KINETIC STUDY OF REDUCTION OF BIS(PENTANE-2,4-DIONATO) DIAQUO MANGANESE (III) COMPLEX WITH SODIUM THIOSULPHATE

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Kinetics of several oxidation-reduction reactions pertaining to manganese have been reported but very few of them involve manganese (III) in perchloric acid. This may be because free manganic ions can not exist in significant concentration in aqueous solutions. Manganese (III) forms a number of complexes with fluoride, chloride, phosphate, pyrophosphate, sulphate, porphyrin, heteropoly anions (Baker 1961; Brauer 1963; Kemmit 1973)

We have now investigated the kinetics and mechanisms of the reduction of bis (pentane 2,4-dionato) diaquo manganese (III) complex by sodium thiosulphate. Kinetic investigation of the electron transfer reactions of metal complexes of β-diketones are sparse and this presentation is one of the few studies of such reactions using simple reductant.

The tris (pentane-2,4-dionato) manganese (III) complex [Mn(pd)$_3$] was prepared as previously described (Charles and Bryant 1963). Bis (pentane 2,4-dionato) diaquo manganese (III) complex [Mn(pd)2(H$_2$O)$_2$]$^+$ was prepared from tris (pentane-2,4-dionato) manganese (III) complex by substitution reaction method reported earlier (Cartledge 1952).

Molar absorptivity value of reduced form of complex was determined to convert the absorbence rate data to the concentration rate data. It was found to be 90.2 lit mol^{-1} cm^{-1} at λ_{max} = 298.5nm

Absorption spectra were recorded at 298.5nm by using Shimadzu UV-160, UV-visible spectrophotometer.

Different combinations of both complex and reductant (sodium thiosulphate) were prepared by taking constant concentration of complex and varying the concentration of the reductant. Perchloric acid was used as a source of hydrogen ion for the pH range of 2-2.5 and all solutions were adjusted to an ionic strength of 0.5 mole dm^{-3} by the addition of NaClO$_4$.

The absorbance of each set of reaction mixture was recorded at 298.5nm. Mn (III) was analyzed potentiometrically. In this technique the complex [Mn (pd)$_3$] was reduced by L-ascorbic acid and potential differences were read with the aid of a potentiometer (Kent EIL 7020). Analysis of the above complex gave Mn 17.1%, where as calculated amount is 15.6%.

Data were collected using initial rate method by plotting the

Table 1
Kinetic rate data between the reaction of $S_2O_3^{2-}$ with Mn (pd)$_2$ (H$_2$O) $^+_2$, NaClO$_4$=0.5M

S.No	Composition of reaction mixture (ml)			[Complex] M 10^4	[Thiosulphate] M 10^4	Initial rate A Sec^{-1}	k$^{'}$ Sec^{-1} Calculated	k$^{'}$ Sec^{-1} Graphical
	NaClO$_4$	Complex	Thiosulphate					
A	2.3	0.5	0.2	8.33	6.66	1.083	Rate is independent of the initial	
B	2.2	0.5	0.3	8.33	10	1.083	concentration of thiosulphate	
C	2.1	0.5	0.4	8.33	13.3	1.089		
D	2.0	0.5	0.5	8.33	16.6	1.08	14.37	
E	2.4	0.1	0.5	1.66	16.6	0.244	16.29	13.3
F	1.8	0.7	0.5	11.66	16.6	1.40	13.31	
G	1.6	0.9	0.5	15.0	16.6	1.749	12.92	

λ max= 298.5 nm; Complex = 0.005M; S$_2$O$_3^{2-}$= 0.01M; pH= 2-2.5; ε= 90.2 lit mol^{-1} cm^{-1}

experiments (A-D) with constant complex, [bis(Pentane-2,4-dionato) diaquo manganese (III)] and variable reductant (sodium thiosulphate) concentrations and another four experi-

ments (D-G) with constant reductant and variable complex concentration, lead to the results reported here in.

In the first case (experiments A-D) with constant complex concentration, the plot shows that there is no change in the
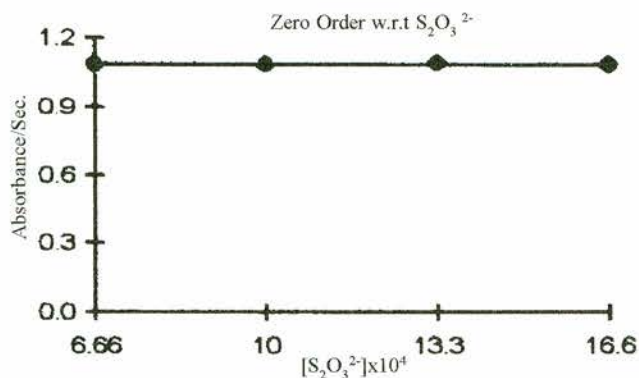
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Fig 1(a). of Table 1. Plot of rate Vs concentration at constant complex and variable reductant concentration

