Potentiometric studies on electrolytically generated manganese(III) acetate in aqueous acetic acid: Oxidation of thiosemicarbazide, its metal complexes and thiosemicarbazones

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Conditions for generating manganese(III) acetate electrochemically with high current efficiency have been determined in aqueous acetic acid solutions. Nature of the manganese species formed has been elucidated spectrophotometrically. Conditions for potentiometric determination of thiosemicarbazide (TSC), its metal complexes and thiosemicarbazones have been investigated. Thiosemicarbazide has been found to undergo four electron oxidation whereas its metal complexes $M(TSC)_2SO_4$, participate in eight electron redox process, indicative of the number of TSC-ligands present in the complexes. All the thiosemicarbazones with the exception of salicylaldehyde thiosemicarbazone, undergo four electron redox process with the regeneration of the respective aldehydes. Salicylaldehyde thiosemicarbazone reacts in two stages namely four electron oxidation of thiosemicarbazone with the regeneration of salicylaldehyde which is further oxidised at elevated temperature to salicylic acid. The formal redox potentials of Mn(III)-Mn(II) couple at various percentages (v/v) of acetic acid and in the presence of anions CH_3COO^-, Cl^-, F^-, ClO_4^- have been determined and compared with the earlier work involving manganic sulphate in H_2SO_4-HOAc medium. The reactive species envisaged in the present system are the undecomposed manganese(III) acetate or the complex, $Mn(OAc)_4^-$, while the earlier system contains free aquo manganic ions, Mn^{3+} aq. or $MnOH^{2+}$ aq. as evident from spectral and redox potential values.

Quite recently we have used anodically generated manganese(III) sulphate in aqueous sulphuric acid for the oxidation of amino acid[1], semicarbazides[2] and thiosemicarbazide derivatives[3]. In the last men-

tioned case, it was found that the number of electrons involved was altered by varying solvent composition, thereby showing the selectivity of manganese(III), as an oxidising agent. That observation prompted us to know, as to how the changes in coordination environment of Mn(III) can influence its redox potential, electrochemical reactivity and mechanism of the related reactions. Hence the title investigation was undertaken.

Experimental

The electrolysis was carried out in an undivided cell with a platinum foil anode of generation area, 4 cm^2. The cathode of generation circuit was a thin platinum spiral of effective area, less than 0.2 cm^2. The electrolyte was 0.05 mol dm^{-3} solution of manganese(III) acetate in aqueous acetic acid (90% v/v, also containing 0.5 mol dm^{-3} potassium acetate). Potassium acetate not only enhances the conductivity of the electrolytic solution but also helps by increasing the solubility of manganese(III) acetate due to the formation of acetato complex[4], $Mn(OAc)_4^-$. The current-potential graphs of the anode showed that Mn(II) was oxidised at a less positive potential as [HOAc] was decreased or as [Mn(II)] was increased.

Electronic absorption spectra of the freshly prepared manganese(III) acetate at different [acetic acid] and [KOAc] were recorded. It has been observed that a manganic complex was formed in the presence of higher concentration of acetate, possibly the one in which water ligand is replaced by acetate ion[4]. The evidence was the change in the visible spectra of manganic acetate which showed enhanced absorption at 420 ṅm (Fig. 1).

Propionaldehyde thiosemicarbazone (PTSC), benzaldehyde thiosemicarbazone (BTSC), salicylaldehyde thiosemicarbazone (STSC) and p-nitrobenzaldehyde thiosemicarbazone (p-NBTSC) were prepared by the method described elsewhere[3]. The thiosemicarbazones were characterised by the elemental analysis and I.R. spectra. The metal complexes, $Ni(TSC)_2SO_4$, $Zn(TSC)_2SO_4$ and $Cd(TSC)_2SO_4$ were prepared[5] by mixing aqueous solutions of thiosemicarbazide and the corresponding salts in the molar ratio 2:1, evaporating slowly at 60°C on a water bath and then cooling in ice, whereupon crystals of the complex appeared. All the above complexes were recrystallised from hot water.

