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The estimation, with titanium (III) chloride, of azo dyes containing a 3-carboxypyridinium group

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Abstract

The strengths of a number of monoazo dyes, each containing a (3-carboxypyridinium) triazinyl reactive group, were assessed by titrimetric reduction of the azo groups with a standard solution of titanium (III) chloride. The results obtained by this method initially appeared at variance with those by elemental analysis and to indicate that the strengths of the samples were greater than 100%. Further investigation revealed that the 3-carboxpyridium quaternary salt itself, in addition to the azo group, was being reduced, probably to an *N*-triazinyl dihydropyridine.

Keywords: Reactive dyes; Titanium (III) chloride; Reduction; *N*-Triazinyl-3-carboxypyridinium salts

1. Introduction

Several analytical methods have been described for determining the purity, or effective agent content, of dyes: however, there is no single procedure applicable to all types of dye. Most methods are based on reduction, oxidation or precipitation reactions and include the following [1].

(a) Reduction with titanium (III) chloride (titanous chloride).
(b) Oxidation with acidic potassium dichromate.
(c) Oxidation with cerie sulphate in acid solution.
(d) Acid–base titration; for example, of acid dyes with basic compounds.
(e) Absorptiometric analysis.

Of these methods, reduction with titanium (III) chloride is the most widely used. However, this reagent suffers from two main disadvantages [2–4]. Sometimes reduction of the dye being estimated can be slow and thus accurate detection of the true end point may be difficult. Also, titanium (III) chloride in aqueous solution is readily oxidised by oxygen and thus solutions of this reagent must be stored under an inert atmosphere such as carbon dioxide. This tendency to undergo facile oxidation makes it necessary to assess the strength of the titanium (III) chloride immediately before use [2–4]. Oxidation with potassium dichromate is also commonly used for the determination of dye strength [5], however the apparatus is more complex and requires a highly experienced operator. Again elimination of air from the apparatus is essential to avoid error and ensure consistent results. Oxidation with eerie sulphate is a clean and simple method, but is not widely applicable [6]. Absorptiometric analysis can give relative values only, for accurate quantitative

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analysis a sample of pure product is required for comparison [1].

Other methods include elemental analysis [5]; however, this is generally used simply to confirm the structure of pure samples. Ash determination [7] and flame photometry [8] are also used to obtain very accurate results but require pure control samples. By contrast, reduction with titanium (III) chloride is a simple, economic and reliable method of determining the effective agent content of azo dyes. Ebelmen discovered, in 1847, that titanium (III) chloride reduces copper and iron to their lowest states of oxidation [9]. Knecht first used titanium (III) chloride for the quantitative analysis of dyes in 1903 [10–14]. Knecht and Hibbert [4] described a series of analytical applications of titanium (III) chloride and the subject was subsequently reviewed, over the period 1903 to 1960 [15].

Nowadays, the titrimetric estimation of azo dyes with titanium (III) chloride is widely used to determine the purity of azo dyes. Using this method, each mole of azo group is reduced to two amino aryl residues with the formal uptake of four moles of hydrogen. However, there have been no reports of the use of this reagent for the analysis of dyes containing a pyridinium triazinyl reactive group (Fig. 1). The use of quaternary ammonium triazinyl derivatives as reactive groups for cellulose, especially those derived from 3-carboxypyridine, nicotinic acid, has been widely reported [16–20] and bis(3-carboxypyridinium)triazines [21–24], prepared by quaternisation of 3-carboxypyridine with bis(monochlorotriazines) have been commercialised (Kayacelon React dyes).

The present paper describes the estimation of the strength of monoazo dyes which contain a (3-carboxypyridium-)-*s*-triazinyl reactive group, with titanium (III) chloride, and reports that the reactive group itself is rapidly reduced with this reagent.

