

## Kinetics of electron transfer between bis(2,2'-bipyridine)manganese(III) complex and thioureas in aqueous perchlorate media

Mahammad Ali<sup>†</sup>, Sumana Gangopadhyay, Amitava Dutta & Pradyot Banerjee\*

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India

Received 6 December 1993; revised and accepted  
8 August 1994

Kinetics of the redox interactions of thiourea and its N-substituted derivatives with manganese(III) complex of 2,2'-bipyridine has been investigated in aqueous solution by a stopped-flow technique in the acid range  $[H^+]$ , 0.10-0.50 mol dm<sup>-3</sup> at  $I=1.0$  mol dm<sup>-3</sup> (NaClO<sub>4</sub>) and at 30°C. A rapid initial increase in absorbance is followed by a slower decay of the formed species for all the four thioureas. Both the reaction steps are analysed and an inner sphere mechanism has been proposed for these reactions. The reactivity order for these thiourea derivatives is: ptu > tu > mtu > atu, and this bears a consequence to their substituent effects.

The electron transfer reactions of biologically relevant thiols have received much attention of late. In general, oxidation of thiols to disulphide occurs through (i) electron transfer preceded by the formation of intermediate complex of significant thermodynamic stability<sup>1-6</sup> and (ii) simple electron transfer without prior complex formation<sup>7-9</sup>.

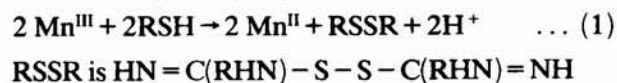
Recently we reported the oxidation of substituted thioureas with  $[Mn^{III}(cdta)]^-(H_4cdta = trans\text{-cyclohexane-1,2-diamine-N,N,N',N'-'tetraacetic acid})$  both in acidic and alkaline media<sup>10</sup>. The kinetic observations were explained successfully in terms of inner sphere mechanism. In continuation to this study we have investigated the reduction of  $[Mn^{III}(bpy)_2]_{(aq.)}^{2+}$  with these thiourea derivatives in aqueous acidic media. The aim of this study is to discriminate between the two probable mechanisms and also to compare the kinetic observations with those obtained in the reaction of  $[Mn^{III}(cdta)]^-$ .

## Experimental

Solutions of the complex bis(2,2'-bipyridine)manganese(III),  $[Mn(bpy)_2]_{(aq.)}^{3+}$  was prepared and standardised by the electrochemical oxidation of  $[Mn^{II}(bpy)_3]^{2+}$  just prior to the kinetic studies and hereafter designated as Mn<sup>III</sup> unless mentioned specifically.

Thiourea (tu), phenyl thiourea (ptu), methyl thiourea (mtu) and allyl thiourea (atu) were of reagent grade and recrystallised twice from alcohol before use. Doubly recrystallised sodium perchlorate and reagent grade perchloric acid were used to maintain the ionic strength and acidity of the reaction solutions. Doubly distilled water was used throughout. Other analytical procedures are the same as reported earlier<sup>10</sup>.

The stoichiometries of the reactions of Mn<sup>III</sup> complex with thioureas were determined spectrophotometrically by estimating the unreacted manganese(III) complex remaining immediately after the reaction with a known concentration of the reductant and a 1:1 stoichiometry for all the thioureas is suggestive under the kinetic conditions of excess reagents over  $[Mn^{III}]$ . The products were the respective disulphides for the reactions of all thioureas with Mn<sup>III</sup> as revealed from the comparison of their melting points to the respective disulphides obtained from their bromine oxidation<sup>11,12</sup>. The corresponding decomposition melting points of disulphides found are:  $110 \pm 2$ ,  $200 \pm 2$ ,  $78 \pm 2$  and  $95 \pm 5^\circ C$  for  $(CSN_2H_3R)_2Br_2$  with R = -CH<sub>2</sub>-CH=CH<sub>2</sub>, -CH<sub>3</sub>, -H, and -C<sub>6</sub>H<sub>5</sub> respectively. The stoichiometric reaction can thus be given by Eq. (1).



