

Trifluoro(oxalato)manganate(III) Oxidations of Thiosemicarbazide, Semicarbazide and their Derivatives

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Potassium trifluoro(oxalato)manganate(III) ($E'_0 = +1.07$ V) is quite stable in the solid state but undergoes decomposition in aqueous solution. The solution stability of the complex in different acid media is studied. The oxidation reactions of potassium trifluoro(oxalato)manganate(III) with substrates like thiosemicarbazide, thiosemicarbazones, semicarbazide, semicarbazones and metal complexes of thiosemicarbazide have been investigated. The reactions have been followed titrimetrically and also potentiometrically in some cases. The stoichiometries of the reactions are established and the oxidation products identified.

Manganese(III), one of the less stable oxidation states, is being increasingly used as selective oxidant for both inorganic and organic substrates¹. Manganese(III) oxalate system which is quite unstable², can be stabilised in presence of flouride ions³. Though in the solid state trifluoro(oxalato)manganate(III) is quite stable, but in solution it undergoes decomposition. An aqueous solution of the complex in 0.03 M HF was found to be reasonably stable at 5° and used as an oxidant. The standard electrode potential of 1.07 V of the system in HF media indicates that the trifluoro(oxalato)manganate(III) should be a reasonably good oxidant. Literature survey revealed the use of manganese(III) acetate⁴, manganese(III) sulphate⁵ and manganese(III) pyrophosphate⁶ as oxidants for amino acids⁷, thiocyanate⁸, thiosemicarbazide^{4,5}, semicarbazide⁹ and pyridoxine hydrochloride¹⁰ and dipeptide¹¹. In continuation of our study of manganese(III) oxidations, we report herein the oxidations of thiosemicarbazide, thiosemicarbazones, semicarbazide, semicarbazones and metal complexes of thiosemicarbazide by trifluoro(oxalato)manganate(III).

Results and Discussion

Potassium trifluoro(oxalato)manganate(III) in dry state appears to be stable indefinitely, but its aqueous solutions are quite unstable. The solution of trifluoro(oxalato)manganate(III) undergoes decomposition to manganese(II) stage at all temperatures. Maintaining lower temperature increased the stability of the manganese(III) species (Fig. 1). While the decomposition is as much as 63% in 0.01 M sulphuric acid medium immediately on dissolution, the rate was lower in HCl and HF medium. To prevent hydrolysis of the complex in solution, a 0.005 mol dm⁻³ solution should contain about 0.15 cm³ of 40% HF and the solution should be maintained at 5° or below. At this temperature pH of the solution was found to be 4.5. The concentration of manganese(III) in solution was determined by add

ing excess of 5% KI solution and quickly titrating the liberated iodine against standard sodium thiosulphate solution using starch as indicator.

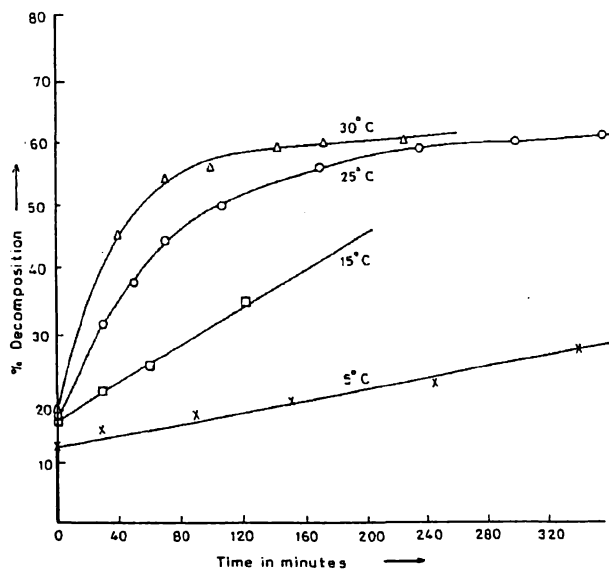


Fig. 1. Percentage decomposition of $K_2[MnF_3(C_2O_4)] \cdot H_2O$ in 0.03 M HF.

The formal redox potential of $Mn^{III}-Mn^{II}$ couple is a measure of the oxidising power of the oxidant. In freshly prepared solution of the complex, the concentration of manganese(III) can be estimated iodometrically. As the complex undergoes decomposition with time, the concentration of Mn^{III} at fixed intervals of time was measured and hence the concentration of Mn^{II} computed. The e.m.f. of the solution at these fixed intervals of time is measured using combination of platinum and calomel electrode assembly. The Nernst equation in which E (mV vs SCE) indicates equilibrium potential, can be presented by equation (1),

$$E \text{ (mV vs SCE)} = E'_0 + \frac{2.303 RT}{nF} \log \frac{[\text{Mn}^{\text{III}}]}{[\text{Mn}^{\text{II}}]} \quad (1)$$

where, $R = 8.314 \text{ J mol}^{-1}$, $T = 278 \text{ K}$, $n = 1$ and $F = 96500 \text{ C mol}^{-1}$.