2. Experimental

Elemental analyses for carbon, hydrogen, nitrogen and sulphur were carried out using a Carlo Erba 1108 elemental analyser. UV/visible spectra of aqueous solutions of dyes were recorded using 1-cm cells and a Phillips PU 8700 spectrophotometer. All samples were essentially pure organically as judged by h.p.l.c and t.l.c. High performance liquid chromatography analyses were performed using a Hewlett-Packard 1100 liquid chromatograph with a 10 cm. Purospher RP-18 (5jLLm) packing and a LiChroCART 125-4 HPLC column cartridge. The mobile phase was 0.25% CHAP solution (dicyclohexylammonium phosphate)/acetonitrile (70/30). Thin layer chromatography was conducted using aluminium plates coated with silicagel 60 F 54 (Merck): the eluent was *iso*-butanol:*n*-propanol:ethyl acetate:-water (2:4:1:3).

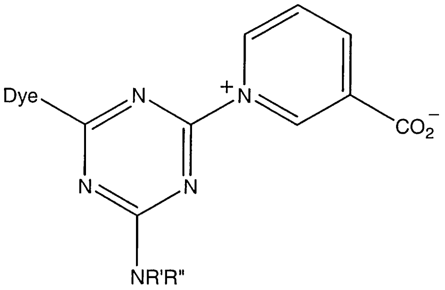


Fig. 1.

2.1. Preparation of dyes

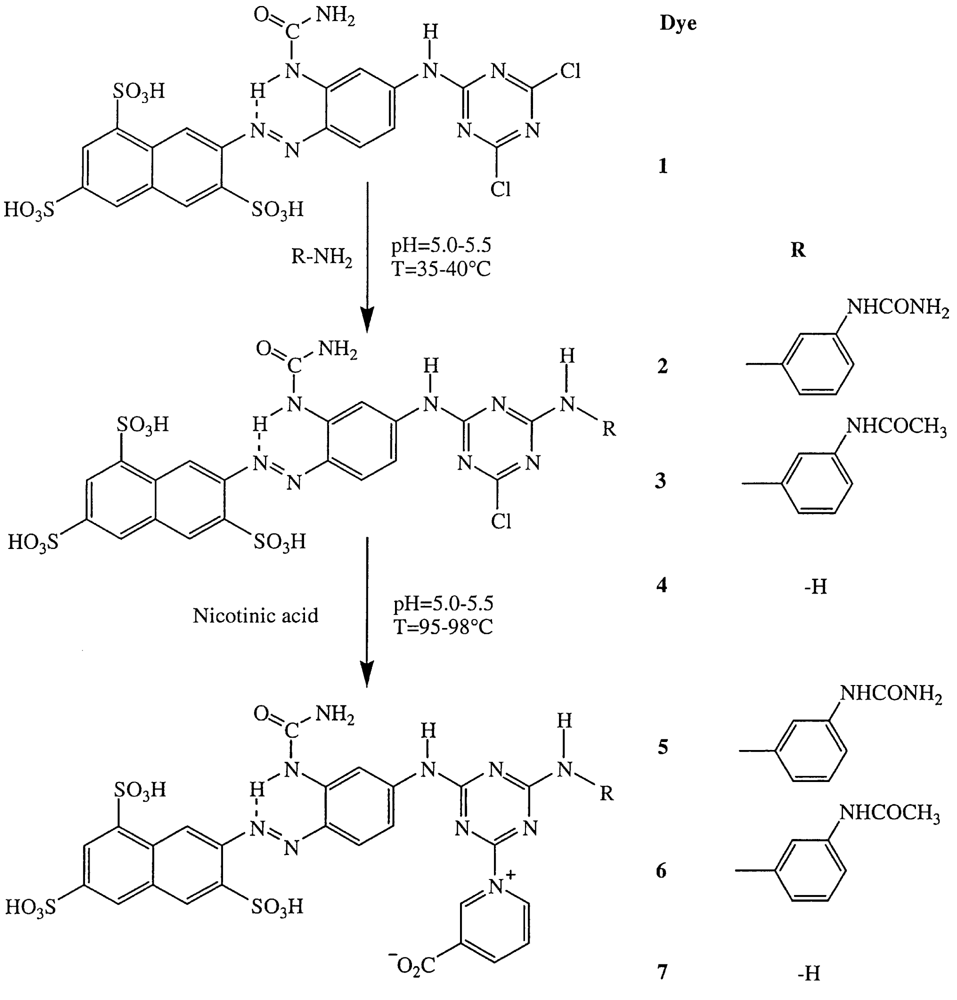
The dichlorotriazinyl dye, **1**, was selected as the starting point for the preparation of the yellow quaternary salts **5–7**. This was readily prepared by coupling the diazonium salt derived from 2-aminonaphthalene-3,6,8-trisulphonic acid onto *m*-ureideoaniline and reacting the resulting dyebase with cyanuric chloride. This in turn was converted to the monochlorotriazines **2–4** which, on treatment with 3-carboxypyridine, furnished the desired quaternary salts as depicted in Scheme 1.

