Journal of the Iranian Chemical Society, Vol. 1, No. 2, December 2004, pp. 122-127.

JOURNAL OF THE
Iranian
Chemical Society

Study of the Kinetics and Activation Parameters of Reduction of Mn(III) to Mn(II) by SO_3^{2-} Ion in $(MnSiW_{11}O_{40}H_2)^{5-}$ Heteropoly Ion

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(Received 29 September 2003, Accepted 10 November 2003)

In order to gain an insight into the mechanism of reduction of Mn(III) heteropoly ions, and also to establish the conditions for use of some of these ions as oxidizing agent, following measurements have been made. The pseudo-first order rate constants, k_{obs}, have been determined and specific rate constants, k, were calculated from the plots of k_{obs} against SO_3^{2-} concentrations. A plot of $\ln(k_2/T)$ against inverse temperature gives enthalpy of activation as 10.67 kJ mol^{-1} and entropy of activation as -237.90 J K^{-1} mol^{-1}. Effects of ionic strength and pH have also been studied over a limited range.

Keywords: Heteropoly ion, Stopped-flow, MPLIX program, Rate constant, Enthalpy, Entropy

INTRODUCTION

Heteropoly anions are a special class of compounds of V(V), Nb(V), Ta(V), Mo(VI) and W(VI). When the anions contain only one transition metal and oxygen such as $Mo_7O_{24}^{6-}$ and $Nb_6O_{19}^{8-}$ they are known as isopolyanions, whereas when the anions contain additional metal or non metal, they are known as heteropoly anions, such as $[Co^{II}_2W_{12}O_{42}]^{8-}$. The heteropoly anions in which Mn(II), Mn(III) and Mn(IV) are present as one of the addenda atom with Nb, W or Mo as metal atoms have been reported [1]. Most of the Mn(III) compounds are fairly unstable and usually disproportionate into Mn(II) and Mn(IV). The standard oxidation potentials for Mn(III)/Mn(II) system are given below [2]:

$$Mn^{2+}_{(aq)} \longrightarrow Mn^{3+}_{(aq)} + e^- \qquad E^0 = -1.5\ V$$

$$Mn^{2+}_{(aq)} + 2H_2O \longrightarrow MnO_2 + 4H^+ + e^- \qquad E^0 = -1.239\ V$$

$$Mn(OH)_2 + OH^-_{(aq)} \longrightarrow Mn(OH)_3 + e^- \qquad E^0 = +0.2\ V$$

The hydrated Mn(III) ion is an oxidizing agent and unstable with respect to Mn(II) and Mn(IV). Mn(III) is stable only in highly acidic solutions [3].

Kinetic studies show that a rapid equilibrium is established for the disproportionation reactions of Mn(III) in aqueous medium according to the following reaction [4,5]:

$$2Mn^{3+} \rightleftarrows Mn^{4+} + Mn^{2+}$$

The reported equilibrium constant for the reaction is 1.8 × 10^5 in 2.4 to 7.4 M H_2SO_4. In less acidic solutions (*i.e.*, above pH 5.5) Mn(III) disproportionates into Mn(II) and MnO_2. However, the trivalent ion can be stabilized in neutral solution by pyrophosphate to give the complex ion $[Mn(H_2P_2O_7)_3]^{3-}$, which can be used as an oxidizing agent [4].

Mn(III) is also stable in solutions containing large excess of phosphoric acid, due to the formation of phosphates [6]. The majority of Mn(III) complex ions are octahedral and high spin. A very few low spin octahedral complexes such as hexacyanomanganese(III) ion and dimethylaminotroponiminto manganese(III) are known [7]. The heteropoly ions containing

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Mn(III) are generally very stable in solid state and in solution over a pH range of 1 to 7 [8,10].

The use of inorganic electron acceptors, such as Br_2, MnO_4^- [11] and inorganic peroxides [12], is often encountered in polyoxometalates (POM) synthesis. Taking advantage of the oxidative stability of many POM anions, researchers have also used ozone in this respect [13]. The Co(III) ion in $[Co^{III}W_{12}O_{40}]^{5-}$ is substitutionally inert. Thus it is reasonable to expect that this ion will be reduced via outer sphere pathways [14].

