

Oxidation of Hydroxylamine by a Tetranuclear Manganese Complex in Aqueous Acidic Medium– Proton Coupled Electron Transfer

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Abstract

Hydroxylamine and its mono protonated conjugate acid form are both quantitatively oxidized to nitrous oxide by a quadrinuclear tetravalent manganese complex $[\text{Mn}_4(\mu\text{-O})_6(\text{bipy})_6]^{4+}$ (**1**, bipy = 2,2'-bipyridine) and its conjugate acid form $[\text{Mn}_4(\mu\text{-O})_5(\mu\text{-OH})(\text{bipy})_6]^{5+}$ (1H^+) in water in the pH range of 2.0-6.0. NH_2OH and its conjugate acid NH_3OH^+ are the active reducing agents, which are oxidized into N(+I) state. As usual, the oxo-bridge protonated metallic oxidant 1H^+ reacts at a faster rate than **1**. An aqueous solution of complex **1** shows extreme stability over a wide pH range and no ligand dissociation equilibria are monitored in its solution, irrespective of different conditions like varying ligand or reducing agent concentrations. The reaction exhibits noticeable kinetic isotope effect by decreasing the reaction rate in D_2O media. A Hydrogen Atom Transfer (HAT), i.e., one electron and one proton (1e , 1H^+ ; electroprotic) transaction, is suitable to elaborate the isotope effect.

Keywords: Hydroxylamine; Isotope Effect; Kinetics; Manganese

Introduction

Dioxygen evolved in green biosystems by the process of photosynthesis in presence of a higher valent multinuclear manganese complex termed as oxygen evolving complex (OEC) which is usually structured by a set of three or four manganese atoms coordinated to each other (Kirby *et al.*, 1981; McEvoy & Brudvig, 2004). During the process of oxygen evolution, this Mn tetramer smoothly transitions between five separate oxidation levels, demarked as $S_0 - S_4$ as we came to know in the groundbreaking work of Kok *et al.* (1970) involving di to tetra valency of metal (Dekker *et al.*, 1984). The metal ions in the reactive core are formed by di- μ -oxo units, which may be either oxo or carboxylate linkage. The targeted oxidant $[\text{Mn}_4(\mu\text{-O})_6(\text{bipy})_6]^{4+}$ (**1**, Figure 1, bipy = 2,2'-bipyridine) of title kinetic investigation is structurally identical to the model proposed by OEC (Yachandra *et al.*, 1993). Generated one-electron reduced complex, which is a mixture of two Mn atoms at different oxidation states, ($\text{Mn}^{\text{IV}}_3\text{Mn}^{\text{III}}$) structurally parallel to EPR-spectral model for the S_2 state of the OEC (Philouze *et al.*, 1994).

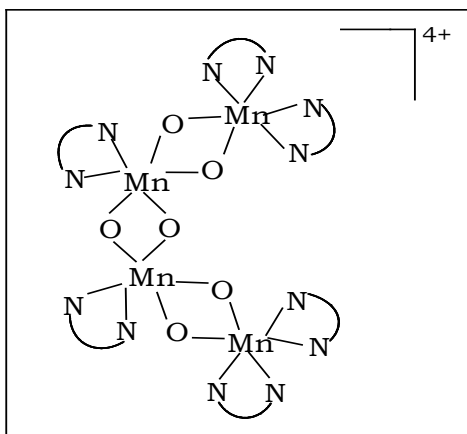


Figure 1: Structural Framework $[\text{Mn}_4(\mu\text{-O})_6(\text{bipy})_6]^{4+}$ is 2,2'-bipyridine

Oxidation of Hydroxylamine by Mn Complex

It is previously reported in the study that the chosen reducing agent, hydroxylamine (NH_2OH), acts as a reducing agent of the Manganese ions of OEC in PS II (Beck & Brudvig, 1987). The bond dissociation energy values of N–H bond in NH_2OH (92 kcal mole⁻¹) and O–H bond in tyrosine attached to the OEC are very close to each other (Blomberg *et al.*, 1997). Therefore, it is interesting to study the NH_2OH reduction where it can be compared with tyrosine for the mechanism of proton coupled electron transfer, like tyrosine activity in PS II. With reference to the activity of tyrosine in PS II, the oxidation-reduction study of this title work will be worthy enough for creating a clear perception of electron transfer mechanism in PS II.

