

## Mechanistic Aspects of Reduction of *tris*(Pyridine-2-carboxylato) Manganese(III) by $S_2O_3^{2-}$ in Na(pic)-picH Buffer

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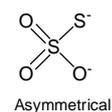
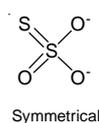
The oxidation of thiosulfate ion by *tris*(pyridine-2-carboxylato) manganese(III) in picolinate-picolinic acid buffer occurs according to the equation  $2S_2O_3^{2-} + 2Mn^{III} \rightarrow S_4O_6^{2-} + 2Mn^{II}$ . The reaction was studied under pseudo-first order conditions. The rate of the reaction is first order with respect to  $[S_2O_3^{2-}]$  and  $[Mn^{III}]$  with no evidence of 1:1 complex formation between the reactants. The influence of pH on the reaction rate is insignificant. The rate of the reaction decreases with the increase in acrylamide concentration. The influence of temperature was studied in the temperature range 288-303 K. The values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  have been calculated to be  $33 \pm 2 \text{ kJ mol}^{-1}$  and  $-137 \pm 7 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively. A one-equivalent electron transfer from  $S_2O_3^{2-}$  to  $Mn^{III}$  takes place to give  $Mn^{II}$  and free radical, the latter subsequently is transformed to  $S_4O_6^{2-}$ . An attempt has been made to compare the results of the oxidation of some other sulfur, phosphorous and nitrogen containing inorganic compounds by this oxidant.

**Keywords:** *tris*(Pyridine-2-carboxylato) manganese(III), Na(pic)-picH buffer, Thiosulfate, Electron transfer reaction.

### INTRODUCTION

Thiosulfate ion is known to react with large number of metal ions to give complexes and considerable amount of work has been done<sup>1</sup> on the determination of instability constants of thiosulfate complexes by potentiometry, spectrophotometry and polarography. Thiosulfate is also a moderately strong reducing agent. The standard redox potential ( $E_0$ ) relative to potential of standard hydrogen electrode at 298 K for the reaction  $S_4O_6^{2-} + 2e \rightarrow 2S_2O_3^{2-}$  is 0.08 volt<sup>2</sup>. The quantitative estimation of  $S_2O_3^{2-}$  via its oxidation by iodine to form tetrathionate and iodide is the basis for the iodometric titration in volumetric analysis<sup>3</sup>, although stronger oxidant like  $MnO_4^-$  oxidizes thiosulfate to sulphate<sup>4</sup>. Thus thiosulfate may be oxidized to tetrathionate or sulfate depending upon the oxidant and experimental conditions. Kinetic studies of the oxidation of  $S_2O_3^{2-}$  by  $Fe^{III}$ ,  $Ag^{III}$ ,  $Os^{VIII}$  and  $Pt^{IV}$  have been reported<sup>5-8</sup>. Kinetics of the oxidation of thiosulfate by copper(II) in aqueous ammonia solution, by hydrogen peroxide in presence of  $[Ru^{III}(edta)(H_2O)]^-$  as catalyst, by  $Fe(CN)_6^{3-}$  in aqueous perchloric acid medium and also by  $FeO_4^-$  in aqueous medium have been studied<sup>9-12</sup>. Thiosulfate ion contains two sulfur atoms and the tracer study with  $^{35}S$  has established the nonequivalence of the two sulfur atoms. Thiosulfate may decompose to  $SO_3^{2-}$  and S and then the oxidation of  $SO_3^{2-}$  to  $SO_4^{2-}$  may occur.

Alternatively thiosulfate may be oxidized directly to tetrathionate. There is no literature data involving the oxidation of thiosulfate by manganese(III) although the oxidations of some inorganic reducing substrates have been studied earlier<sup>13-16</sup>. The present communication deals with the oxidation of  $S_2O_3^{2-}$  by *tris*(pyridine-2-carboxylato) manganese(III) in picolinate-picolinic acid buffer medium. The purpose of this study is to elucidate the mechanism of the reaction and also to correlate the results obtained earlier with the other redox reactions<sup>13-16</sup> by this oxidant. The structure of thiosulfate may be expressed in two different ways.



Of the two canonical structures which participates in the reaction with manganese(III) is yet to be ascertained. It will therefore be interesting to see whether the reaction takes place between symmetrical or asymmetrical form of the reductant.

### EXPERIMENTAL

Sodium thiosulfate (Glaxo, India) was used. A stock solution of thiosulfate was prepared by dissolving sodium

thiosulfate in water and then standardized by known procedure. Picolinic acid (Lancaster) was used without purification and its sodium salt was prepared by the addition of the requisite amount of sodium hydroxide. The Na(pic)-picH buffer, in which the reactions were carried out, was prepared by mixing picolinic acid ( $pK_a = 5.52$ ) with its sodium salt in calculated amounts. The pH of each buffer solution remained unaltered for a considerable period of time, indicating that the buffer solutions are stable in the pH range studied. Thiosulfate solutions are stable in the pH range 5-12. All solutions were made in doubly distilled water.