## Results and discussion

Spectral traces of a mixture of Mn<sup>III</sup> and thiourea or its N-substituted derivatives at 400 nm showed a rapid initial increase in absorbance within the time period ca. 20-30 ms followed by a slower decay of the formed species. It is reasonable to consider that the initial rise in optical density is due to the intermediate complex formation between Mn<sup>III</sup> and thioureas while the slower decay corresponds to the electron transfer process from ligand to the complex resulting in the conversion of Mn<sup>III</sup> → Mn<sup>II</sup>. This observation was

<sup>†</sup>Present address: Department of Chemistry, Vidyasagar College, 39, Sankar Ghosh Lane, Calcutta 700 006, India.

further supported by the spectrum generated by observing the rise in optical density as a function of wavelength in the range 340-800 nm (20 nm interval) which showed that the intermediate formation has a dependence on wavelength for a given reactant concentration in the oxidation of thiourea. The spectrum showed a shoulder peak at 400 nm characteristic of the parent complex. Since the rate of formation of the intermediate is more than 10 times greater than the corresponding electron transfer rate at a particular reaction condition, the interference due to redox decomposition would not significantly hamper the determination of the formation rate (vide supra). Again, the systematic interference from the instrument's dead time and monitoring time will not also tell upon such determination of formation rate as Union RA-401 stopped flow spectrophotometer (used in this investigation) has a very small dead time (0.50 ms at room temperature under nitrogen pressure of 7-8 kg/cm<sup>2</sup>).

The kinetics of the redox interactions between Mn<sup>III</sup> and RSH were carried out under pseudo-first order conditions keeping at least ten fold excess of reagent over the oxidant at a constant ionic strength,  $I=1.0 \text{ mol dm}^{-3}$  (NaClO<sub>4</sub>) and temperature, 30°C. The conventional plots of  $-\log(A_\infty - A_t)$  versus time (>50% of the total reactions) for the initial formation step and  $-\log(A_t - A_\infty)$  versus time (>70%) for the decay step (all the signs have their usual significances) were all linear indicating a first order dependence of rate on [Mn<sup>III</sup>] for both the steps. Variation of reductant concentrations was carried out in the range 0.001-0.15 mol dm<sup>-3</sup> at [H<sup>+</sup>]=0.50 mol dm<sup>-3</sup> and  $I=1.0 \text{ mol dm}^{-3}$  and at 30°C for the four thioureas. Analysis of the first step shows that a plot of  $k_{\text{obs}}$  versus [RSH] is a limiting curve of decreasing slope with a positive intercept on the rate axis (data in Table 1). On the other hand, for the second reduction step, it is also a limiting curve of the same kind but with zero intercept (Fig. 1). The effect of acidity on the reaction rate was tested in the [H<sup>+</sup>] range, 0.10-0.50 mol dm<sup>-3</sup> and found to have very negligible effect.

The initial complex formation is assumed to occur through the displacement of the coordinated water molecule by the thiourea ligands. Proton is being released on coordination from the sulphhydryl (-SH) group of the ligands. (The  $pK$  for thiourea is reported to be  $> -2.0$  and that for N-substituted derivatives is  $< -1.50$  (ref. 10). In the experimental acidity the protonation of thiourea and its derivatives would be very negligible, and RSH could be considered as the only reacting

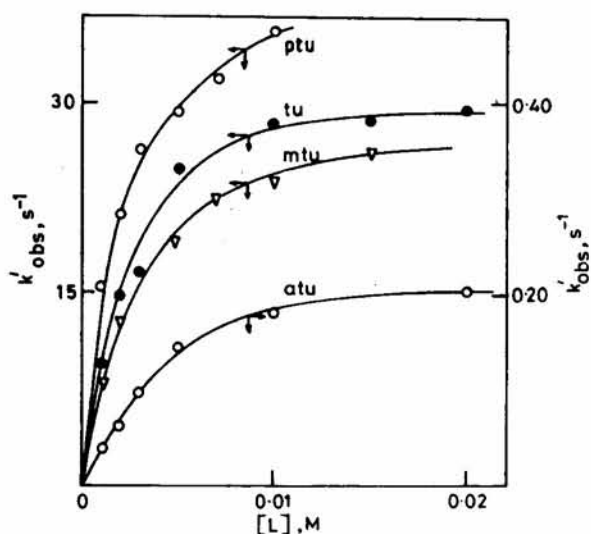


Fig. 1—Plots of  $k_{\text{obs}}$  versus [L], (electron transfer step) for the oxidation of four thioureas by  $[\text{Mn}^{\text{III}}(\text{bpy})_2(\text{H}_2\text{O})(\text{OH})]^{2+}$  with  $[\text{Mn}^{\text{III}}]=2.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{H}^+]=0.50 \text{ mol dm}^{-3}$ ,  $I=1.0 \text{ mol dm}^{-3}$  and at 30°C.

Table 1—Pseudo-first order rate constants for the formation step in the oxidation of thiourea derivatives by  $[\text{Mn}(\text{bpy})_2(\text{H}_2\text{O})(\text{OH})]^{2+}$  at  $[\text{Mn}^{\text{III}}]=2.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{H}^+]=0.5 \text{ mol dm}^{-3}$ ,  $I=1.0 \text{ mol dm}^{-3}$  (NaClO<sub>4</sub>) and temp. 30°C.

