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Reductive Cleavage of Certain Azo Dyes byElectrolytically Generated Vanadium(II) in Aqueous Acid Media

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Vandium(II) species has been electrolytically generated by the reduction of vanadium(V) sulphate over mercury cathode under nitrogen atmosphere and characterised by literature methods. The reductive estimation of certain commercially important azo dyes using V(II) was carried out and the conditions were standardised. The reduction products were identified by TLC-PC methods. The advantages of this method over the Ti(III) reduction have been highlighted.

INTRODUCTION

Azo compounds are an important class of compounds which find a wide range of applications as acaricides, biological stains, analytical indicators, catalysts, dyes and complexing agents[1, 2]. Reductive cleavage of these compounds leads to the formation of primary amines, which have diagnostic importance[3]. The estimation and identification of these amines provides an insight into the structure of the parent molecule. Different reducing agents have been employed by the early workers for the cleavage of azo bonds for synthetic and analytical purposes[4–7]. In the present work, we report an efficient analytical procedure for quantitative estimation of a few azo dyes. The results obtained compare well with those of accepted methods.

V(II) in aqueous acid media has been found to be an efficient reducing agent for a variety of organic as well as inorganic compounds[8]. It can be prepared from the vanadium salts of higher oxidation states either by electroreduction[9] or by chemical reduction using zinc amalgam[10] under nitrogen atmosphere. As a part of analytical and kinetic studies with various metal ion redox systems, we present herein the results of the reduction of certain commercially important azo dyes using V(II) species.

EXPERIMENTAL

Diphenyldiazine (azobenezene, AB), phenylazo-β-naphthol (PABN), 4-(phenylazo)-1,3-benzenediamine (chrysoidine—CD, CI.11270), 4[[(4-dimethylamino)phenyl]azo] benzene sulphonic acid sodium salt (methyl orange, MO, CI13025), 2-[[(4-dimethylamino)phenyl]azo] benzoic acid (methyl red, MR, CI.13020), *p*-(phenylazo) benzenamine (*p*-amino azobenzene, PAAB CI.11000), 2-methyl-4[(2-methylphenyl)azo] benzenamine (*o*-amino azo-toluene-OAAT, CI.11160). 4-[(2-hydroxy, 1-naphthalenyl)azo] benzene sulphonic acid monosodium salt [β-naphtholorange, BNO, CI.15510] were prepared by diazo coupling reaction and purified by literature methods[11, 12]. 1-[[(4-phenylazo)phenyl]azo]-2-

naphthalenol (solvent red-23, SR.23, CI.26100) 1-[(2-methyl-4-[(2-methylphenyl)azo]phenyl]azo]-2-naphthalenol (solvent red-24, SR-24, CI.26105), 3,3′-[[1,1′-biphenyl]-4,4′-diylbis(azo)] bis[4-amino-1-naphthalene sulphonic acid] disodium salt (congo red, CR, CI.22120), 4-[(2,4-dihydroxyphenyl)azo] benzenesulphonic acid monosodium salt [tropaeolin-O-acid orange, AO, CI.14270] were obtained from Konspec Ltd., Mangalore and used without purification.

Assay Method

Titanium(II) chloride was prepared by the method suggested by Ingraham *et al.*[13], and standardised. The absolute strength of the dye sample was determined by the method suggested by Knecht and Hibbert using $TiCl_3$ as the reducing agent[14]. This method has been adopted by the National Formulary, and Biological Stain Commission, U.S.A.[15, 16]

The V(II) solution was prepared, stored and used in the same manner as described in our earlier communication[17]

Determination of Azo Groups

A. Back Titration Method: A known amount of the dye sample was weighed accurately in a four-necked flat-bottomed titration cell, and dissolved in 15 mL of glacial acetic acid. 15 mL of conc. hydrochloric acid and 5 mL of THF were added, and oxygen-free nitrogen gas was bubbled for about 15 min through the solution. A known excess of V(II) solution (V_1 mL, 0.25 mol dm^3) was run down from the burette. The mixture was stirred magnetically till the disappearance of the dye colour. Dearated ammonium iron(III) sulphate solution (V_2 mL, 0.05 mol dm^{-3}) was pipetted out and the resulting mixture was titrated against standard V(II) solution using 10% ammonium thiocyanate as the indicator till the reddish colour changed to clear light green at the end point. A blank titration was performed by taking same aliquot of V(II) against the same titrant (V_3 mL). The whole experiment was carried out under nitrogen blanket. The number of electrons involved in the reaction was calculated by

$$n = \frac{[V_1 - (V_3 - V_2)]M_1}{M}$$

where M_1 is the molar concentration of V(II) in mol dm^{-3} and M is the moles of the substrate used.