The complex *tris*(pyridine-2-carboxylato)manganese(III) was prepared by dissolving 2.5 g  $MnCl_2 \cdot 6H_2O$  in 25 mL of water. The solution was warmed and 25 mL of hydrogen peroxide was added which was followed by the addition of 1 g of sodium hydroxide in 25 mL water and then stirred vigorously for a period of 0.5 h. The precipitated  $MnO_2$  was filtered through a sintered glass crucible, washed thoroughly with water and then warmed with an aqueous solution of excess picolinic acid with stirring finally to filter through a sintered glass crucible. The scarlet red filtrate deposited red crystals of *tris*(pyridine-2-carboxylato)manganese(III) on cooling. Found: C = 49.2; H = 3.3; N = 9.4 %. Calculated for  $[Mn^{III}(C_5H_4NCO_2)_3] \cdot H_2O$ , C = 49.2; H = 3.2; N = 9.6 %. 10 mg of the solid product was heated at a rate of 10 °C per min and analyzed thermogravimetrically. From the calculation based on the weight loss of  $[Mn^{III}(C_5H_4NCO_2)_3] \cdot H_2O$ , it was confirmed that one water molecule is lost in one step.

The structure of the manganese(III) complex has been reported<sup>17</sup> to be a tetragonally distorted octahedron. The room temperature magnetic moment (25 °C) of the solid compound has been found to be 4.92 BM (lit value 4.90 BM<sup>18</sup>). The cyclic voltammogram of the manganese(III) complex exhibited an irreversible response at 0.8 v and the corresponding response was observed at -0.47 v ( $\Delta E_p = 330$  mV,  $E_{1/2} = -0.63$  v).

The manganese(III) solution was estimated<sup>19</sup> as follows. To a solution (25 mL) containing  $[Mn^{III}(C_5H_4NCO_2)_3] \cdot H_2O$  a known excess of a standard Mohr salt solution was added. The excess of Mohr salt was determined by titration against standard potassium dichromate solution using phosphoric acid and diphenylamine sulfonate as an indicator.

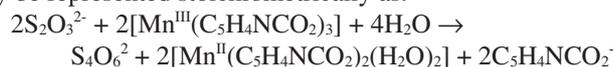
Absorbances were measured on a Systronics (India) spectrophotometer. C, H and N analysis were performed by the Microanalytical Laboratory using a Perkin-Elmer 240 C, H, N Analyser. Thermogravimetric studies were performed on a Shimadzu Corporation (Japan) TG 50 in normal atmospheric environment. The cyclic voltametric experiment was performed under dry nitrogen using a Bio-Analytical System (BAS) CV27 electrochemical analyser and a BAS model X-Y recorder at 298 K. A standard three electrode electrochemical cell consisting of a platinum disc working electrode (BAS), a

platinum wire auxiliary electrode and a Ag/AgCl reference electrode was used. EPR spectra were recorded with a Varian EPR Spectrometer.

**Kinetic measurements:** The progress of the reaction was followed at 350 nm ( $\epsilon = 2710 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$ ) since manganese(III) complex exhibits two weak shoulders at 21900 and 24800  $\text{cm}^{-1}$  ( $\epsilon = 257$  and  $407 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$ ). The complex absorbs appreciably at the low concentration range of  $(1-6) \times 10^{-4} \text{ mol dm}^{-3}$ . Beer's law is obeyed in this concentration range. The kinetic studies were carried out under pseudo-first order conditions, where substrate was in large excess over that of the oxidant. Freshly prepared thiosulfate solutions were always used to ensure reproducibility of the data. Requisite volumes of the reactants at the appropriate temperature were mixed and the mixture was immediately transferred to a cell of 1 cm path length. The cell compartment of the spectrophotometer was kept at constant temperature. The rate of decrease of manganese(III) was followed for at least two half lives. Pseudo-first rate constants ( $k_{obs}$ ) were calculated from  $\log A$  ( $A = \text{absorbance}$ ) versus time plots. The maximum error in the measurement of rate constant was 5 % depending upon the experimental conditions. However, for most experiments duplicate measurements were reproducible to  $\pm 3$  %.

**Stoichiometry and product analysis:** The stoichiometries of the reactions were studied keeping  $[S_2O_3^{2-}]$  in excess over  $[Mn^{III}]$  at pH 5.63 and at room temperature (298 K). After completion of the reactions the excess substrate was determined. The consumption ratio ( $\Delta[Mn^{III}]/\Delta[S_2O_3^{2-}]$ ) was found to be 1 (Table-1).

The formation of tetrathionate in the oxidation of thiosulfate was confirmed by the purple colouration of  $[Cu(en)_2(S_4O_6)]$  on treatment of the reaction mixture with requisite amount of cupric sulfate and ethylenediamine<sup>20</sup>. It is also known that oxidants with  $E_0 < 1.0$  v oxidize  $S_2O_3^{2-}$  to tetrathionate<sup>3,5,8</sup> whereas those with  $E_0 > 1.0$  v oxidize  $S_2O_3^{2-}$  to sulfate<sup>4</sup>. The cyclic voltammogram of the  $Mn^{III}$  complex exhibited an irreversible reductive response at 0.8 v, thus supporting the above observation. No trace of sulfide or sulfate could be detected in the reaction mixture by the usual tests nor did any opalescence or odour indicate the formation of  $H_2S$  or free sulfur. All these rule out the possibility of  $S_2O_3^{2-}$  disproportionating under the experimental conditions. The existence of  $Mn^{II}$  in the reaction mixture has been confirmed by the appearance of typical six line e.p.r spectra<sup>13</sup>. On the basis of the stoichiometry and product studies, the reactions may be represented stoichiometrically as.