2.1.1. Sodium salt of 4-(3,6,8-trisulphonaphth-2-ylazo)-2-ureido-N-(6-[m-ureidophenylamino]-4-[3-carboxypyridinium]-[1,3,5]-triazin-2-yl) aniline (5)

Freshly prepared 4-(3,6,8-trisulphonaphth-2-ylazo)-3-ureido-*N*-(4,6-dichlorotriazinyl)-aniline (**1**, 39.5 g, 0.025 mole, M.I. = 1580) was dissolved in distilled water (200 ml) with stirring. The resulting solution was added to 3-ureidoaniline (66%, 6 g, 0.026 mole) and the pH was adjusted to 6.5. The mixture was stirred at this pH and 35–40 °C for 2 h, with control by t.l.c. The resulting precipitated product was collected and dissolved in distilled water (200 ml) together with nicotinic acid (99%, 4.61 g, 0.0375 mole). The mixture was stirred for 3 h at pH 5.5 and 95–98 °C. After cooling to room temperature sodium chloride (20% w/v) was added with stirring. The resulting precipitated solid was collected and dried. Yield 15.41 g (54%), M.I. (by titration vs. $TiCl_3$) 1134; λ_{max} (water) 424 nm; ε_{max} 27,910 $mole^{-1}\,cm^{-1}\,l$.

2.1.2. Sodium salt of 4-(3,6,8-trisulphonaphth-2-ylazo)-2-ureido-N-([6-m-acetylamino phenylamino-]-4-[3-carboxypyridimum])-[1,3,5]-triazin-2-yl-aniline (6)

This material was prepared by a procedure similar to that described for **5**. Yield 15.25 g (55%), M.I. = 1112; λ_{max} (water) 426 nm; ε_{max} (water) 27,660 $mole^{-1}\,cm^{-1}\,l$.



Scheme 1.

2.1.3. *Sodium salt of 4-(3,6,8-trisulphonaphth-2-ylazo)-2-m-ureidophenyl-N-(6-amino-4-[3-carboxypyridinium])-[1,3,5]-triazin-2-yl-aniline (7)*

4-(3,6,8-Trisulphonaphth-2-ylazo)-2-*m*-ureidophenyl-*N*-(6-amino-4-chlorotriazin-2-yl)aniline, Procion Yellow P-3R, (24.75 g, 0.015 mole, M.I. = 1650) was dissolved in distilled water (300 ml) with stirring. Nicotinic acid (99%, 2.46 g, 0.02 mole), was added, the pH was adjusted to 5.5 with sodium carbonate and the temperature raised to 95–98 °C. After 3 h the reaction was essentially complete, the solution was allowed to cool to room temperature and sodium chloride (20% w/v) was added with stirring. The resulting precipitated solid was collected and dried. Yield 13.18 g (79%), M.I. by TiCl$_3$ 1112; Mass (MALDI) m/z 759(M+); $\lambda_{\max}$ (water) 431 nm, $\varepsilon_{\max}$ (water) 30,400 mole^{-1} cm^{-1} l.

2.2. *Desalination of dyes*

After isolation, a sample (2 g) of each dye was dissolved in distilled water (50 ml) and desalinated by dialysis using Visking tubing. The tubing containing the dye solution was put in a 2000 ml beaker containing distilled water (ca. 500 ml). The water in the beaker was changed periodically (ca. every 15 min) until chloride ions could no longer be detected, with silver nitrate, in the eluate. The sample was then removed from the Visking tubing and water removed under reduced pressure, the resulting solid was dried in an oven at less than 50 °C.