$10^3 [\text{Reductant}]$ (mol dm <sup>-3</sup> )	$k_{\text{obs}}$ (s <sup>-1</sup> )			
	ptu <sup>i</sup>	tu <sup>j</sup>	mtu <sup>k</sup>	atu <sup>l</sup>
1	325(325)	231(233)	205(206)	165(166)
2	435(434)	290(288)	250(248)	178(181)
2.5		315(314)		
3	531(531)			201(196)
5	695(695)	425(425)	350(352)	222(222)
7	830(830)		410(408)	
10	990(990)	585(586)	477(478)	274(276)
15		696(697)	567(567)	
20		780(779)		352(351)

Parentetical values represent calculated values.

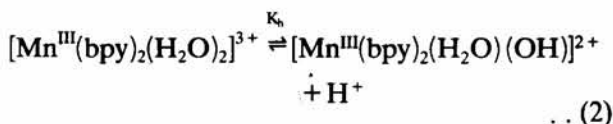
<sup>i</sup>a=(2.97 ± 0.01); <sup>b</sup>=(21.6 ± 0.01) × 10<sup>2</sup>;  
<sup>c</sup>=(1.48 ± 0.01) × 10<sup>-2</sup>;  $k_1=201 \text{ s}^{-1}$ ;  $k_2=19.5 \times 10^2 \text{ s}^{-1}$ ;  
 $Q_1=67.7 \text{ dm}^3 \text{ mol}^{-1}$ ;  $Q_2=9.72$  and  $K=Q_1Q_2=658 \text{ dm}^3 \text{ mol}^{-1}$ .

<sup>j</sup>a=(2.99 ± 0.02); <sup>b</sup>=(13.09 ± 0.02) × 10<sup>2</sup>;  
<sup>c</sup>=(1.74 ± 0.01) × 10<sup>-2</sup>;  $k_1=172 \text{ s}^{-1}$ ;  $k_2=11.37 \times 10^2 \text{ s}^{-1}$ ;  
 $Q_1=57.5 \text{ dm}^3 \text{ mol}^{-1}$ ;  $Q_2=6.61$  and  $K=Q_1Q_2=380 \text{ dm}^3 \text{ mol}^{-1}$ .

<sup>k</sup>a=(3.05 ± 0.03); <sup>b</sup>=(11.1 ± 0.01) × 10<sup>2</sup>;  
<sup>c</sup>=(1.90 ± 0.01) × 10<sup>-2</sup>;  $k_1=160 \text{ s}^{-1}$ ;  $k_2=9.23 \times 10^2 \text{ s}^{-1}$ ;  
 $Q_1=52 \text{ dm}^3 \text{ mol}^{-1}$ ;  $Q_2=5.77$  and  $K=Q_1Q_2=300 \text{ dm}^3 \text{ mol}^{-1}$ .

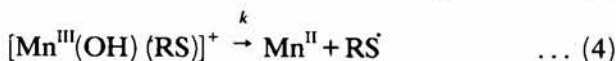
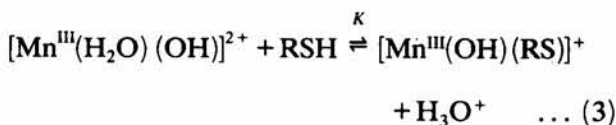
<sup>l</sup>a=(4.38 ± 0.07); <sup>b</sup>=(6.48 ± 0.09) × 10<sup>2</sup>;  
<sup>c</sup>=(2.93 ± 0.03) × 10<sup>-2</sup>;  $k_1=149.5 \text{ s}^{-1}$ ;  $k_2=4.98 \times 10^2 \text{ s}^{-1}$ ;  
 $Q_1=34 \text{ dm}^3 \text{ mol}^{-1}$ ;  $Q_2=3.33$  and  $K=Q_1Q_2=114 \text{ dm}^3 \text{ mol}^{-1}$ .

species towards  $\text{Mn}^{\text{III}}$ . Again, in the experimental  $[\text{H}^+]$ ,  $K_{\text{h}}[\text{H}^+]^{-1} \gg 1$  (though the value of  $K_{\text{h}}$  is not reported in the literature), where  $K_{\text{h}}$  is defined<sup>13</sup> by Eq. (2)



and so  $[\text{Mn}^{\text{III}}(\text{bpy})_2(\text{H}_2\text{O})_2]^{3+}$  would be of negligible existence leaving  $[\text{Mn}^{\text{III}}(\text{bpy})_2(\text{H}_2\text{O})(\text{OH})]^{2+}$  as the sole reacting species (hereafter designated as  $[\text{Mn}^{\text{III}}(\text{H}_2\text{O})(\text{OH})]^{2+}$ ).