The liberation of picolinate ion as a result of the oxidation of these sulfur compounds was confirmed<sup>21</sup> by the yellow colouration formed on addition of a reagent containing

TABLE-1  
STOICHIOMETRIC RESULTS OF THE OXIDATION OF  $S_2O_3^{2-}$  BY  $Mn(III)$

Initial $[Mn^{III}]$ ( $10^3 \text{ mol dm}^{-3}$ )	Initial $[S_2O_3^{2-}]$ ( $10^3 \text{ mol dm}^{-3}$ )	Final $[Mn^{III}]$ ( $10^3 \text{ mol dm}^{-3}$ )	Final $[S_2O_3^{2-}]$ ( $10^3 \text{ mol dm}^{-3}$ )	$\Delta[Mn^{III}]/\Delta[S_2O_3^{2-}]$
0.30	1.00	0.00	0.71	1.02
0.40	2.00	0.00	1.60	1.01
0.50	5.00	0.00	4.52	1.05

$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$  (1 g) and KF (0.5 g) in 100 cm<sup>3</sup> of 0.1 N acetic acid to the reaction mixture. The pH of the reaction mixture was checked before and after the reaction and it was found that the presence of a slight excess of ligand does not alter the pH of the solution.

## RESULTS AND DISCUSSION

The reactions were studied at varying initial concentrations of  $Mn^{III}$  in the range  $(2-8) \times 10^5$  mol dm<sup>-3</sup> but at constant  $[S_2O_3^{2-}]$ , pH and temperature of  $1 \times 10^{-3}$  mol dm<sup>-3</sup>, 5.63 and 293 K, respectively. The average pseudo-first order rate constant is  $(6.43 \pm 0.06) \times 10^{-4}$  s<sup>-1</sup> (Table-2). The reaction is thus first-order with respect to  $[Mn^{III}]$ .

TABLE-2

EFFECT OF  $[Mn^{III}]$  AND pH ON THE PSEUDO-FIRST ORDER RATE CONSTANT OF THE OXIDATION OF  $S_2O_3^{2-}$  AT 293 K

$10^5 [Mn^{III}]$ (mol dm <sup>-3</sup> )	$10^3 [S_2O_3^{2-}]$ (mol dm <sup>-3</sup> )	pH	$10^4 k_{obs}$ (s <sup>-1</sup> )
2.0	1.0	5.63	6.45
3.0	1.0	5.63	6.49
4.0	1.0	5.63	6.43
5.0	1.0	5.63	6.39
6.0	1.0	5.63	6.41
8.0	1.0	5.63	6.40
6.0	1.2	5.22	7.73
6.0	1.2	5.30	7.69
6.0	1.2	5.42	7.74
6.0	1.2	5.50	7.76
6.0	1.2	5.75	7.72
6.0	1.2	6.10	7.67

The pseudo-first order rate constants were also determined for different substrate concentrations in the concentration range  $(0.2-1.2) \times 10^{-3}$  mol dm<sup>-3</sup> at four different temperatures but at constant  $[Mn^{III}]$  and pH of  $5 \times 10^{-5}$  mol dm<sup>-3</sup> and 5.63, respectively. At a constant temperature an increase in  $[S_2O_3^{2-}]$  was found to increase the rate of reaction (Table-3). The plots of  $k_{obs}$  versus  $[S_2O_3^{2-}]$  however, are linear and pass through the origin at different temperatures (Fig. 1) indicating that the reaction is first order with respect to  $[S_2O_3^{2-}]$ . The quotients,  $k_2 = k_{obs}/[S_2O_3^{2-}]$  are found to be constant at each temperature. The values of  $k_2$  for the oxidation of thiosulfate are recorded in Table-3.

The effect of changing  $[H^+]$  on pseudo-first order rate constant ( $k_{obs}$ ) was studied in the pH range 5.22-6.10 and at  $[Mn^{III}]$ ,  $[S_2O_3^{2-}]$  and temperature of  $6 \times 10^{-5}$  mol dm<sup>-3</sup>,  $1.2 \times$

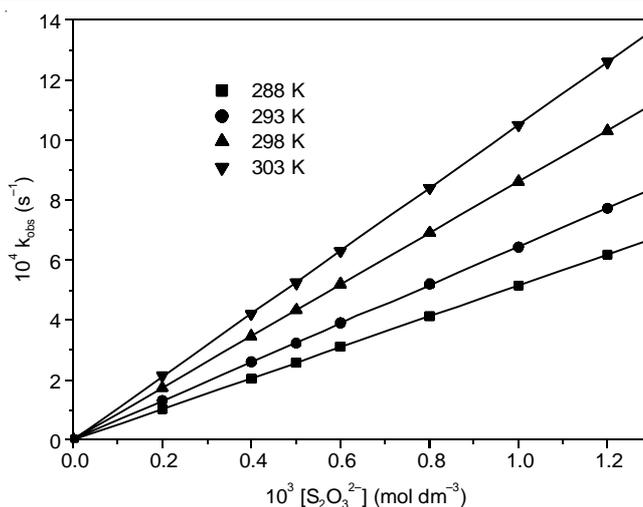


Fig. 1. Variation of reaction rate with  $S_2O_3^{2-}$  concentration. Plots of  $k_{obs}$  versus  $[S_2O_3^{2-}]$  at four different temperatures.  $[Mn^{III}] = 5 \times 10^{-5}$  mol dm<sup>-3</sup> and pH = 5.63

$10^{-3}$  mol dm<sup>-3</sup> and 293 K, respectively. The values of  $k_{obs}$  were found to be independent of changing pH of the reaction medium (Table-2).