3. Results and discussion

3.1. *Estimation of dye strength (M.I.)*

Usually water-soluble dyes synthesised and isolated under laboratory conditions contain water and inorganic salts. The strength or effective agent content of such dyes is often described in terms of Mole In (M.I.). This is defined as the number of grams of material which contains one mole of dye. For example, if a technical grade sample of dye of molecular weight 500

(M.W. = 500) is of 50% effective agent strength, then the M.I. of the sample is 1000.

3.2. Titration using titanium (III) chloride

Titanium (III) chloride, when used as a reducing agent, itself undergoes oxidation.

$$Ti^{3+} \rightarrow Ti^{4+} + e^-$$

Nitro-, nitroso-, azo-compounds, quinones; indophenols and many dyes such as indigo, triarylmethane and azo dyes can be reduced with titanium (III) chloride.

Examples are depicted below [4,14,15,25,26].

$$R{-}NO + 4H^+ + 4Ti^{3+} \rightarrow 4Ti^{4+} + R{-}NH_2 + H_2O$$

$$R{-}NO_2 + 6H^+ + 6Ti^{3+} \rightarrow 6Ti^{4+} + R{-}NH_2 + 2H_2O$$

$$R_1{-}N{=}N{-}R_2 + 4H^+ + 4Ti^{3+} \rightarrow 4Ti^{4+} + R_1{-}NH_2 + R_2{-}NH_2$$

$$\text{Quinones} + 2H^+ + 2Ti^{3+} \rightarrow 2Ti^{4+} + \text{Hydroquinones}$$

$$\text{Dyes} + xH^+ + Ti^{3+} \rightarrow xTi^{4+} + \text{Leucocoumpounds}$$

Reduction of a monoazo dye with titanium chloride can be depicted as follows ($R_1\backslash R_2$ = [hetero] aromatic group).

$$\begin{array}{lcll}
4T\,i^{3+} & \rightarrow & Ti^{4+} + 4e^- & (1) \\
R_1\text{-}N{=}N\text{-}R_2 + 4\,H^+ + 4e^- & \rightarrow & R_1\text{-}NH_2 + R_2\text{-}NH_2 & (2) \\
\hline
R_1\text{-}N{=}N\text{-}R_2 + 4Cl^{3+} + 4H^+ & \rightarrow & 4\,Ti^{4+} + R_1\text{-}NH_2 + R_2NH_2 & (1)+(2)
\end{array}$$

The reduction of one mole of a monoazo dye thus formally requires four gram atoms of hydrogen; that is, the azo group has a hydrogen factor of 4.

3.3. Estimation of dye strength

A dye of known strength was titrated against a solution of titanium (III) chloride in order to determine the strength (titanous factor, Tf) of the titanium (III) chloride solution immediately before use. The sample of dye of unknown strength (ca. 0.2 g) was dissolved in distilled water (100 ml) in a conical flask together with potassium sodium tartrate buffer (20%, 20 ml). The contents of the flask were heated to boiling and then titrated against freshly standardised titanium (III) chloride solution (ca. 0.1 N). The results were taken as the mean of three readings. The M.I. was calculated as described below.

3.4. Calculation

A standard sample of dye, ca. 0.2 g, of known M.I. and structure, was dissolved in water (100 ml) in a conical flask (fitted with a side tube filled with solid carbon dioxide). Potassium sodium tartrate buffer (20%, 20 ml) was added. The contents of the flask were heated to boiling and then titrated against titanium (III) chloride solution. The results were taken as the mean of three readings. Formula (1) was used to determine the titanous factor (Tf), related to the strength of the titanium (III) chloride solution.

$$\text{Titanous factor (Tf)} = \frac{\text{Weight taken (g)} \times \text{Hf} \times 10{,}000}{\text{Volume of titre (ml)} \times \text{M.I.}} \tag{1}$$

The procedure was repeated titrating a solution containing a known weight of the speculative dye of unknown strength against the freshly standardised titanium (III) chloride solution. The M.I. of the speculative dye was calculated using Formula (2)

$$\text{M.I.} = \frac{\text{Weight taken (g)} \times \text{Hf} \times 10{,}000}{\text{Volume of titre (ml)} \times \text{Tf}} \tag{2}$$

where

M.I. = Mole In, i.e. the number of grams of dye containing one mole of dye.
Hf = Hydrogen factor, i.e. the number of gram atoms of hydrogen formally required to reduce one mole of dye. For one azo bond the Hf is 4, for two azo bonds the Hf is eight and so on.
Tf = Titanous factor.