Experimental**Materials**

Target oxidant is prepared in pure crystalline form with molecular formula $[\text{Mn}_4(\mu\text{-O})_6(\text{bipy})_6](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$ (**1**) according to the reported method (Philouze *et al.*, 1994). The complex makes a clear transparent solution in water, and the spectral patterns of these solutions remain unchanged for a long period of time over a wide pH range up to pH 6.0. Pure Hydroxylamine nitrate was prepared in situ by double decomposition of hydroxylamine sulphate (G. R., E. Merck) with barium nitrate (G. R., E. Merck) and purity of the reductant is checked by oxidation with KBrO_3 in dilute H_2SO_4 medium (Jeffery, 1989). The strength of the stock solutions remains unaltered for long period of time when kept at $\sim 10^\circ\text{C}$.

NaNO_3 solution was standardized by a common acid-based titration and for this purpose, it was passed through a Dowex cation-exchange resin (in acid form) and the acidic eluate was estimated by an acid base titration reaction using standard sodium hydroxide solution and phenolphthalein as indicator. Solid 2,2'-bipyridine of G. R., E. Merck, was purchased and used in the process. D_2O (99.9 atom % D) and DNO_3 (99+ atom % D) were used in the experiment and purchased from Sigma. Used other chemicals and reagents were of reagent grade quality. Doubly distilled deionized water was useful for the depicted reaction setup.

Equilibrium Measurements

Acid dissociation constants (K_a) of the reductant NH_3OH^+ cation in 95% D_2O media were determined by pH-metric titration using a Metrohm 736-GP-Titrino autotitrator at $I = 1.0\text{ M}$ (NaNO_3) at 25°C . The reported $\text{p}K_a$ value (Lumme *et al.*, 1965) in H_2O media for NH_3OH^+ cation was used. Same type of pH metric titration was executed several times in the working pH range of the reaction to evaluate any $\text{p}K_a$ value for the protonation of oxo-bridges of Mn tetramer.

Stoichiometric Measurements

Stoichiometry of the title reaction was resolute in both kinetic (when reagent concentration is more than the complex concentration) and non-kinetic situations (when complex is more than the reagent in same volume). Solutions for kinetic study used 8 – 15 times more hydroxylamine than the colored Manganese tetramer for a complete reaction and ended up without any visible color (absorbance at 420 nm was less than 0.01). In this reaction setup, unused N(-I) was determined by a titration procedure with standard KBrO_3 , where Mn^{II} , bipy and ClO_4^- had no interference. Existence of nitrite or nitrate anions as the oxidation product was nullified after testing the coupling reaction of sulfanilic acid and α -naphthylamine where no characteristic red azo dye was reported.

Complexometric EDTA-EBT (at pH 10) titration method was deployed to measure the exact amount of Mn^{2+} ions formed after the complete reduction of the tetravalent complex.

It was also tested that no interferences were noted by any other reaction components existing in the solution. In non-kinetic situation, less than stoichiometric amount of measured hydroxylamine was allowed to react with the complex at similar reaction condition and after a finite time gap, the absorbance value of

unreacted complex from the equilibrated reaction mixtures was monitored at 420 nm ($\epsilon=7.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) to calculate the unreacted quantity of tetramer that remains.

Physical Measurements and Kinetics

All physical parameters, like absorbances and spectra of the described reaction, were recorded with a Shimadzu (1601 PC) spectrophotometer using 1.00 cm quartz cells. The kinetics were monitored *in situ* with the instrument in “kinetic mode” at 420 nm in an electrically controlled thermostated 25.0 (± 0.1) °C cell housing (CPS –240 A).

A Shimadzu (1601 PC) spectrophotometer with 1.00 cm quartz cells was utilized to follow the described kinetics spectrophotometrically. The machine worked in thermostated mode at 25.0 (± 0.1) °C. Apart from the Mn(IV) tetramer no other substance absorbs any radiation in the 420 nm range. The medium ionic strength was usually fixed at 1.0 M with Sodium nitrate. Excess (range 1 – 80 mM) bipy concentration, ($C_{\text{bipy}} = [(\text{Hbipy})^+] + [\text{bipy}]$) maintained in all the kinetics serves the roll of a good buffer in the reactions medium. It was possible that the hydroxylamine cation could act as an additional buffering agent with the excess ligand bipy. NH_3OH^+ ($\text{pK}_a = 6.00$) would impart its buffering action at higher pH extremes. The pH of the reacting solutions was watched at both initiation and ending of every set by using an Orion – Ross combined-electrode system -model 81-02. Calibration of the pH meter was performed with standard HNO_3 solutions, also maintaining a medium unit molar ionic strength with sodium nitrate. Accurate comparison of kinetic studies in similar pH in D_2O media and in H_2O media was done by selecting solutions with a 0.4-unit higher value of pH in deuterated environment than that in aqueous medium (Covington *et al.*, 1966). To maintain first-order kinetics, concentration of the reducing agent keeps high throughout, and the rate constants (k_0) were calculated by using the techniques of least square slopes of $\log_{10}(\text{abs})$ versus time plots. Rate measurements were usually done at 25.0 °C and at $I = 1.0 \text{ M}$ (NaNO_3) unless stated specifically.