The polymerization tests were carried out with different concentration of acrylamide ( $0.0-0.6$  mol dm<sup>-3</sup>) at 298 K keeping  $[Mn^{III}]$ ,  $[S_2O_3^{2-}]$  and pH constant at  $4 \times 10^{-5}$  mol dm<sup>-3</sup>,  $0.8 \times 10^{-3}$  mol dm<sup>-3</sup> and 5.63, respectively. The rate of the reaction decreases with the addition of acrylamide (Table-4). The onset of polymerization could not be determined by the appearance of turbidity in the initially clear solution. However, a cloudy suspension formed on standing in presence of methanol, indicating the intervention of free radicals during the reactions<sup>22</sup>. Cationic and anionic polymerizations have been ruled out under the conditions at which the reactions were studied<sup>22</sup>. Blank experiments from which either the  $S_2O_3^{2-}$  or  $Mn^{III}$  was excluded gave no polymeric product.

The reactions have been studied at different temperatures in the 288-303 K regions. The pseudo-first order rate constant was found to increase with increase in temperature (Table-3). The overall enthalpy of activation ( $\Delta H^\ddagger$ ) and entropy of activation ( $\Delta S^\ddagger$ ) were calculated from the linear plot of  $\log(k_2/T)$  versus  $1/T$  (Fig. 2) using the relationship:

$$\log(k_2/T) = [\log(k_B/h) + \Delta S^\ddagger/2.303R] - \Delta H^\ddagger/2.303 RT \quad (2)$$

where,  $k_B$  is the Boltzmann constant and the other terms have their usual significances. The values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are  $33 \pm 2$  kJ mol<sup>-1</sup> and  $-137 \pm 7$  JK<sup>-1</sup> mol<sup>-1</sup>, respectively.

TABLE-3

EFFECT OF VARIATION OF  $[S_2O_3^{2-}]$  ON THE PSEUDO-FIRST ORDER RATE CONSTANT AT DIFFERENT TEMPERATURES. FIGURE IN THE PARENTHESES REPRESENT THE VALUES OF SECOND-ORDER RATE CONSATANTS;

$k_2 = k_{obs}/[S_2O_3^{2-}]$  (dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>).  $[Mn^{III}] = 5.0 \times 10^{-5}$  mol dm<sup>-3</sup> AND pH = 5.63

$10^3 [S_2O_3^{2-}]$ (mol dm <sup>-3</sup> )	$10^4 k_{obs}$ (s <sup>-1</sup> )			
	288 K	293 K	298 K	303 K
0.2	1.04 (0.52)	1.32 (0.66)	1.74 (0.87)	2.15 (1.07)
0.4	2.05 (0.51)	2.60 (0.65)	3.45 (0.86)	4.19 (1.05)
0.5	2.57 (0.52)	3.22 (0.64)	4.32 (0.86)	5.24 (1.05)
0.6	3.10 (0.52)	3.89 (0.65)	5.20 (0.87)	6.30 (1.05)
0.8	4.11 (0.51)	5.20 (0.65)	6.90 (0.86)	8.40 (1.05)
1.0	5.15 (0.52)	6.43 (0.64)	8.61 (0.86)	10.5 (1.05)
1.2	6.19 (0.52)	7.71 (0.64)	10.3 (0.86)	12.6 (1.05)

TABLE-4  
EFFECT OF ACRYLAMIDE CONCENTRATIONS ON THE  
PSEUDO-FIRST ORDER RATE CONSTANT.  $[Mn^{III}] =$   
 $4 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[S_2O_3^{2-}] = 0.8 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $pH = 5.63$   
AND TEMPERATURE = 298 K

[Acrylamide] (mol dm <sup>-3</sup> )	10 <sup>4</sup> k <sub>obs</sub> (s <sup>-1</sup> )
0.0	6.90
0.1	6.72
0.3	6.31
0.5	5.84
0.6	5.34
0.7	4.94

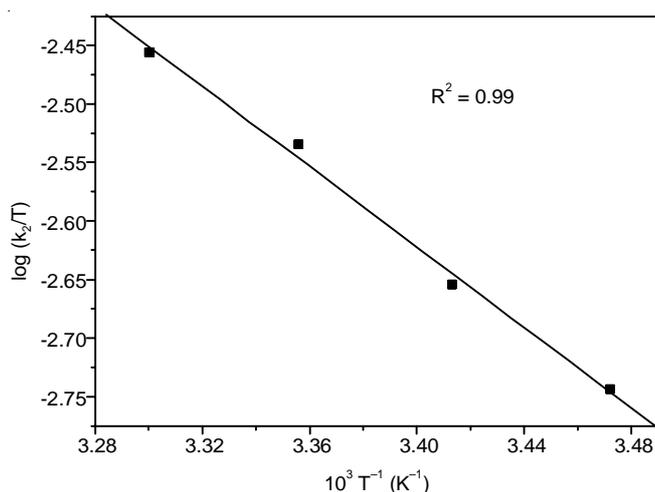
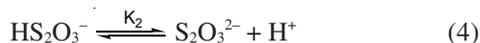
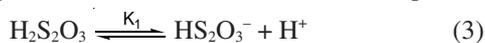