The plot of E against $\log [\text{Mn}^{\text{III}}]/[\text{Mn}^{\text{II}}]$ gave a straight-line with intercept equal to $[E'_0 - E_{\text{calomel}}]$. Taking E_{calomel} for standard KCl at 278 K as 0.2548 V¹¹, the formal redox potential of $\text{Mn}^{\text{III}}-\text{Mn}^{\text{II}}$ couple, E'_0 was determined. The redox potential of trifluoro(oxalato)manganate(III) was found to be 1.07 V.

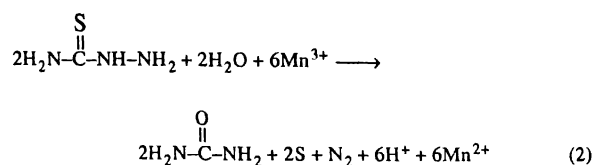
TABLE I—VOLUMETRIC DETERMINATION OF PROBABLE NUMBER OF ELECTRONS INVOLVED IN THE OXIDATION OF COMPOUNDS BY TRIFLUORO(OXALATO)MANGANATE(III) AT $5 \pm 1^\circ$

Temp = $5 \pm 1^\circ$ Compd. (range in mg)	Time for completion of reaction min	Number of electron participating in redox reaction	
		Calcd.	Found $\pm \text{SD}^a$
Thiosemicarbazide (0.29–1.34)	15	3.0	2.98 ± 0.03 (2.92 ± 0.02) ^b
Vanilline thiosemicarbazone (0.45–1.70)	120	5.0	4.93 ± 0.03
Furfuraldehyde thiosemicarbazone (0.42–2.54)	60	2.0	2.05 ± 0.01
Benzaldehyde thiosemicarbazone (0.49–2.69)	180	2.0	1.91 ± 0.03
Anisaldehyde thiosemicarbazone (0.52–3.14)	120	2.0	1.96 ± 0.02
3,4,5-Trimethoxybenzaldehyde thiosemicarbazone (0.67–4.04)	150	2.0	1.94 ± 0.04
Zn(TSC) ₂ SO ₄ (0.34–1.73)	05	6.0	6.08 ± 0.02
Cd(TSC) ₂ SO ₄ (0.39–1.95)	05	6.0	6.04 ± 0.03
Semicarbazide (0.29–1.71)	30	1.0	1.01 ± 0.04 (1.02 ± 0.04) ^b
Vanilline semicarbazone (0.52–3.14)	30	3.0	2.91 ± 0.02
Furfuraldehyde semicarbazone (0.38–2.30)	No reaction		
Benzaldehyde semicarbazone (0.41–2.45)	No reaction		
Anisaldehyde semicarbazone (0.48–2.90)	No reaction		
3,4,5-Trimethoxybenzaldehyde semicarbazone (0.63–3.80)	No reaction		

^aStandard deviation for five determinations. ^bPotentiometric method.

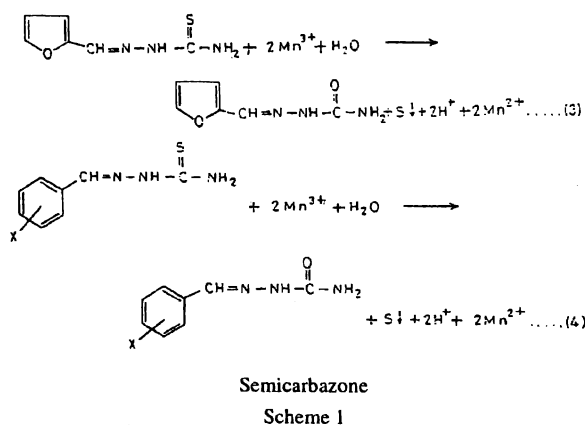
Potassium trifluoro(oxalato)manganate(III), $\text{K}_2[\text{MnF}_3(\text{C}_2\text{O}_4)] \cdot \text{H}_2\text{O}$, reacts with thiosemicarbazide, semicarbazide and their derivatives. The results are presented in Table 1. The redox reactions of trifluoro(oxalato)manganate(III) are stoichiometric, but the number of electrons involved depends on the nature of the reductant molecule. The reaction has been studied by using different known quantities of the substrate and excess of trifluoro(oxalato)manganate(III) solution.

Trifluoro(oxalato)manganate(III) solution oxidises thiosemicarbazide with a three-electron change with urea, nitrogen and elemental sulphur as the products as represented by equation (2).



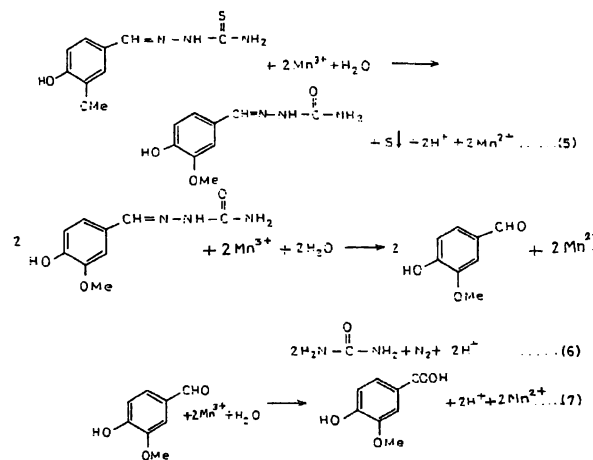
Sulphur is identified by the appearance of turbidity and quantitatively determined by converting it to sulphate and estimating as barium sulphate gravimetrically. Urea does not undergo further oxidation and this has been confirmed by attempting the reaction between urea and the oxidant.