Bearing in mind the kinetic and stoichiometric observations the following probable reaction scheme [Eqs (3) and (4)] involving also the redox step could be postulated from the second reaction trace as



The free radical thus generated will initiate the polymerisation observed<sup>10</sup> and in the absence of monomer is probably removed by the rapid reaction with another radical as in Eq. (5)



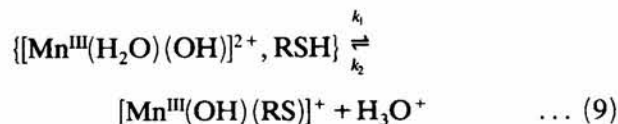
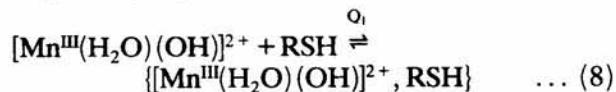
The general rate law corresponding to the above reaction scheme could be given by Eq. (6)

$$k_{\text{obs}} = \frac{kK[\text{RSH}]}{1 + K[\text{RSH}]} \quad \dots (6)$$

A plot of  $k_{\text{obs}}^{-1}$  versus  $[\text{RSH}]^{-1}$  is linear with slope =  $1/kK$  and intercept =  $1/k$ . The parameter evaluated by means of a least squares computer-fit programme for the four thioureas are:  $k = 39.4 \pm 0.2$ ,  $35.3 \pm 0.12$ ,  $31.7 \pm 0.01$ ,  $0.34 \pm 0.01 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , and  $K = 645 \pm 20$ ,  $364 \pm 15$ ,  $330 \pm 10$  and  $119 \pm 21 \text{ dm}^3 \text{ mol}^{-1}$  for phenyl thiourea, thiourea, methyl thiourea and allyl thiourea respectively. The values of  $K$  for the four thioureas are large enough to justify for an inner sphere complex formation. Considering the initial formation step alone, a plot of pseudo-first order rate constant,  $k_{\text{obs}}$  versus  $[\text{RSH}]$  yields a non-linear curve of decreasing slope with a positive intercept on the rate axis, and the corresponding rate law could be framed by Eq. (7)

$$k_{\text{obs}} = k_1 + \{k_2 Q_1[\text{RSH}]\}/\{1 + Q_1[\text{RSH}]\} \quad \dots (7)$$

The reaction scheme corresponding to Eq. (7) can be given by Eqs (8) and (9)

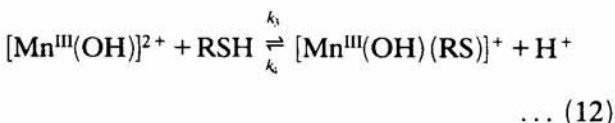
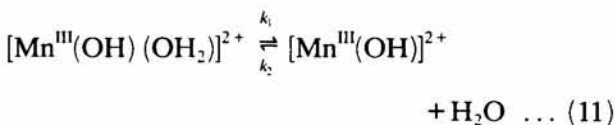


It is to be noted here that  $K$  in Eq. (3) should be replaced by  $Q_1 Q_2$ , where  $Q_2 = k_1/k_2$ . Eq. (7) could be rearranged to Eq. (10) with  $a = k_1/Q_1$ ,  $b = k_1 + k_2$  and  $c = 1/Q_1$ .

$$k_{\text{obs}} = \frac{a + b[\text{RSH}]}{c + [\text{RSH}]} \quad \dots (10)$$

Experimental data were fit to Eq. (10) by means of a non-linear least squares computer-fit programme and values of  $a$ ,  $b$  and  $c$ , and hence the respective values of rate parameters and formation equilibrium constants for the oxidation of thiourea derivatives evaluated are listed in Table 1. It is interesting to note that  $K$  and  $Q_1 Q_2$  obtained from the analysis of the respective traces of redox and formation steps are agreeable in all the thiourea derivatives supporting the proposed mechanism strongly.