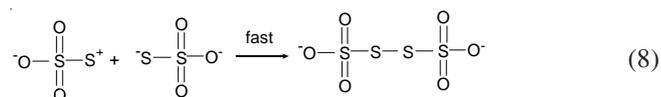
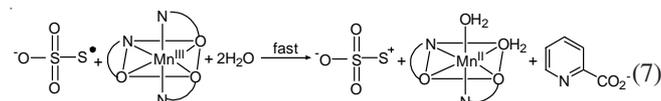
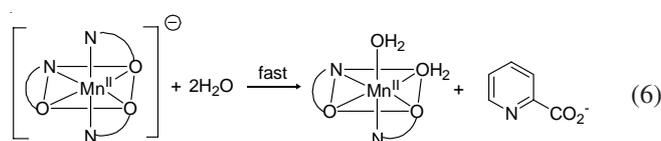
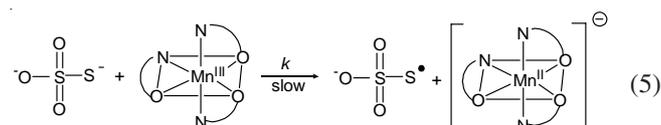
Fig. 2. Influence of temperature on the second-order rate constant. Plot of  $\log(k_2/T)$  versus  $1/T$ .  $[Mn^{III}] = 5 \times 10^{-5} \text{ mol dm}^{-3}$  and  $pH = 5.63$

The reaction is first order in each  $[S_2O_3^{2-}]$  and  $[Mn^{III}]$  but independent of  $[H^+]$ . The pseudo-first order rate constant was found to remain constant ( $(5.20 \pm 0.04) \times 10^{-4} \text{ s}^{-1}$ ) in the presence of varying  $NaClO_4$  concentration in the region (0.05-0.60)  $\text{mol dm}^{-3}$ , indicating that the variation of ionic strength has no influence on the rate. This is contrary to the observation made earlier during the oxidation of  $S_2O_3^{2-}$  by  $PtCl_6^{2-}$  where the rate increases considerably with increase in ionic strength<sup>8</sup>. There are two consecutive proton binding<sup>23,24</sup> steps (3) and (4) in thiosulfate in acid media with  $pK_a$  values of 1.74 ( $pK_1$ ) and 0.6 ( $pK_2$ ), respectively at 25 °C. Of the two species monoprotonated form is comparatively stable in aqueous solution whereas the doubly protonated species is unstable<sup>25</sup>. The latter decomposes to give sulfite, elemental sulfur and other species.

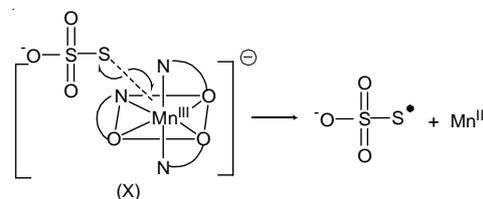


Since the reaction has been carried out in the pH range 5.22-6.10, it is suggested that  $S_2O_3^{2-}$  is the predominant and reactive reductant species. Since  $S_2O_3^{2-}$  is an effective one-electron reductant it reduces  $Mn(III)$  to  $Mn(II)$  in the first step itself being oxidized to the thiosulfuryl radical  $S_2O_3^{\bullet}$ . Oxidation of thiosulfate by metal ions frequently results in the production of thiosulfuryl radicals<sup>5</sup> when the oxidant can act as a one-electron oxidant. There are literature evidences for the existence of the  $S_2O_3^{\bullet}$  radical from e.p.r. and IR spectroscopy<sup>7</sup>. In the second step  $S_2O_3^{\bullet}$  gets further oxidized to  $S_2O_3^+$  by a second molecule of the  $Mn(III)$  complex. The combination of  $S_2O_3$  and  $S_2O_3^{2-}$  leads to the formation of product tetrathionate

