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Reductive Deoximation of Certain Oximes by Electrolytically Generated Vanadium(II) in Aqueous Sulphuric Acid Media

K. VASANTKUMAR PAI, P. VASUDEVA NAYAK* and B.S. SHEREGARA
Department of Studies in Industrial Chemistry
Kuvempu University, Shankaraghatta-577 451, India

Vanadium(II) species generated by the cathodic reduction of vanadium(II) sulphate using mercury pool cathode under nitrogen atmosphere has been characterised by UV-visible spectra and by the determination of redox potential of V(III)/V(II) couple. The purity of V(II) species has been tested by potentiometric titration with standard cerium(IV) solution where the species gets oxidised to V(V) in three steps corresponding to three equivalent points. The reductive estimation of hydroxylamine hyrochloride and its keto and aldehyde oxime derivatives using V(II) was carried out. The reaction products were isolated, indentified and characterised by the literature methods. The utility of V(II) as a reductant in analytical studies has been highlighted.

INTRODUCTION

Oximes are the derivatives of carbonyl compounds with hydroxylamine or its salts. These are most widely studied for the identification and determination of the parent carbonyl groups.[1] The reduction of oximes proceeds through hydroxylamine to the end product amine. The synthetic applications of the reductive cleavage of oximes by V(II) species have been studied by Olah *et al.*[2] These reductive products occupy a unique position in synthetic organic chemistry and biochemistry. In literature, standard analytical techniques are rarely available for the estimation of industrially important oximes. Hence, in the present work, we report an efficient analytical procedure for the quantitative estimation of a few oximes.

V(II) species in aqueous acid media have been reported to be efficient reducing agents for a variety of organic as well as inorganic compounds.[3, 4] The thermochemistry, electrochemistry, spectroscopic and magnetic properties of vanadium species have been well documented.[5–7] The standard redox potential of V(III)/V(II) couple has been reported to be –0.255 V. V(II) can be prepared from its salts of higher oxidation states by electrolytic reduction[8] or by chemical reduction using zinc amalgam under nitrogen atmosphere.[9] Being a typical d^3 ion, it is kinetically inert but undergoes electron transfer reactions readily.[10]

As a part of analytical kinetic studies with various metal ion redox systems, we present here in the result of reduction of certain oximes with electrolytically generated vanadium(II) sulphate in aqueous sulphuric acid media containing 50% (v/v) ethanol-water.

EXPERIMENTAL

Laboratory grade (E-merck) hydroxylamine hydrochloride (HAH),

α-benzoinoxime (ABO), dimethylglyoxime (DMG), salicylaldoxime (SAO) were used after recrystallizations from alcohol. Acetoxime (AO), cyclohexanoneoxime (CHO), benzophenoneoxime (BPO), vanillinoxime (VO), diacetylmonoxime (DAMO), acetaldoxime (AAO) and furfuraldoxime (FAO) were prepared and purified by literature methods.[11, 12] The purity of these compounds was checked by the determination of m.p./b.p. and by TLC methods.

Vanadium (V) oxide was prepared by heating ammonium metavanadate (Reanal, Budapest) at a temperature of 400°C in a muffle furnace.[13] 4.5 g (0.025 mol) of this oxide, 28 mL of concentrated sulphuric acid and 40 mL of water were stirred, heated on a water bath for 30 min, and diluted to 500 mL with water. This was used for the preparation of V(II) solution. A three-necked kettle of pyrex glass with IC joints was used for the reduction. This arrangement of apparatus based on the work of Piccini[14] with a slight modification ensures air-free conditions. The anolyte, 15 mL of 1 mol dm^{-3} sulphuric acid, was placed in a vertical tube with a sintered glass bottom of 1×10^{-4} m^2 area. The anode was 1.28×10^{-4} m^2 foil of platinum and the cathode was mercury pool.