In Mn(III) heteropoly ion, Mn(III) lies at the center of the six oxygen atoms and surrounded by silicon atom (addenda), so that the gain of electron should be difficult. This work was carried out to reduce Mn(III) heteropoly ion by a strong reducing agent (SO_3^{2-}) and suggest a possible mechanism of the reduction.

The sulfite ion contains sulfur in tetravalent positive formal oxidation state and, in oxyanions, the most stable oxidation state of sulfur is hexavalent; the sulfite ion is rendered a strong reducing agent. The sulfite ions are either oxidized to $S_2O_6^{2-}$ or SO_4^{2-} ions depending upon the nature of the reaction.

It has been observed that the inert oxidants usually oxidize S(IV) to SO_4^{2-}, whereas the labile oxidants usually produce an appreciable quantity of $S_2O_6^{2-}$ ion. Two suggestions have been made to account for these observations:

1. There should be a reduced metal-S(V) complex.
2. An intermediate is formed, consisting of an unreduced oxidant metal-S(V) complex that leads to dithionate. However, this complex would not form if the oxidant was inert. Another possible mechanism for the formation of dithionate could occur when an unreduced oxidant metal-S(IV) complex reacting with intermediate metal-S(V) complex. Similar pathways might be important in some other systems.

The kinetics of the oxidation of SO_3^{2-} by H_2O_2 has been reported by stopped-flow spectrophotometry over the pH range 4-8 [9].

The preceding discussion suggests that the SO_3^{2-} ion has been used to reduce the metal ion through many pathways but mostly SO_3^- (intermediate) seems to be involved in the electron transfer reaction. The unusual stability of Mn(III) heteropoly ions and the reducing ability of SO_3^{2-} ions demands the study of the kinetics and mechanism of their reaction. Since many pathways have been proposed for the reductions involving SO_3^{2-} ions, it would be useful to analyze this reaction for its kinetics. Attempt has been made to deduce the mechanism of reaction, to determine the activation parameters and to study the effect of changes in pH and ionic strength of solution on the rate of such reaction. For the purpose of this study the potassium(II) tungstomangano(III) silicate $K_5[SiMn^{III}W_{11}O_{40}H_2].16H_2O$ was selected. The reduction of these ions by sodium sulfite was studied by a stopped-flow spectrophotometric technique.

EXPERIMENTAL

All solutions were prepared in deionized distilled water. The heteropoly anion, potassium-tungsto mangano(III) silicate was synthesized according to the standard procedure [10].

The solution of $K_5[SiMn^{III}W_{11}O_{40}H_2].16H_2O$ of 1.22×10^{-3} M was kept in a well stoppered bottle. Fresh solutions of Na_2SO_3 with concentrations ranging from 1.22×10^{-2} M to 8.5×10^{-3} M in acetate buffer of pH 4-5.5 were prepared for every new set of experiments, as the solution of Na_2SO_3 decomposed on standing .

For each kinetic run, 50 ml of the heteropoly anion stock solution was placed in a conical flask. A weighed amount of solid Na_2SO_4 was added to heteropoly anion in order to maintain the ionic strength of the final solution. The pH of the solution was adjusted to 5.0. 50 ml of freshly prepared solution of Na_2SO_3 in acetate buffer at pH = 5 was placed in a conical flask. Both flasks were placed in a thermostatically controlled water bath for 15 min to ensure the attainment of the required temperature. Equal volumes of Mn(III) heteropoly anion and Na_2SO_3 solutions were mixed in a reaction cell to measure the absorbance. The absorbance data were changed into equivalent potential with the aid of digital analog, and k_{obs} values were calculated using computer program MPLIX. Since the rate of reaction was very fast, a stopped-flow technique was used. Change in absorbance was in the visible region. The MPLIX program allowed us to save the records of individual kinetic runs in files with voltage output of a Spectronic 21 instrument.

The reaction was carried out with different concentrations of Mn(III) heteropoly anion ranging from 1.22×10^{-3} to 6.1 ×

10^{-4} M. Each solution of the heteropoly anions was made to react with a series of Na_2SO_3 solutions ranging from 1.22 × 10^{-2} to 8.5 × 10^{-3} M, to maintain the pseudo first order condition. These reactions were carried out at 308, 313, 318, 323, and 328 K. The ionic strength was maintained by Na_2SO_4, ranging from 0.1 to 0.3 M. The concentration of Mn(III) heteropoly anion, Na_2SO_3 and Na_2SO_4 were taken twice of the required concentration so that on mixing the appropriate concentration is attained in the reaction cell.