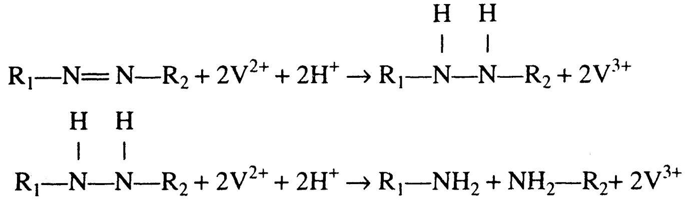
B. Potentiometric Back Titration Method: The titration cell consisted of a flat-bottomed closed vessel of 100 mL capacity with five vents of IC joints for the free flow of oxygen-free nitrogen, for SCE-Pt assembly and for the introduction of the titrant. An Equip-tronic model EQ-600 digital potentiometer was used to measure the potential. A known amount of the dye sample to get about 1 mmol was introduced into the cell and dissolved in 15 mL glacial acetic acid. 15 mL of conc. HCl and 5 mL of THF were added. Nitrogen gas was bubbled through this cell continuously. V(II) solution was introduced into the cell and stirred magnetically until decolouration of the dye. Chloroamine-T (CAT, 0.05 mol dm^{-3}) was added from a microburette in small quantities and the e.m.f. values were noted after each increment of the tittrant. A potential jump of about 350 mV to 750 mV (–ve to +ve) per 0.05 mL of the titrant was observed at the end point. A blank titration was carried out under identical conditions but in the absence of the substrate. The number of electrons involved in the reaction was obtained by

$$n = \frac{(V_1 - V_2)M_1}{M}$$

where M_1 is the molar concentration of the reductant and M is the number of moles of the azo sample used. V_1 and V_2 are volume of the reductant used for the blank and sample respectively.

RESULTS AND DISCUSSION

The azo groups of the dye are quantitatively reduced by V(II) in presence of THF at room temperature to the corresponding amines according to the reaction:



$$R_1—N{=}N—R_2 + 2V^{2+} + 2H^+ \rightarrow R_1—\overset{\overset{H}{|}}{N}—\overset{\overset{H}{|}}{N}—R_2 + 2V^{3+}$$

$$R_1—\overset{\overset{H}{|}}{N}—\overset{\overset{H}{|}}{N}—R_2 + 2V^{2+} + 2H^+ \rightarrow R_1—NH_2 + NH_2—R_2 + 2V^{3+}$$

TABLE-1

Sl. No.	Dye sample	No. of electrons involved in the reaction		
		Theoretical value	Volumetric* n ± sd	Potentiometric* n ± sd
1.	AB	4	4.02	4.01
2.	PABN	4	4.04	4.02
3.	CD	4	4.03	4.01
4.	MO	4	4.04	4.03
5.	MR	4	4.05	4.03
6.	PAAB	4	4.03	4.04
7.	OAAT	4	4.05	4.03
8.	BNO	4	4.05	4.02
9.	SR-23	8	8.08	8.05
10.	SR-24	8	8.09	8.05
11.	CR	8	8.08	8.04
12.	AO	4	4.04	4.03

*Average of six trials.

The reaction between V(II) and the mono azo dyes follow 1 : 4 stoichiometry corresponding to four electron transfer, whereas the diazo dyes follow 1 : 8 stoichiometry. The presence of other susceptible groups such as nitro, nitroso, oxime, azoxy interfere in the analysis. Hence the azo compounds containing these groups in the parent molecule have been avoided. The halogen containing azo dyes do not undergo reduction quantitatively by V(II). This is because V(II), being a typical d^3 ion, is substitutionally inert and the direct transfer of electrons from a V(II) t_{2g} orbital to an antibonding oxidant follows outer-sphere route[18, 19]

The V(II) reduction method for the determination of the absolute strength of the azo compounds is advantageous compared to the accepted method with Ti(III), in that the reduction occurs at room temperature owing to the high redox potential of $[V(THF)_6]^{2+}$ and no need of addition of hydrofluoric acid. The results obtained compare well with the accepted methods.

In the potentiometric method. CAT has been employed as the oxidant for the back titration of V(II) which is quantitative and instantaneous[20]. The oxidant (CAT) does not affect the reduction products in the presence of V^{3+} ions. The results obtained are accurate and reproducible.

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