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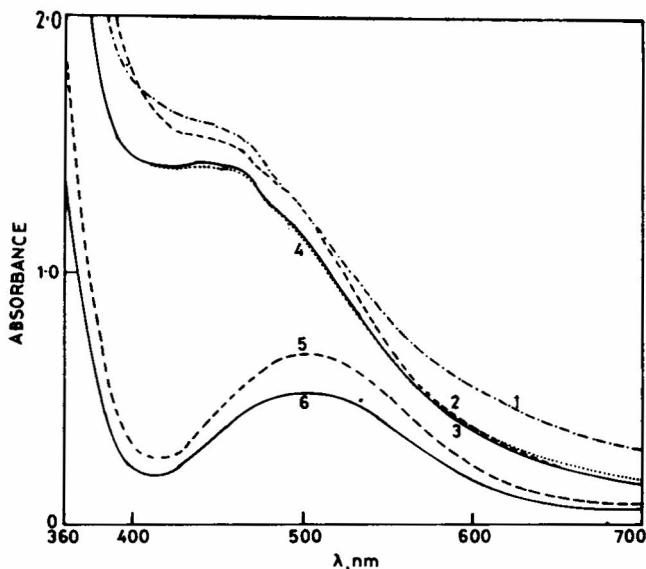§St. Aloysius College, Mangalore, India.

Fig. 1—Visible absorption spectra of manganese(III) acetate:
{(1) 0.05 mol dm^{-3} manganese(II) acetate, 5.0×10^{-3} mol dm^{-3} manganese(III) acetate in 100% HOAc

(2) 0.05 mol dm^{-3} manganese(II) acetate, 5.0×10^{-3} mol dm^{-3} manganese(III) acetate, 0.6 mol dm^{-3} KOAc in 80% (v/v) HOAc

(3) 0.05 mol dm^{-3} manganese(II) acetate, 5.0×10^{-3} mol dm^{-3} manganese(III) acetate, 0.6 mol dm^{-3} KOAc in 100% HOAc

(4) 0.05 mol dm^{-3} manganese(II) acetate, 5.0×10^{-3} mol dm^{-3} manganese(III) acetate, 0.3 mol dm^{-3} KOAc in 100% HOAc.

(5) 0.2 mol dm^{-3} manganese(III) sulphate in the mixture H$_2$SO$_4$ (2.5 mol dm^{-3}) + HOAc (50% v/v)

(6) 0.2 mol dm^{-3} manganese(III) sulphate with 5.0 mol dm^{-3}, H$_2$SO$_4$}

Glacial acetic acid (Glaxo, SQ), was refluxed with chromic oxide and distilled.

A Digisun (India) model 801 digital potentiometer with platinum-calomel electrode assembly was used for the pontentiometric study throughout this work.

Direct potentiometric titrations of thiosemicarbazide (TSC) with manganese(III) acetate in aqueous acetic acid were moderately fast in the beginning but became very slow in the vicinity of the end point. Hence back titration with hydroquinone was employed. To a known amount of the reductant (5.0 cm^3 of 0.005 mol dm^{-3}) was added a known excess of the oxidant (25.0 cm^3 of 0.01 mol dm^{-3}) both in aqueous acetic acid (80% v/v); the mixture was allowed to stand for about one hour in stoppered flask and the excess oxidant was back-titrated potentiometrically with 0.01 mol dm^{-3} hydroquinone in aqueous acetic acid (80% v/v). In case of *p*-nitrobenzaldehyde thiosemicarbazone and salicylaldehyde thiosemicarbazone the reaction mixture was allowed to stand for about 3 hr at 70°C and then titrated. The titrations gave well-defined curves of

sigmoid form (Fig. 2). There was large well defined potential change (400-500 mV per 0.1 cm^3 of the titrant added) at the end point.

Results and discussion

It was noticed that 0.01 mol dm^{-3} solution of manganese(III) acetate was stable in acetic acid-water medium containing acetic acid about 75% (v/v) for about 48 hr, thereafter disproportionation slowly set in and black particles of Mn(IV) were formed[6].

$$2Mn(III) \rightleftharpoons Mn(II) + Mn(IV)$$

The acetic acid concentration was varied in the range 40-90% (v/v) and the extent of disproportionation was recorded by estimating [Mn(III)] in solution by iodometry.