The strength of dyes was calculated by applying Formula (3).

$$\text{Strength (\%)} = \frac{\text{Molecular weight of dye}}{\text{M.I.}} \times 100 \tag{3}$$

Initially, the effective agent contents of the monoazo yellow dyes **5–7**, which had not been subjected to a desalination procedure, were assessed by titration against titanium (III) chloride, assuming a hydrogen factor of 4 for each dye. It was noted that the Mole In (M.I.), as determined by this method, was less than the molecular weight. This is clearly impossible and prompted further evaluation of the method. The dye structures, estimated M.I. values and calculated molecular weights are listed in Fig. 2.

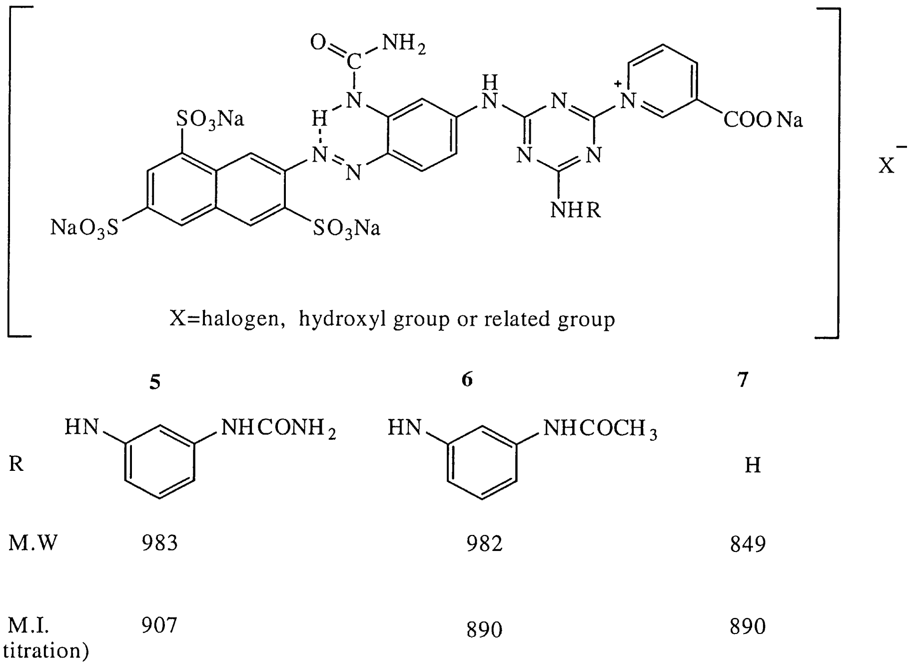


Fig. 2. Dye structures and the results of M.I. calculations.

In an attempt to explain these observations, samples of each of these dyes were re-precipitated carefully from aqueous solution with sodium chloride. This technique furnished dyestuffs which were essentially pure, organically, but which were still contaminated with inorganic salt and water. The samples so obtained were desalinated and isolated as described above. Microanalysis results are listed below.

3.4.1. Product 5

Molecular formula $[C_{33}H_{23}N_{12}Na_4O_{13}S_3]^+X^-$. M.W. = 983 + X.
Elemental analysis: found C = 37.5%; H = 2.75%; N = 16.1%.
$[C_{33}H_{23}N_{12}Na_4O_{13}S_3]^+OH^-\cdot 3H_2O$ requires C = 37.57%; H = 2.94%; N = 15.93%.