In this study four sets of experiments were performed. In the first two sets of experiments, the temperature, pH and ionic strength were kept constant. In one series, the concentration of sulfite ion was varied while that of Mn(III) heteropoly ion was kept constant. In the second series, the SO_3^{2-} ion concentrations were kept constant while the Mn(III) heteropoly ion concentration was varied. All of these experiments were performed at 308, 313, 318, 323, and 328 K at pH 5 and ionic strength 0.15 M.

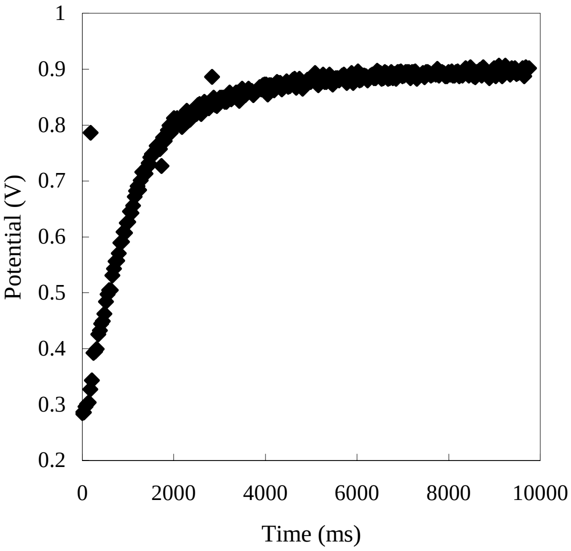

Fig. 1. Sample plot of change in potential as a function of time.

Table 1. The Observed Rate Constants, $10^4 k_{obs}$ (s^{-1}), at Various Concentrations of Na_2SO_3. Concentration of Heteropoly ion Mn(III) = 6.1 × 10^{-4} M, pH = 5, and μ = 0.15 M

	308 K		313 K		318 K		323 K		328 K	
Na_2SO_3 Conc. (M)	k_{obs} × 10^4	S.D. × 10^6	k_{obs} × 10^4	S.D. × 10^7	k_{obs} × 10^4	S.D. × 10^6	k_{obs} × 10^4	S.D. × 10^6	k_{obs} × 10^4	S.D. × 10^6
3.66 × 10^{-3}	1.39	2.43	1.58	9.10	1.70	1.39	1.83	3.75	1.90	1.19
5.00 × 10^{-3}	1.79	3.66	1.89	11.6	2.13	8.00	2.32	4.40	2.51	1.65
6.10 × 10^{-3}	2.36	2.06	2.49	33.5	2.73	8.76	2.91	2.80	3.18	7.10
7.32 × 10^{-3}	2.59	1.42	2.78	240	3.22	5.19	3.52	7.22	3.70	9.44
8.50 × 10^{-3}	3.19	1.10	3.33	197	3.57	16.4	3.72	3.33	3.86	13.70

Table 2. The Observed Rate Constants, $10^4 k_{obs}$ (s^{-1}), at Various Concentrations of Mn(III) Heteropoly Ion. Concentration of Na_2SO_3 = 6.1 × 10^{-4} M, pH = 5, and μ = 0.15 M

	308 K		313 K		318 K		323 K		328 K	
Mn(III) heteropoly ion Conc. (M)	k_{obs} × 10^4	S.D[1] × 10^6	k_{obs} × 10^4	S.D. × 10^6	k_{obs} × 10^4	S.D. × 10^6	k_{obs} × 10^4	S.D. × 10^6	k_{obs} × 10^4	S.D. × 10^6
0.75 × 10^{-4}	1.39	1.61	2.50	2.80	2.07	5.67	3.50	1.46	3.92	2.23
1.50 × 10^{-4}	1.40	1.06	2.48	5.44	2.13	12.60	3.51	4.10	3.92	1.60
3.00 × 10^{-4}	1.40	1.31	2.51	1.89	2.06	10.80	3.49	3.88	3.92	1.81
4.50 × 10^{-4}	1.40	1.19	2.50	4.01	2.10	4.20	3.51	1.68	3.90	9.55
6.10 × 10^{-4}	1.40	1.31	2.51	1.12	2.13	4.27	3.53	5.41	3.84	15.00

To observe the effect of change of pH and ionic strength on the rate constant, in a set of experiments, the pH and ionic strength were varied keeping the concentration of the reactants and temperature constant. Each kinetic run was repeated at least five times. The results are shown in Tables 1-4.