Acetic acid being a strong donor solvent, higher percentage (v/v) of HOAc increases the stability of Mn(III). Our previous work[7] has shown that, in lower percentage of acetic acid, manganese(III) deteriorated at a fast rate, but its stability could be enhanced by adding higher amount of manganese(II) acetate.

The formal redox potential, E_0' of Mn(III)-Mn(II) couple is a measure of its oxidising power and it generally alters on anionic complexation. Various ratios of manganese(III) acetate and manganese(II) acetate were taken and the electrode potential was measured each time. The Nernst equation in which E(mV vs SCE) indicates equilibrium potential can be represented by Eq. (1).

$$E(mV \text{ vs SCE}) = E_0' + \frac{2.303\,RT}{nF} \log \frac{[Mn(III)]}{[Mn(II)]} \quad \ldots (1)$$

where R = 8.314 J mol^{-1}, T = 298 K, n = 1, F = 96, 500 C mol^{-1}. Plot of E(V vs SCE) against log $\frac{[Mn(III)]}{[Mn(II)]}$ was linear with intercept = [$E_0' - E_{calomel}$].

Taking $E_{calomel}$ for saturated KCl at 298 K as 0.241, E_0' could be found out. The measurements are made in the absence and presence of added anions, CH$_3$COO$^-$, Cl$^-$, F$^-$ and ClO$_4^-$ and E_0', in the changed environment was computed (Table 1). Variation in percentage of HOAc (v/v) in the reaction mixture did not affect the formal redox potential. But there was a small but significant change in the formal redox potential due to the added anions, possibly because of the changes in coordination environment of the oxidising species.

As can be seen from the Table 2, the number of electrons exchanged in the oxidation of thiosemi-
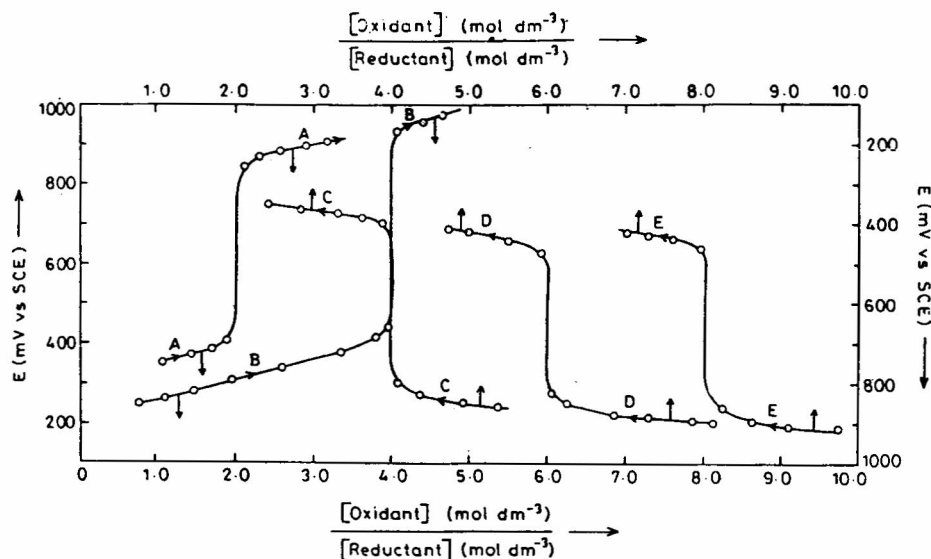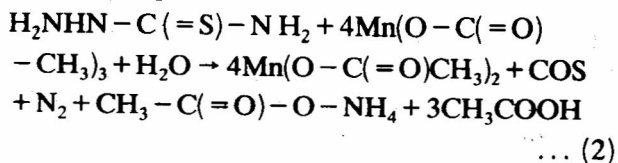
Fig. 2—Direct potentiometric titration curves of
(A) hydroquinone titrated with manganese(III)acetate
(B) thiosemicarbazide titrated with manganese(III)acetate
(C, D and E) Indirect potentiometric titration curves of thiosemicarbazide, salicylaldehyde, thiosemicarbazone and metal complexes of thio-semicarbazide titrated with manganese(III)acetate with hydroquinone as back titrant

[Manganese(III)acetate] = 1.0×10^{-2} mol dm^{-3},
[hydroquinone] = 1.0×10^{-2} mol dm^{-3},
[thiosemicarbazide] = 1.0×10^{-3} mol dm^{-3},
[salicylaldehyde thiosemicarbazone] = 1.0×10^{-3} mol dm^{-3},
[Metal complexes of thiosemicarbazide, Zn(TSC)$_2$SO$_4$] = 1.0×10^{-3} mol dm^{-3},
medium = aqueous acetic acid 80% (v/v)
temp = 25°C with thiosemicarbazide and 70°C with salicylaldehyde thiosemicarbazone.