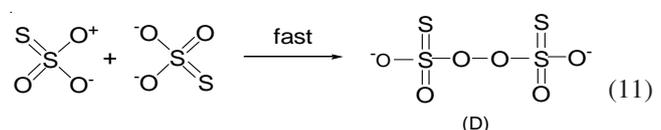
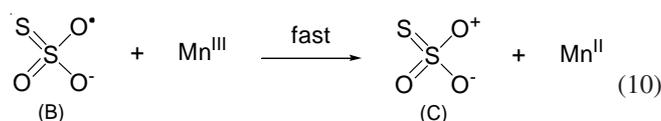
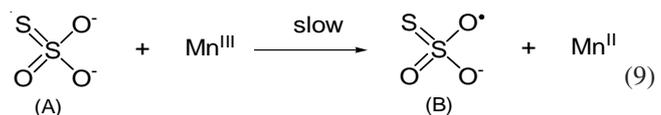
and is consistent with the observed stoichiometry,  $(\Delta[Mn^{III}]/\Delta[S_2O_3^{2-}]) = 1.0$ .  $S_2O_3^{2-}$  is known to be an excellent nucleophile for electron deficient sulfur species while  $S_2O_3$  acts as an acceptor in reactions with various nucleophiles like  $S_2O_3^{2-}$ ,  $SO_3^{2-}$ ,  $I^-$  and  $CN^-$ <sup>26</sup>. Tetrathionate has been considered to be a donor-acceptor complex of  $S_2O_3^{2-}$  and  $S_2O_3$ . Alternatively  $S_2O_3^{\bullet}$  may also react with  $S_2O_3^{2-}$  to give  $S_4O_6^{3-}$ . The latter subsequently by reacting with  $Mn(III)$  gives  $Mn(II)$  and  $S_4O_6^{2-}$ . It is still to be ascertained which one of the two canonical structures actually participates in the reaction with  $Mn(III)$  complex. The following steps have been suggested which might throw some light on the reaction mechanism.



Electron transfer from  $S_2O_3^{2-}$  to  $[Mn^{III}(C_5H_4NCO_2)_3]$  occurs through the formation of an unstable transition state. (X) followed by its decomposition to give free radicals.



The reaction has been shown to occur through the asymmetric form of the thiosulfate ion. If the reaction occurs by the other form (symmetric, A) of the substrate a free radical ion (B) will be generated which subsequently by reacting with manganese(III) would give (C). The latter will be transformed to (D) by reacting with unreacted form (A) of the substrate.



Since tetrathionate contains S-S linkage such a possibility has been discounted.

The  $E^0$  values and  $pK_{a1}$  of different reducing substrates are recorded in Table-5. The values indicate that the substrates are characterized by wide range of  $E^0$  values and  $pK_{a1}$ .

Correlations of activation enthalpy with  $pK_{a1}$  of the reductants are found for a number of reactions in acid medium. In an attempt to check the validity of the equation,  $\Delta H^\ddagger = b pK_{a1} + a$  as suggested by Nikolov<sup>27</sup> we have plotted  $\Delta H^\ddagger$  against  $pK_{a1}$  of the reductants. The plot is not linear rather scattered points are obtained. It may be that the present investigation has been carried out in weakly acid medium unlike those reported by Nikolov<sup>27</sup> in highly acidic media. On the other hand, an attempt was made to plot  $\Delta S^\ddagger$  against  $pK_{a1}$  and better correlation has been obtained (Fig. 3).

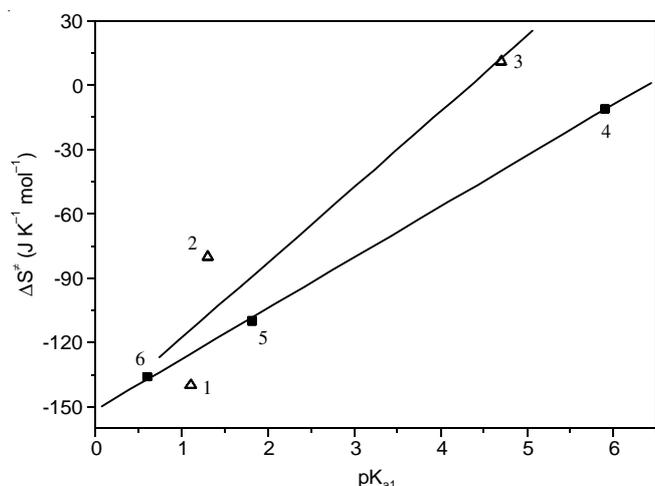


Fig. 3. Correlation between  $pK_{a1}$  and  $\Delta S^\ddagger$  for the oxidation of different inorganic compounds by Mn(III). Plot of  $pK_{a1}$  versus  $\Delta S^\ddagger$ . (1)  $H_2PO_2^-$ ; (2)  $H_2PO_3^-$ ; (3)  $N_3^-$ ; (4)  $NH_2OH^+$ ; (5)  $SO_3^{2-}$  and (6)  $S_2O_3^{2-}$

Two different plots one for phosphorus and  $N_3^-$ , the other for  $SO_3^{2-}$ ,  $S_2O_3^{2-}$  and  $NH_2OH$  are obtained. It may be mentioned

that the intermediate formation of 1:1 complex is formed between the reactants with phosphorus compounds or  $N_3^-$  and oxidant. These reactions are characterized by higher activation enthalpies in the region (52-91)  $kJ mol^{-1}$ . The isokinetic nature of the reactions has been confirmed from the plot of  $\Delta S^\ddagger$  against  $\Delta H^\ddagger$  (Fig. 4).