RESULTS AND DISCUSSION

The plots of ln($A_{t\ -}\ A_x$) against time turn out to be straight lines over many half-lives. This indicates that the system is first order with respect to both SO_3^{2-} and Mn(III) heteropoly ion. The slope of this line is the pseudo first order rate constant (k_{obs}). For each concentration of heteropoly ion and SO_3^{2-}, twenty kinetic runs were performed to determine (k_{obs}). A sample graph for the kinetic rows is shown in Fig. 1. The values of these rate constants are given in (Tables 1and 2). In one set of experiments, the SO_3^{2-} concentration was varied, while in other sets of experiments, the Mn(III) heteropoly ion concentration was varied, keeping all other parameters constant.

The reaction involved SO_3^{2-} ion as reducing agent have been extensively studied and two mechanisms namely the outer sphere and inner sphere electron transfer have been proposed for various systems.

The Mn(III) containing heteropoly ions have a complex cage structure where Mn(III) ions are surrounded by the neighboring oxygen and thus lose their reactivity, since they are unable to form a direct linkage with the other reagents. Probably this the reason why the oxidation of Mn(II) heteropoly ions by peroxodisulfate seems to proceed through an outer sphere electron transfer mechanism resulting in the formation of SO_4^{2-} ion radicals. The formation of SO_3^{2-} radical has been proposed in case of reduction of $[Fe(CN)_6]^{3-}$ [15].

The inner sphere electron transfer mechanism requires either a direct contact between SO_3^{2-} and the species being reduced or through a bridge, as proposed in the case of reduction of $[Fe(CN)_6]^{3-}$ [15]. In case of heteropoly ions, the inner sphere electron transfer seems to be somewhat unlikely, since they do not conveniently form charge transfer complexes as cyanide (CN^-) or NO^+. The outer sphere electron transfer requires the formation of SO_3^- ion radical as an intermediate, which may dimerize to dithionate $S_2O_6^{2-}$ or take one OH^-, which may dimerize to dithionate $S_2O_6^{2-}$ or take one OH^- ion forming HSO_4^-:

$$[Mn^{III}x]^{5-} + SO_3^{2-} \longrightarrow [Mn^{II}x]^{6-} + SO_3^- \quad (1)$$

$$2SO_3^- \longrightarrow S_2O_6^{2-} \quad (2)$$

$$SO_3^- + 2OH^- \longrightarrow SO_4^{2-} + H_2O + e \quad (3)$$

$$e + [Mn^{III}x]^{5-} \longrightarrow [Mn^{II}x]^{6-} \quad (4)$$

where $[SiMn^{III}W_{11}O_{40}H_2]^{5-} = [Mn^{III}x]^{5-}$.

In case of excess of SO_3^{2-} ion concentration, the reaction (2) has been proposed to dominate over (3) and (4), as suggested [15] and confirmed [9]. Since the SO_3^{2-} concentration in this study is varied from 3.66×10^{-3} to 8.5×10^{-3} M and pH has been retained at 5.00, the reactions (3) and (4) cannot be contributed to a great extent as compared to reaction (2). The rate equation, however, comes out to be as following:

$$d[Mn^{III}x] / dt = k\,[SO_3^{2-}]\,[Mn^{III}x] \quad (5)$$

Since SO_3^{2-} ions were present in large excess, we can define k_{obs} as

$$k_{obs} = k\,[SO_3^{2-}] \quad (6)$$

The values of k_{obs} are summarized in Tables 1and 2.

When k_{obs} values are plotted against the concentration of SO_3^{2-} ion, they give a straight line graph for at each temperature (Fig. 2). The slope of the line corresponds to k, the rate constant in equation (5). The agreement between the rate equation and the experimental data supports the ion radical mechanism. Keeping the concentration of Mn(III) heteropoly and SO_3^{2-} ion constant, the pH and the ionic strength was varied in order to observe the effects of changes in these parameters.