Table 1—Effect of complexing agents on the formal electrode potential of Mn(III)-Mn(II) couple
Temp = 298K; acetic acid: 80% (v/v); [complexing agent] = 0.05 mol dm^{-3}

[Mn(OAc)$_3$] (mol dm^{-3})	[Mn(OAc)$_2$] (mol dm^{-3})	E(mV vs SCE)					
		−	CH$_3$COO$^-$	Cl$^-$	F$^-$	ClO$_4^-$	H$_2$SO$_4^-$
0.00467	0.00967	896	864	916	877	906	—
0.00467	0.01717	865	836	885	853	877	—
0.00467	0.02967	836	806	855	825	848	—
0.00467	0.03467	825	796	842	815	836	—
Formal redox potential, E$_0'$ (mV):		1157	1126	1181	1140	1169	1520

[a]Analyst, 116 (1991) 285

carbazide by manganese(III) acetate in acetic acid water medium was four. The reaction may be represented by Eq. (2).

$$H_2NHN - C(=S) - NH_2 + 4Mn(O-C(=O)$$
$$-CH_3)_3 + H_2O \rightarrow 4Mn(O-C(=O)CH_3)_2 + COS$$
$$+ N_2 + CH_3 - C(=O) - O - NH_4 + 3CH_3COOH$$
$$\qquad \ldots (2)$$

The product, carbonyl sulphide (COS) being a gas, is known to undergo slow hydrolysis in acid medium to give carbon dioxide and hydrogen sulphide[8] (Eq. 3).

$$COS + H_2O \rightarrow CO_2 + H_2S \qquad \ldots (3)$$
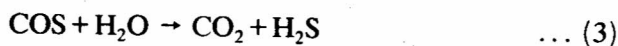
H$_2$S was ascertained by the addition of lead acetate to the resulting solution which turned black gradual-

Table 2—Potentiometric titration of thiosemicarbazide (TSC), its metal complexes, M(TSC)$_2$SO$_4$, and thiosemicarbazones, propionaldehyde thiosemicarbazone (PTSC), benzaldehyde thiosemicarbazone (BTSC), salicylaldehyde thiosemicarbazone (STSC) and p-nitrobenzaldehyde thiosemicarbazone (p-NBTSC) in acetic acid-water medium at 30°C

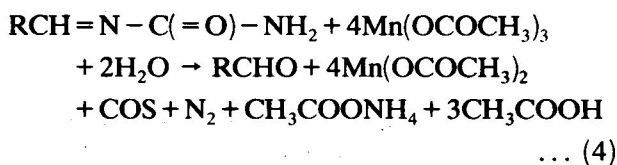| Compound	Acetic acid % (v/v)	Electrons participating in the reaction		Standard deviation
		Calc.	Found[a]	
TSC	80	4	3.99	0.04
	70	4	3.96	0.05
	60	4	3.91	0.05
Ni(TSC)$_2$SO$_4$	80	8	8.02	0.06
Zn(TSC)$_2$SO$_4$	80	8	7.98	0.05
Cd(TSC)$_2$SO$_4$	80	8	7.99	0.04
PTSC	80	4	4.02	0.03
BTSC	80	4	3.98	0.03
STSC[b]	80	6	6.09	0.06
p-NBTSC[b]	80	4	3.94	0.05

