O—P linkage are characterized by the presence of absorption bands in the spectral region 980–900 cm^{-1} [29,31-4] and also near 750 cm^{-1}.[33] Infrared analysis of the compound with R_f 0·12 was not possible because of the presence of overlapping bands.

The chromatographic studies indicate that the reaction mechanism between phosphonic dye and cellulose in the presence of dicyandiamide can be represented[23] by Scheme 2. Product **IV** is formed when the



Scheme 2

phosphonic dye is heated at 210 °C in the presence of dicyandiamide. Product **IV** reacts at 210 °C with cellulose to give **V**.

From studies on the preparation of tetraesters of pyrophosphoric acid from diesters of phosphoric acid by means of exchange reactions,[35] it is evident that the pyrophosphate **IV** is converted by cellulose into compound **V**. Compound **V** is more stable than **IV**, because the phosphonic dye is a stronger acid than Cell—OH and in consequence the derived anhydride is less reactive, and more stable than that formed by two moles of phosphonic dye.

3. EXPERIMENTAL

Materials

All dyes used were commercial phosphonated Procion T dyes, supplied by ICI. They were derived from *m*-aminophenyl phosphonic acid and were of general structure **I**. Their structures were not known precisely except for Procion Red T-2B, **II**. This was prepared by diazotizing the *m*-aminophenyl phosphonic acid,[36] coupling with acetyl-H-acid (commercial Bayer product), acidifying to pH 0·5 with HCl, isolating, drying at 50 °C under vacuum, dissolving in CH_3OH–H_2O and passing through an ion exchange in the acid form.[37] The UV (H_2O) and IR (KBr) spectra of the compound so prepared was similar to that of commercial Procion Red T-2B.

All measurements were carried out using the dyes in the form of free acids. The UV absorption of the dyes in H_2O is shown in Table 1. Dicyandiamide was the commercial Aldrich product.

Dyeings

The Procion T dyes were applied to pure cotton cloth by the methods described. The sequence of the colouration process was:

$$\text{Pad} \rightarrow \text{dry} \rightarrow \text{thermofixation} \rightarrow \text{wash-off} \rightarrow \text{dry}$$

Padding on cotton was carried out at approximately 75 % expression.

In order to determine the amount of the chemically bonded dye, the padded cotton was washed in water at 50 °C for 10 min to remove all the unreacted dye, rinsed in cold water and dried. The dye content of the

washed dyeings was determined by dissolution of the cotton in 95% sulphuric acid at 0–5 °C. After 2 h the solution was diluted with water and the dye content of the solutions was determined spectrophotometrically at the wavelengths reported in Table 1, comparing the OD with that of test solutions containing undyed cotton.

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