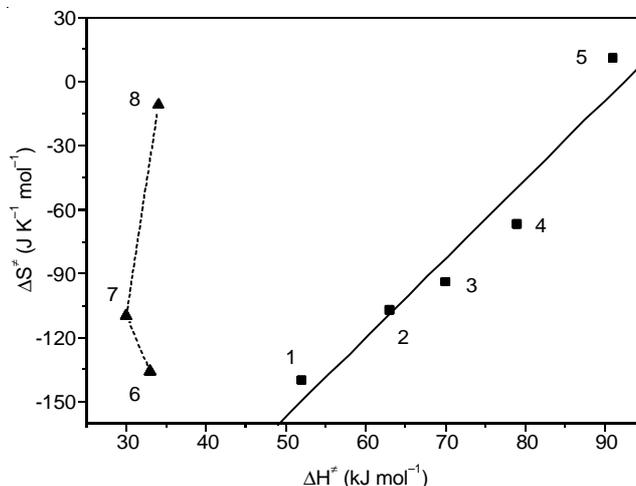


Fig. 4. Isokinetic correlation for the oxidation of different inorganic substrates by Mn(III). Plot of  $\Delta S^\ddagger$  versus  $\Delta H^\ddagger$ . (1)  $H_2PO_2^-$ ; (2)  $PhPO_2H$ ; (3)  $D_2PO_2^-$ ; (4)  $H_2PO_3^-$ ; (5)  $N_3^-$ ; (6)  $S_2O_3^{2-}$ ; (7)  $SO_3^{2-}$  and (8)  $NH_2OH^+$

The plot of  $\Delta S^0$  against  $\Delta H^0$  (where  $\Delta S^0$  and  $\Delta H^0$  are thermodynamic parameters associated with the equilibrium steps) also shows linear relationship (Fig. 5). On the other hand with other three substrates like  $SO_3^{2-}$ ,  $S_2O_3^{2-}$  and  $NH_2OH$  the reactions which are first order in each [substrate] and  $[Mn^{III}]$  activation enthalpy are found in the region (30-34)  $kJ mol^{-1}$ .

The lower activation enthalpy of  $24.5 \pm 0.1 kJ mol^{-1}$  has been found in the oxidation of  $S_2O_3^{2-}$  by copper(II) in aqueous ammonium solution. Consequently irrespective of which mechanism is operative it has been confirmed that picolinate

TABLE-5  
THE VALUES OF DIFFERENT REACTIONS PARAMETERS FOR THE OXIDATION OF DIFFERENT INORGANIC REDUCTANTS BY Mn(III) IN ACID MEDIUM

Reductant	Reaction	$E_0(v)$ [Ref 2]	$pK_{a1}$	$\Delta H^0$ ( $kJ mol^{-1}$ )	$\Delta S^0$ ( $JK^{-1} mol^{-1}$ )	$\Delta H^\ddagger$ ( $kJ mol^{-1}$ )	$\Delta S^\ddagger$ ( $JK^{-1} mol^{-1}$ )
$N_3^-$	$3N_2 + 2H^+ + 2e \rightleftharpoons 2HN_3$	-3.1	4.75	$-61 \pm 4$	$-169 \pm 14$	$91 \pm 4$	$11 \pm 14$
	$3N_2 + 2e \rightleftharpoons 2N_3^-$	-3.4	[Ref 3]	[Ref 13]	[Ref 13]	[Ref 13]	[Ref 13]
$NH_2OH$	$N_2 + 2H_2O + 4H^+ + 2e \rightleftharpoons 2NH_2OH \cdot H^+$	-1.87	5.95	-	-	$34 \pm 2$	$-11 \pm 7$
			[Ref 27]			[Ref 14]	[Ref 14]
$H_3PO_2$	$H_3PO_3 + 2H^+ + 2e \rightleftharpoons H_3PO_2 + H_2O$	-0.50	1.1	$30 \pm 2$	$135 \pm 7$	$52 \pm 2$	$-140 \pm 7$
			[Ref 28]	[Ref 15]	[Ref 15]	[Ref 15]	[Ref 15]
$H_3PO_3$	$H_3PO_4 + 2H^+ + 2e \rightleftharpoons H_3PO_3 + H_2O$	-0.276	1.3	$19 \pm 1$	$103 \pm 3$	$79 \pm 4$	$-67 \pm 13$
			[Ref 28]	[Ref 15]	[Ref 15]	[Ref 15]	[Ref 15]
$SO_3^{2-}$	$SO_4^{2-} + 4H^+ + 2e \rightleftharpoons H_2SO_3 + H_2O$	0.172	1.81	-	-	$30 \pm 4$	$-110 \pm 13$
			[Ref 3]			[Ref 16]	[Ref 16]
$S_2O_3^{2-}$	$S_4O_6^{2-} + 2e \rightleftharpoons 2S_2O_3^{2-}$	0.08	0.6	-	-	$33 \pm 2$	$-137 \pm 7$
			[Ref 23, 24]			(present study)	(present study)
$D_2PO_2^-$	-	-	-	$27 \pm 2$	$127 \pm 7$	$70 \pm 4$	$-94 \pm 13$
				[Ref 15]	[Ref 15]	[Ref 15]	[Ref 15]
$PhPO_2H$	-	-	-	$25 \pm 2$	$122 \pm 7$	$63 \pm 2$	$-107 \pm 7$
				[Ref 15]	[Ref 15]	[Ref 15]	[Ref 15]