250 mL of the V(V) solution was charged into the kettle and oxygen-free nitrogen gas was bubbled for 15 min. A current of 2.5 amp at 9 V was applied for 4 h. Since the reduction was exothermic, the kettle was cooled by water during the process.The V(II) solution thus obtained was directly discharged into a burette through the stopcock at the side of the kettle, and standardised by Fe(III) solution volumetrically using thiocyanate ion as the indicator[9] and also by potentiometric titration with Ce(IV) solution using SCE-Pt electrode assembly.[15]

Determination of oximes

A: Black titration method—To a known volume (V_1 mL 0.001 mol dm^{-3}) of the sample in 1 : 1 (v/v) water-ethanol mixture, 25 mL of 1 mol dm^{-3} sulphuric acid solution was added, and a known excess of V(II) solution (V_2 mL 0.005 mol dm^{-3}) was run down from the burette. The mixture was stirred with a magnetic stirrer for about 10 min for the reduction to be completed. Deaerated ammonium(III) sulphate solution (V_3 mL 0.05 mol dm^{-3}) was pipetted out and the resulting mixture was titrated against standard V(II) sulphate solution using 10% ammonium thiocyanate as the indicator till the reddish orange colour changed to clear light green at the end point. A blank titration was performed by taking the same aliquot of V(II) against ammonium iron(III) sulphate solution (V_4 mL). The whole experiment was carried out under nitrogen blanket. The number of electrons involved in the reaction was calculated as under:

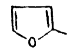
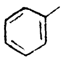
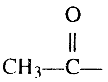
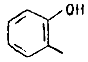
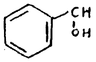
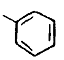
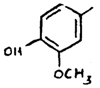
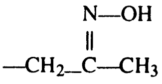
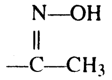
$$n = \frac{\text{number of moles of the reductant}}{\text{number of moles of the substrate}}$$

$$= \frac{[V_2 - (V_4 - V_3)]M_2}{V_1 M_1}$$

where M_1 and M_2 are the molar concentration of V(II) and substrate, respectively. The results are presented in Table-1.

TABLE-1

REDUCTION OF CERTAIN OXIMES BY V(IV) IN 1 MOL DM^{-3} AQUEOUS SULPHURIC ACID MEDIA AT 25°C

Substrate*	R_1	R_2	Product	No. of electrons in redox reaction			Maximum Percentage error
				Theoretical	Found± SD†		
					Titrimetic	Potentiometric	
1. HAH			Ammonia	2	1.98±0.02	1.99±0.01	1.00
(A) Monoximes							
2. AO	CH_3—	—CH_3	Amine	4	3.98±0.01	1.99±0.01	1.00
3. CHO		—	Amine	4	3.97±0.02	1.99±0.01	1.25
4. A'AO	CH_3—	—H	Amine	4	4.01±0.02	3.99±0.02	0.50
5. FAO		—H	Amine	4	3.99±0.03	3.99±0.01	0.75
6. BPO			Amine	4	3.96±0.04	3.99±0.01	0.75
7. DAMO	 $CH_3—C(=O)—$	—CH_3	Amine	4	3.94±0.03	3.99±0.01	1.50
8. SAO		—H	Amine	4	3.95±004	3.98±0.02	1.00
9. VO			Hydroxylamine	2	1.98±0.03	1.99±0.02	2.00
10. ABO		—H	Hydroxylamine	2	1.99±0.01	1.98±0.01	1.50
(B) Dioximes							
11. AADO	CH_3—	 $—CH_2—C(=N—OH)—CH_3$	Diamine	8	8.02±0.02	8.00±0.02	1.25
12. DMG	CH_3—	 $—C(=N—OH)—CH_3$	Diamine	8	7.97±0.03	7.99±0.03	1.25

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 the Pt-SCE assembly and for the introduction of the titrant. An Equip-Tronic model Eq-600 digital potentiometer was used to measure the potential. The cell was charged with 50 mL of 1 mol dm^{-3} sulphuric acid and 20 mL of 1 mol dm^{-3} of KCl solution. Nitrogen gas was bubbled through the solution continuously. V(II) solution (10 mL, 0·025 mol dm^{-3}) was introduced into this cell followed by a known volume of the substrate (2.5 mL, 0.01 mol dm^{-3}). This mixture was stirred magnetically and deaerated chloramine-T(CAT) solution (0.05 mol dm^{-3}) was added in small quantities and the emf values were noted after each increment of the titrant. A potential jump of 350–750 mV (–ve potential 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 end point was determined graphically. The number of electrons involved in the reaction were obtained from:

$$n = \frac{(V_2 - V_3)M_2}{V_1M_1}$$

where M_1 and M_2 are the molar concentration of the substrate and CAT respectively, V_1 = volume of the substrate, V_2 = volume of the CAT for blank titration and V_3 = volume of CAT in back titration.