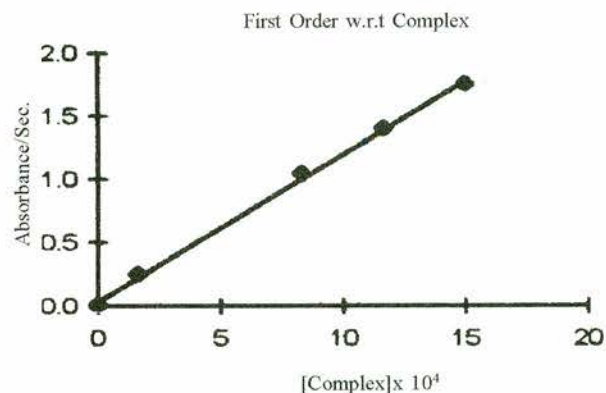
Fig 1 (b). of Table 1.Plot of rate Vs concentration at constant reductant and variable complex concentration
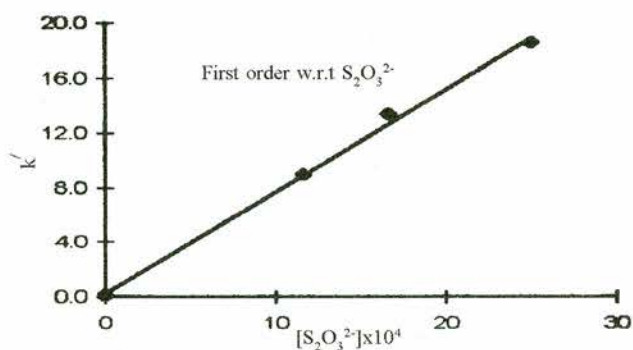

Fig 2(a). of Table 2. Plot of pseudo- first order rate constant Vs reductant concentration at constant complex concentration
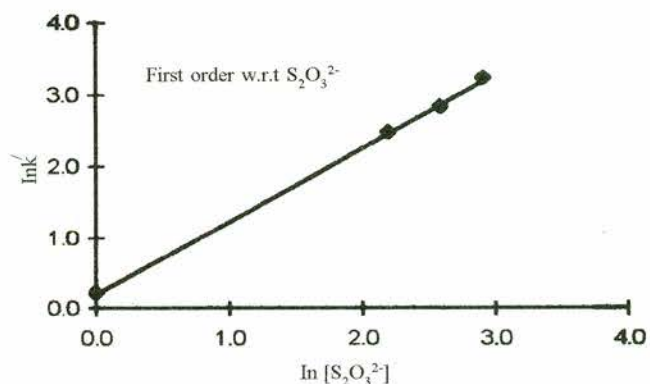

Fig 2(b). of Table 2. Plot of pseudo- first order rate constant Vs In [reductant] at constant complex concentration

Table 2

Indirectly determination of order of reaction of reductant at constant complex concentration

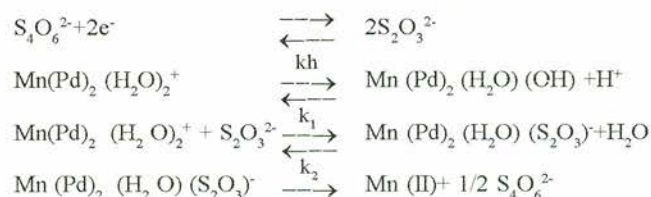| S.No	[Complex]M 10^4	[Thiosulphate]M 10^4	$k^{/}$ Sec^{-1} Graphical	In $k^{/}$	In [thiosulphate]
1	8.33	16.66	13.3	2.59	2.81
2	8.33	11.66	8.9	2.2	2.46
3	8.33	25	18.5	2.91	3.22

rate when the concentration of the reductant is varied. So, the order of reaction with respect to reductant is zero. As shown in Table 1 and in Fig 1(a). In the second case (experiments D-G), rate (absorbance persecond) increases in a linear manner with the concentration of the complex as shown in Table 1 and in Fig 1(b). This shows that order of reaction with respect to complex is first order and that the overall order of reaction is pseudo-first order.

When the pseudo-first order rate constants, k$^{/}$ determined graphically, given in Table 2, of previous different set of experiments are plotted versus the reductant concentrations, as shown in

Fig 2(a), a straight line is obtained passing through the origin. Thestraight line indicates that the order of reaction with respect to reductant is also first order. The slope of this later plot gives the overall second order reaction.

Another approach to determining the order of reaction of the reductant is a l_n-l_n plot as shown in Fig. 2(b). The slope of the plot of In $k^{/}$ versus In [reductant] should equal to 'n' order of reaction. The value of slope determined by this method is equal to '1' so this is again an indication of first order reaction with respect to reductant (sodium thiosulphate) and over all order of reaction is second order. The intercept gives the value of second order rate constant, amounting to 7.5×10^3 $M^{-1}S^{-1}$

In view of the above mentioned experimental results we propose the following mechanism for the reaction.

$$S_4O_6^{2-} + 2e^- \xrightleftharpoons{} 2S_2O_3^{2-}$$

$$Mn(Pd)_2 (H_2O)_2^+ \xrightleftharpoons{kh} Mn (Pd)_2 (H_2O) (OH) + H^+$$

$$Mn(Pd)_2 (H_2O)_2^+ + S_2O_3^{2-} \xrightleftharpoons{k_1} Mn (Pd)_2 (H_2O) (S_2O_3)^- + H_2O$$

$$Mn (Pd)_2 (H_2O) (S_2O_3)^- \xrightarrow{k_2} Mn (II) + 1/2 S_4O_6^{2-}$$

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