If a hydrogen factor of 4 is assumed for the titration against titanium (III) chloride the calculated M.I. value is 844. If a hydrogen factor of 5 is assumed for the titration against titanous chloride the calculated M.I. value is 1055 which is in excellent agreement with a compound of molecular formula $[C_{33}H_{23}N_{12}Na_4O_{13}S_3]^+OH^-\cdot 3H_2O$, molecular weight 1054.

3.4.2. Product 6

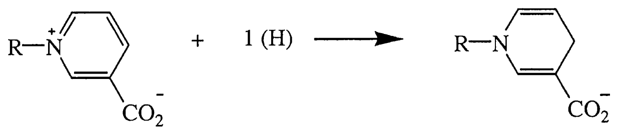
Molecular formula $[C_{34}H_{24}N_{11}Na_4O_{13}S]^+X^-$. M.W. = 982 + X.
Elemental analysis: found C = 41.15%; H = 2.15%; N = 15.35%; S = 9.45%.
$[C_{34}H_{24}N_{11}Na_4O_{13}S]^+OH^-$ requires C = 40.84%; H = 2.50%; N = 15.42%; S = 9.61%.

If a hydrogen factor of 4 is assumed for the titration against titanium (III) chloride the calculated M.I. value is 829. If a hydrogen factor of 5 is assumed for the titration against titanous chloride the calculated M.I. value is 1036. This is in good agreement with a compound of molecular formula $[C_{34}H_{24}N_{11}Na_4O_{13}S]^+OH^-$, molecular weight 999.

3.4.3. Product 7

Molecular formula = $[C_{26}H_{17}N_{10}Na_4O_{12}S_3]^+X^-$. M.W. = 849 + X.
Elemental analysis: found C = 34.95%; H = 2.90%; N = 15.7%; S = 10.15%.
$[C_{26}H_{17}N_{10}Na_4O_{12}S_3]^+OH^-\cdot 2H_2O$ requires C = 34.58%; H = 2.44%; N = 15.52%; S = 10.64%.

If a hydrogen factor of 4 is assumed for the titration against titanium (III) chloride the calculated M.I. is 727.



Scheme 2.

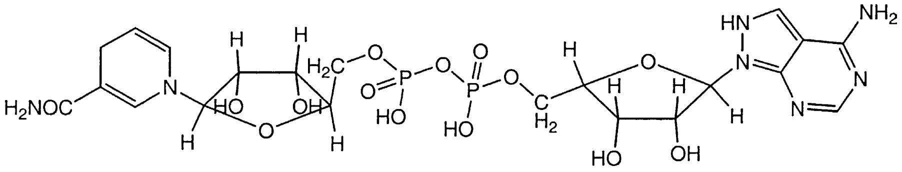


Fig. 3.

If a hydrogen factor of 5 is assumed for the titration against titanium (III) chloride the calculated M.I. is 909. This is in excellent agreement with a compound of molecular formula $[C_{26}H_{17}N_{10}Na_4O_{12}S_3]^+OH^- \cdot 2H_2O$, molecular weight 902.

These results suggest that the mono-(3-carboxypyridinium)triazine group is itself being reduced during titration against titanous chloride. This is in keeping with earlier observations on the chemistry of dihydropyridines, especially their preparation by reduction of quaternary salts with sodium dithionite (Scheme 2) [27].

This type of system also occurs naturally in the hydrogen transferring co-enzyme, reduced nicotinamide adenine dinucleotide NADH [28], shown in Fig. 3.

4. Conclusion

The reduction of one mole of an azo group (with titanous chloride) formally requires four gram atoms of hydrogen to effect reduction. This quantity is referred to as the hydrogen factor. It has been demonstrated that reduction of the 3-carboxypyridinium triazinyl group of reactive dyes also occurs in the presence of titanous chloride and that the hydrogen factor for this process is one. If a hydrogen factor of 5 is assumed for a monoazo dye containing a (3-carboxypyridinium)triazinyl reactive group, excellent agreement is obtained between the titrimetric method and elemental analysis. Also, because the discharge of colour from the azo dye always requires an additional one equivalent of titanium (III) chloride, it can be inferred that reduction of the pyridinium salt is at least as fast as that of the azo group.

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