The thiosemicarbazones of furfuraldehyde, benzaldehyde, anisaldehyde and 3,4,5-trimethoxybenzaldehyde react with a two-electron transfer, leading to the formation of the respective semicarbazones and precipitation of sulphur. The corresponding semicarbazones do not undergo oxidation with trifluoro(oxalato)manganate(III). This fact supports the present scheme of reaction (Scheme 1).

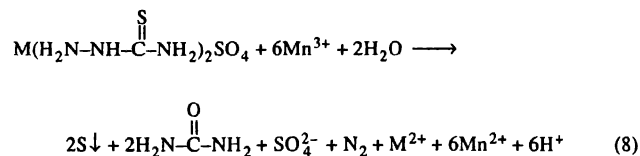


In case of vanilline thiosemicarbazone, the reaction proceeded in two stages, namely, a three-electron oxidation of the thiosemicarbazone to urea, nitrogen and sulphur with the regeneration of vanilline and a further two-

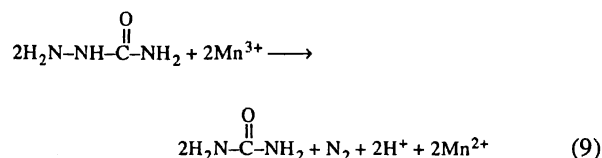
electron oxidation of vanilline to vanillic acid. The five-electron stoichiometry was confirmed by carrying out the oxidation of vanilline to vanillic acid under identical condition (Scheme 2).



Oxidations of aqueous solutions of the metal complexes, viz., $Zn(TSC)_2SO_4$ and $Cd(TSC)_2SO_4$ with trifluoro(oxalato)manganate(III) involved six-electron stoichiometry, confirming the presence of two molecule of thiosemicarbazide per molecule in the complexes.



An aqueous solution of semicarbazide undergoes oxidation with one-electron change per molecule, which can be represented as



But, semicarbazones of furfuraldehyde, benzaldehyde, anisaldehyde and 3,4,5-trimethoxybenzaldehyde do not react with trifluoro(oxalato)manganate(III). This further corroborates the scheme of reactions proposed for thiosemicarbazones.

In the case of vanilline semicarbazone, the reaction can be represented in two steps, namely, one-electron change

for oxidation of the semicarbazone to urea with the release of vanilline and a further two-electron oxidation of vanilline to vanillic acid.

In all the above cases the product, urea, owing to its greater degree of stability, does not show evidence of undergoing further oxidation.

The analytical utility of trifluoro(oxalato)manganate(III) has been studied with reference to thiosemicarbazide, semicarbazide and their derivatives and their stoichiometries have been worked out. The thiosemicarbazones undergo oxidation, but not the semicarbazones (except vanilline semicarbazone) with trifluoro(oxalato)manganate(III). Compared to other manganese(III) species, namely, manganese(III) acetate, manganese(III) sulphate and manganese(III) pyrophosphate, the present reagent is a mild oxidising agent.

Experimental

Potassium trifluoro(oxalato)manganate(III) was prepared by the literature method³. An aqueous solution of ~ 0.005 mol dm^{-3} in ~ 0.03 M HF was prepared and standardised iodometrically. Thiosemicarbazide (TSC) and semicarbazide hydrochloride (SC) (CDH analytical reagent) were used after recrystallisation. Thiosemicarbazones and semicarbazones of vanilline, furfuraldehyde, benzaldehyde, anisaldehyde and 3,4,5-trimethoxybenzaldehyde were prepared by the literature methods^{5,12}. Zinc(II) and cadmium(II) complexes of thiosemicarbazide were prepared by the reported method¹³.

Iodometric method: To a known volume of the reductant (5.0 cm³ of 0.001 mol dm^{-3}) was added a known excess of the oxidant (10.0 cm³ of 0.005 mol dm^{-3}). The mixture was allowed to stand for different intervals of time in a constant temperature bath maintained at $5 \pm 1^\circ$ to ascertain the completion of the reaction. The excess of oxidant was determined by reacting with an excess of KI and then titrating the liberated iodine with standard sodium thiosulphate solution to the starch end-point. A blank titration was performed simultaneously. The determination was repeated with various amounts of reductant.

Potentiometric method: A Digisun (India) DI-101 potentiometer equipped with platinum-calomel electrode assembly was used.

To a known amount of the reductant (5.0 cm³ of 0.001 mol dm^{-3}), was added a known excess of the oxidant (10.0 cm³ of 0.01 mol dm^{-3}). The mixture was allowed to stand for completion of the reaction at $5 \pm 1^\circ$ and the excess oxidant was back-titrated potentiometrically with 0.01 mol dm^{-3} ammonium iron(II) sulphate. A large potential change was observed at the end-point. The determinations were repeated with various amounts of the reductants.

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