The results of the experiments are reported with various amounts of oximes used in Table-1.

RESULTS AND DISCUSSION

The solution of V(II) in aqueous sulphuric acid has been found to be stable for several days under nitrogen atmosphere. The formal redox potential of V(III)/V(II) couple in 1 mol dm^{-3} sulphuric acid media has been found to be -0.152 ± 0.003V at 25°C indicating that it is a good reducing system.

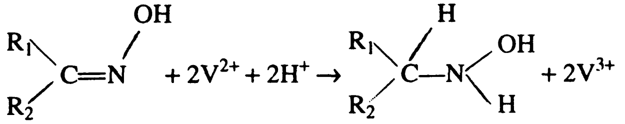
The reduction of HAH by V(II) was instantaneous with 1 : 2 stoichiometry corrosponding to two electron change.

$$H_3N^+OH + 2V^{2+} + 2H^+ \rightarrow NH_4^+ + 2V^{3+} + H_2O$$

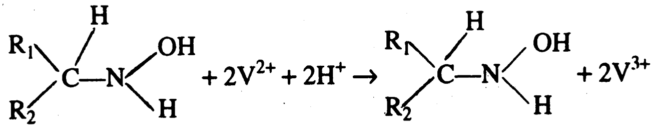
The presence of NH_4^+ was detected by Nessler's test. The reaction proceeds through the formation of NH_2 free radical as an intermediate which was confirmed by the vinyl polymerization of methyl methacrylate.

The reduction of eleven oximes with vanadium(II) was carried out. In general, the reaction stoichiometry with mono-oximes was found to be 1 : 4 corresponding to four electron change resulting in the formation of corresponding mono-amines via hydroxylamine formation. The amines were isolated and characterised by the m.p./b.p. of the products and m.p. of their solid derivatives.

The general reaction mechanism has been proposed as under:



$$R_1R_2C{=}NOH + 2V^{2+} + 2H^+ \rightarrow R_1R_2C(H){-}N(OH)H + 2V^{3+} \quad (i)$$



(ii)

However, in case of VO and ABO the reaction stoichiometry has been found to be 1 : 2 corresponding to two electron change. The reduction of these oximes resulting in the formation of hydroxylamime as the end product was indicated by the formation of silver mirror with Tollen's reagent and by the formation of red precipitate with Fehling's solution.

With dioximes the reaction stoichiometry was 1 : 8 corresponding to eight electron change resulting in the formation of corresponding diamines. The reaction products, diamines could not be isolated as they form hygroscopic sulphates. They were characterised based on the m.p. of their diacetyl derivatives. The end products and their m.p./b.p. of the solid derivatives have been presented in Table-2.

TABLE–2
PHYSICAL CONSTANTS OF THE OXIMES, REDUCTION PRODUCTS AND THEIR DERIVATIVES

Oxime	(m.p./b.p.) °C	Product	(m.p./b.p.) °C	Derivative	(m.p.) °C
1. HAH	151	Ammonia	—	—	—
2. AO	59	Amine	32	Picrate	150
3. CHO	40	Amine	134	Picrate	172
4. AAO	55	Amine	17	Picrate	166
5. FAO	89	Amine	146	Hydrochloride	110
6. BPO	59	Amine	34	Hydrochloride	298
7. DAMO	77	Amine	142	Hydrochloride	210
8. SAO	57	Amine	48	Acetyl	140
9. VO	117	Hydroxylamine	—	Hydrochlorde	—
10. ABO	152	Hydroxylamine	121	Hydrochlorde	193
11. AADO	149	Diamine	—	Diacetyl	168
12. DMG	240	Diamine	—	Diacetyl	199.7

In potentiometric back titration method, the proposed reaction mechanism between CAT and V(II) is[16]:

$$[ArSO_2NNa^+]Cl^- + 2V^{2+} + 2H^+ \rightarrow ArSO_2NH_2 + 2V^{3+} + NaCl$$

where Ar = $C_6H_4CH_3$

The reduction of oximes with V(II) in 1 mol dm^{-3} sulphuric acid media is quantitative and the results are presented in Table-2. Further the quantitative nature of this process has been confirmed by calculating the correlation coefficient of eight replicates with each oxime, which was found to be very close to 1.00.

The results are comparable with those experiments where the oximes were reduced by Ti(III) in aqueous sulphuric acid media.[17]

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