The values of k_{obs} obtained at different pH and ionic strength are summarized in Tables 3 and 4, respectively. The system seems to be insensitive towards changes in pH and ionic strength, indicating that SO_3^{2-} rather than HSO_3^- is involved in the reaction.

The plots of ln(k_2/T) against inverse temperature (Fig. 3)

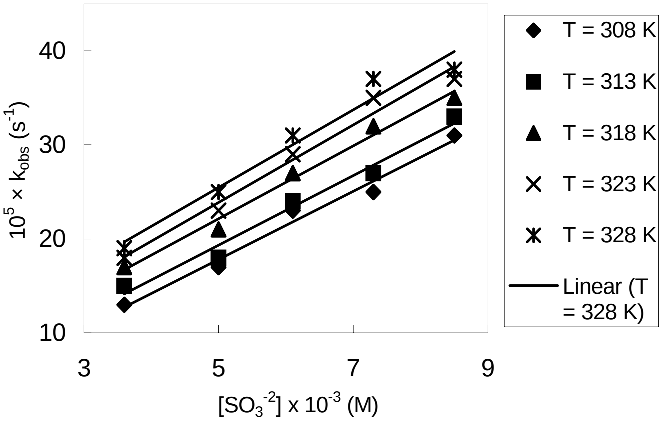

Fig. 2. Plot of k_{obs} as a function of [SO_3^{-2}] at different temperatures, pH = 5, μ = 0.15 M.

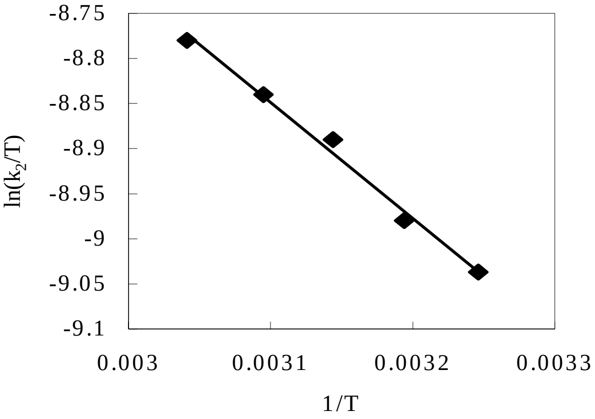

Fig. 3. Plot of ln(k_2/T) as a function of 1/T.

Table 3. The Observed Rate Constants at Various Ionic Strengths. Mn(III) heteroploy ion = 6.1 × 10^{-4} M, Na_2SO_3 = 6.1 × 10^{-3} M, T = 313 K, and pH = 5.0

Ionic strength μ (M)	$k_{obs} \times 10^4$ (s^{-1})
0.10	2.53
0.15	2.52
0.20	2.52
0.25	2.52
0.30	2.53

Table 4. The Observed Rate Constants at Various pH. Mn(III) heteroploy ion = 6.1 × 10^{-4} M Na_2SO_3 = 6.1 × 10^{-3} M, T = 313 K, μ = 0.15 M

pH	$k_{obs} \times 10^4$ (s^{-1})
0.5	2.50
4.0	2.50
4.5	2.51
5.0	2.51
5.5	2.49

gives enthalpy of activation as 10.7 kJ mol^{-1} and entropy of activation as -238 J K^{-1} mol^{-1}.

The change in reaction rates with change in temperature justifies the enthalpy of activation. The reaction requires a close approach of divalent and pentavalent changed ions. The electrostatic repulsion, the changes in solvation at the moment of electron transfer and rearrangement of bond lengths in both ions would increase the enthalpy of the reaction substantially.

In view of the preceding discussion, it can be concluded that $[SiMn^{III}W_{11}O_{40}H_2]^{5-}$ is reduced by SO_3^{2-} through an outer sphere electron transfer mechanism. The product is the Mn(III) heteropoly ion and SO_3^{-} ion radical which may dimerize to produce $S_2O_6^{2-}$ ions. The reaction exhibits first order dependent on either of the reagents and the reaction rate increases with increasing temperature. The rates of reaction are insensitive to change in pH and ionic strength within the range included in this study.

ACKNOWLEDGEMENT

The authors wish to thanks late Prof. Dr. S. A. Zubairi and Prof. Dr. A. M. Qureshi for useful suggestion and guidance in this work.

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