[a]Average values, [b]At 70°C

ly (but not immediately) due to the formation of PbS, thus confirming COS as one of the reaction products. It may be recalled that in the oxidation of TSC by manganese(III) sulphate in sulphuric acid-acetic acid medium[3] a reproducible six electron stoichiometry could be noticed only when [acetic acid] in the mixture was less than 20% (v/v). Further, the reactive species envisaged in that system was the ionic form of trivalent manganese, Mn^{3+} aq. or Mn(OH)$^{2+}$ aq. as evident from the UV, visible absorption spectra (Fig. 1) and the formal redox potential value of 1.52V (Table 1). The present study shows that manganese(III) acetate in aqueous acetic acid reacts differently as the reactive species involved in this reaction are the complexed form of Mn(III), as Mn(OAc)$_3$ or Mn(OAc)$_4^-$. These reactive species were confirmed by the UV visible absorption spectra and the formal redox potential value of 1.16V (Table 1). However, manganese(III) sulphate containing critical amount of acetic acid, namely 40% (v/v) and above oxidises the reductant quantitatively with 4 electron stoichiometry. This again goes to show that the changes in the coordination environment of the oxidising species alter its redox behaviour.

Potentiometric titrations of metal-TSC complex M(TSC)$_2$SO$_4$ where M = Ni^{2+}, Zn^{2+} and Cd^{2+} in aqueous acetic acid medium were also carried out. Eight electron stoichiometry conformed to two TSC ligand molecules present in the complexes.
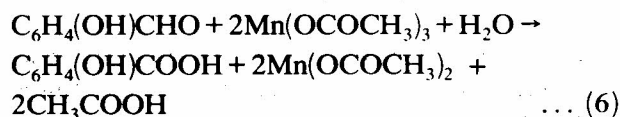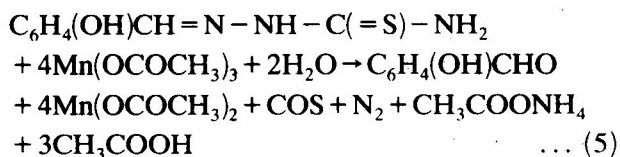
Propionaldehyde and benzaldehyde thiosemicarbazones in aqueous acetic acid medium undergo four electron change redox process with the regeneration of propionaldehyde and benzaldehyde

respectively. The reaction can be represented by Eq. (4).

$$RCH=N-C(=O)-NH_2+4Mn(OCOCH_3)_3$$
$$+2H_2O \rightarrow RCHO+4Mn(OCOCH_3)_2$$
$$+COS+N_2+CH_3COONH_4+3CH_3COOH$$
$$\qquad \dots (4)$$

where R = CH$_3$CH$_2$ − or C$_6$H$_5$ −. The regenerated aldehyde was identified as its 2,4-dinitrophenylhydrazone and could be isolated giving yields up to 90%.

With thiosemicarbazones of hydroxybenzaldehydes the regenerated aldehydes further underwent two electron oxidation to the corresponding hydroxy carboxylic acids at elevated temperature (70°C), as observed in the case of salicylaldehyde thiosemicarbazone (Eqs 5 and 6).

$$C_6H_4(OH)CH=N-NH-C(=S)-NH_2$$
$$+4Mn(OCOCH_3)_3+2H_2O \rightarrow C_6H_4(OH)CHO$$
$$+4Mn(OCOCH_3)_2+COS+N_2+CH_3COONH_4$$
$$+3CH_3COOH \qquad \dots (5)$$

$$C_6H_4(OH)CHO+2Mn(OCOCH_3)_3+H_2O \rightarrow$$
$$C_6H_4(OH)COOH+2Mn(OCOCH_3)_2+$$
$$2CH_3COOH \qquad \dots (6)$$

Manganese(III) sulphate oxidation of salicylaldehyde thiosemicarbazone in sulphuric acid-acetic acid medium could not be investigated because of the formation of an insoluble complex.

It has been observed that in the case of oxidation of semicarbazones the electron transfer to Mn(III) involved the formation of N − Mn(III) intermediates[9] and the electron transfer to Mn(III) was facilitated by the electron donating groups as in the case of salicylaldehyde thiosemicarbazone and retarded by electron withdrawing groups as in the case of p-nitrobenzaldehyde thiosemicarbazone. That was the reason for manganese(III) acetate oxidation of salicylaldehyde thiosemicarbazone to be rapid, compared to that of p-nitrobenzaldehyde thiosemicarbazone, which was very sluggish requiring about 6 hr for direct titration at 70°C. It appears that in the case of aromatic aldehydes a certain degree of electron density in the aromatic ring is necessary for the redox reaction to take place.

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