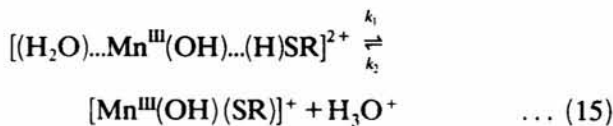
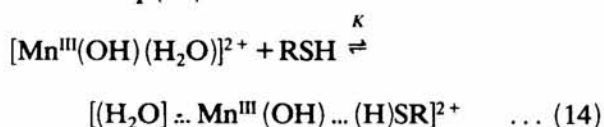
The intermediate complex formation between  $[\text{Mn}^{\text{III}}(\text{H}_2\text{O})(\text{OH})]^{2+}$  and thiourea and its derivatives may be assumed to take place either through a limiting dissociative (D) or an interchange dissociative (Id) mechanism. For D mechanism, Eqs. (11) and (12) apply and  $k_{\text{obs}}$  is related to the rate constants by Eq. (13)



$$k_{\text{obs}} = \frac{k_2 k_4 + k_1 k_3 [\text{RSH}]}{k_2 + k_3 [\text{RSH}]} \quad \dots (13)$$

A plot of  $k_{\text{obs}}$  as a function of  $[\text{RSH}]$  should be hyperbolic, with an intercept on the rate axis equal to  $k_4$ , an initial slope of  $k_1 k_3/k_2$ , and curving at high  $[\text{RSH}]$  value to reach a saturating value,  $k_{\text{sat}}$  and for D mechanism,  $k_{\text{sat}} = k_1$ .

In the case of  $I_d$  mechanism [Eqs (14) and (15)], the observed rate constants given by Eq. (7) is similar to Eq. (13).



Eq. (13) could be modified to Eq. (16) as

$$k_{\text{obs}} = \frac{(k_2 k_4 / k_3) + k_1 [\text{RSH}]}{(k_2 / k_3) + [\text{RSH}]} \dots (16)$$

which is identical to Eq. (10) with  $a = k_2 k_4 / k_3$ ,  $b = k_1$  and  $c = k_2 / k_3$ . The distinction between the two mechanisms is generally not possible. For D mechanism,  $k_1 = k_{\text{sat}}$  corresponds to the unimolecular release of water molecule from the coordination sphere and should be independent of the nature of the incoming ligands. But the evaluation of experimental rate parameters showed that the values of  $b = k_1 = k_{\text{sat}}$  are different for the four thiourea derivatives (Table 1) suggesting the preference for an  $I_d$  over the D mechanism.

The redox interactions of  $[\text{Mn}^{\text{III}}(\text{bpy})_2(\text{H}_2\text{O})(\text{OH})]^{2+}$  with hydrazoic acid<sup>13</sup>, quinol<sup>14</sup>, bromine<sup>15</sup>, hydrogen peroxide<sup>16</sup> and ascorbic acid<sup>17,18</sup> are reported to follow an inner-sphere mechanism. The present investigation also suggests an inner-sphere mechanism for the oxidation of

four thiourea derivatives and it is also consistent with the results obtained in the oxidation of these reductants by  $[\text{Mn}^{\text{III}}(\text{cdta})]^-$  (ref. 10). The reactivity of thiourea and its N-substituted derivatives is in the order  $\text{ptu} > \text{tu} > \text{mtu} > \text{atu}$ . This is in agreement with their substituent effect<sup>10</sup>.

## References

- McCann J P & McAuley A, *J chem Soc, Dalton Trans*, (1975) 783.
- Olatunji M A & McAuley A, *Can J Chem*, 55 (1977) 3335.
- Kujundic N & Everse J, *Biochem Biophys Res Commun*, 82 (1978) 1211.
- Davies G, *Inorg Chem*, 11 (1972) 2488.
- Cristani F & Diaz A, *Inorg chim Acta*, 24 (1977) L7.
- Amjad Z & McAuley A, *Inorg chim Acta*, 25 (1977) 127.
- Martin J F & Spence J, *J phys Chem*, 74 (1970) 2863.
- Ayoko G A & Olatunji M A, *Polyhedron*, 2 (1983) 577.
- Ayoko G A & Olatunji M A, *Inorg chim Acta*, 80 (1983) L15.
- Gangopadhyay S, Saha S K & Banerjee P, *Trans met' Chem*, 16 (1991) 355.
- Kurzer F & Sanderson P M, *J chem Soc*, (1957) 4461.
- Kurzer F & Sanderson P M, *J chem Soc*, (1959) 1058.
- Heyward M P & Wells C F, *J chem Soc, Dalton Trans*, (1988) 1331.
- Heyward M P & Wells C F, *Inorg chim Acta*, 165 (1989) 105.
- Heyward M P & Wells C F, *Inorg chim Acta*, 148 (1988) 241.
- Heyward M P & Wells C F, *J chem Soc Faraday Trans*, 84 (1988) 815.
- Gangopadhyay S, Saha S K, Ali M & Banerjee P, *Int J chem Kinet*, 23 (1991) 105.
- Gangopadhyay S, Ali M & Banerjee P, *Coord chem Rev*, 133 (1994) 000.