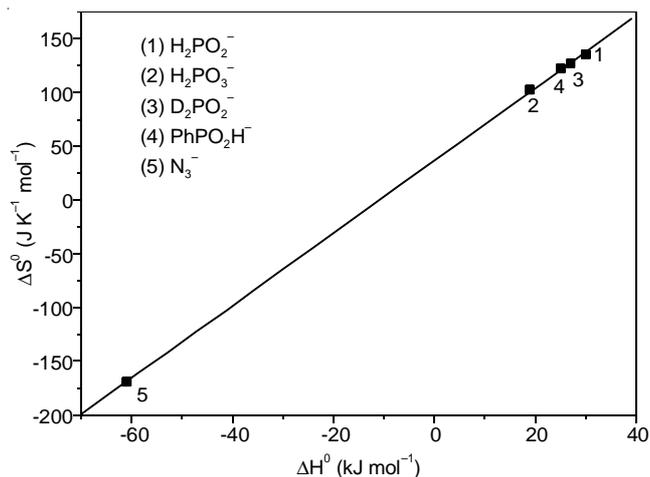


Fig. 5. Correlation plot of the thermodynamic parameters in the oxidation of different inorganic compounds by  $\text{Mn}^{\text{III}}$ . Plot of  $\Delta S^\circ$  versus  $\Delta H^\circ$

ion is generated by the break down of the manganese(III) complex and the reactions occur through inner-sphere mechanism.

### Conclusion

The reaction between  $\text{S}_2\text{O}_3^{2-}$  and *tris*(pyridine-2-carboxylato)manganese(III) occurs through the interaction between the asymmetric form of the thiosulfate ion and  $\text{Mn}(\text{III})$ . The reaction is proposed to take place through the formation of free radical and  $\text{Mn}(\text{II})$  in one electron transfer process and ultimately produces  $\text{S}_4\text{O}_6^{2-}$ .

### REFERENCES

1. B. Yatsimurski and V.P. Vasilev, *Instability Constants of Complex Compounds*, Pergamon Press, Oxford, p. 134 (1960).
2. J. Lurie, *Hand Book of Analytical Chemistry*, Mir Publications, Moscow, p. 311 (1975).
3. F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, edn 3, Wiley Eastern, New Delhi, p. 353, 447 and 453 (1979).
4. K.B. Wiberg, *Oxidation in Organic Chemistry*, Part A, Academic Press, New York, p. 29 (1965).
5. F.M. Page, *Transac. Farad. Soc.*, **49**, 635 (1953); *Transac. Farad. Soc.*, **50**, 120 (1954); *Transac. Farad. Soc.*, **56**, 398 (1960).
6. J.D. Rush and L.J. Kirschenbaum, *Inorg. Chem.*, **24**, 744 (1985).
7. R.K. Panda, G. Neogi and D. Ramaswamy, *Int. J. Chem. Kinet.*, **13**, 1001 (1981).
8. K.K. Sen Gupta, S. Das and S. Sen Gupta, *Transition Met. Chem.*, **13**, 155 (1988).
9. J.J. Byerley, S.A. Fouda and G.S. Rempel, *J. Chem. Soc. (Dalton)*, 889 (1973).
10. D. Chatterjee, S. Shome, N. Jaiswal and S.C. Moi, *J. Mol. Catal. Chem.*, **386**, 1 (2014).
11. R.K. Patil, S.A. Chimatadar and S.T. Nandibewoor, *Indian J. Chem.*, **48A**, 357 (2009).
12. M.D. Johnson and J.F. Read, *Inorg. Chem.*, **35**, 6795 (1996).
13. K.K. Sen Gupta, B. Pal, N. Bhattacharjee and S.P. Ghosh, *Bull. Chem. Soc. Jpn.*, **72**, 1769 (1999).
14. K.K. Sen Gupta and B. Pal, *Inorg. React. Mech.*, **1**, 265 (2000).
15. K.K. Sen Gupta and N. Bhattacharjee, *Transition Met. Chem.*, **25**, 518 (2000).
16. K.K. Sen Gupta and N. Bhattacharjee, *J. Indian Chem. Soc.*, **78**, 284 (2001).
17. S. Ghosh, P.K. Ray, T.K. Bandopadhyay and A.K. Deb, *Z. Naturforsch. B*, **36**, 1270 (1981).
18. M.M. Ray, J.N. Adhya, D. Biswas and S.N. Poddar, *Aust. J. Chem.*, **19**, 1737 (1966).
19. I.M. Kolthoff and R. Belcher, *Volumetric Analysis*, Interscience Publishers, Inc (New York), vol III, p. 648 (1957).
20. G.T. Morgan and F.H. Burstall, *J. Chem. Soc.*, 1259 (1927).
21. F. Feigl, L. Anger and R. Oesper, *Spot Test in Organic Analysis*, Elsevier, New York, edn 7, p. 387 (1966).
22. B. Pal and K.K. Sen Gupta, *Transition Met. Chem.*, **37**, 671 (2012).
23. I.A. Derevenkov, D.S. Salnikov, S.V. Makarov, G.R. Boss and O.I. Koifman, *J. Chem. Soc., Dalton Trans.*, **42**, 15307 (2013).
24. F.M. Page, *J. Chem. Soc.*, 1719 (1953).
25. R. Steudel and Y. Steudel, *J. Phys. Chem.*, **113**, 9920 (2009).
26. J.O. Edwards, *Chem. Rev.*, **50**, 455 (1952).
27. G.S. Nikolov, *Inorg. Chim. Acta*, **5**, 559 (1971).
28. J.R. van Wazer, *Phosphorus and its Compounds*, Interscience Publishers, Inc., New York, vol. 1, p. 360, (1964).