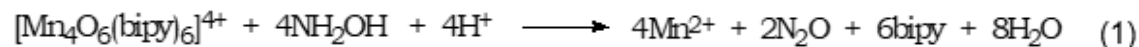
Results and Discussion

Equilibrium Measurements

The pK_a values of the title acid N(-I) in a 95% deuterated media and in aqueous media are found to be 6.40 ± 0.10 and 6.00 ± 0.20 respectively, at 25.0 °C and at $I = 1.0 \text{ M}$ (NaNO_3). Numerous projects were carried out to discover any sort of value of protonation constant for the oxo bridges of the title compound during the reaction conditions. Title oxidant does not exhibit any proper numerical value of protonation or ionization in the reaction condition.

Stoichiometric Measurements

The described kinetics resulted in the following stoichiometry, i.e., $\Delta[\text{Mn}^{\text{IV}}_4]/\Delta[\text{T}_R] = 0.25 \pm 0.03$ and $\text{T}_R = [\text{N}(-\text{I})] = [\text{NH}_2\text{OH}] + [\text{NH}_3\text{OH}^+]$. Tetramer quantitatively reduced into Mn^{II} state as revealed from EDTA titration and exists as a stable Mn^{II} - bipy complex. Formation of Mn^{II} - bipy complex is supported by the study of optical spectra. In similar conditions, a mixture of manganese nitrate and 2,2'-bipyridine generates similar spectral patterns, like reaction product solutions. All the above findings guided to equation (1).



Kinetics

The above-described reaction process in kinetic situation obeys a good first order reaction mechanism for up to a minimum of four half-lives. Kinetic pathways of reduction of colored compounds are tracked spectrophotometrically in the range of 380 nm to 500 nm wavelengths. Facts and findings revealed that the first order reaction kinetics are independent of the selected wavelength. Each k_0 value reported is an

average value of three self-reliant resolutions when the individuals rate constant having maximum of 3% the coefficients of variation (CV). The first order rate constants are determined from the slope of straight-line fitting graph of $\log_{10}(\text{absorbance})$ versus time plots. For title redox k_0 increase with an increase in pH but this trend is just reversed at high acidic region. The reaction rates remain unaltered with the variation of concentration of additional free bipyridine ligand (3 – 80 mM) which clearly precluded the prospect of any sort of equilibrium of the complex which set free bipy ligand from compound to the solution. The described kinetics highly displays first-order relation with the total concentration of the reducing species throughout the pH range it studied. The experimentally derived rate constants are unaltered by the switching of compound concentration in varied concentration, like 0.05 – 0.2 mM or presence or absence of ambient light in the reaction medium. The effect of increasing ionic strength of the medium increases the oxidation rate significantly at lower pH regions, ca. at pH 2.1 or 3.6, indicating the reaction between similarly charged species. Whereas the first-order rates remain unchanged during ionic strength variation when the oxidation reaction is carried out in higher pH (~ 5 - 6) region.

Table 1: Some Illustrative Data Representing First-Order Rate Constants of the Described Kinetics

pH	T _R , M	C _{bipy} , mM	10 ⁴ k ₀ , s ⁻¹
2.04	0.01	5.0	3.60 (3.58)
2.37	0.01	5.0	1.95 (1.92)
3.02	0.01	5.0	0.79 (0.84)
3.20	0.01	5.0	0.73 (0.76)
3.42	0.01	5.0	0.74 (0.74)
4.00	0.01	5.0	1.19 (1.12)
4.41	0.01	5.0	1.98 (2.10)
4.84	0.01	5.0	4.52 (4.69)
5.35	0.01	5.0	12.2 (12.4)
6.00	0.01	5.0	32.0 (32.2)
3.61	0.02	5.0	1.51 (1.58)
3.62	0.04	5.0	3.23 (3.18)
3.61	0.10	5.0	7.79 (7.90)
4.11	0.01	1.0	1.21 (1.30)
4.10	0.01	10	1.23 (1.28)
4.13	0.01	20	1.29 (1.34)
4.12	0.01	40	1.37 (1.32)
4.12	0.01	60	1.42 (1.32)
5.95	0.01	5.0	30.1 ^a
5.93	0.01	5.0	30.5 ^b
2.11	0.01	5.0	2.61 ^a
2.12	0.01	5.0	2.08 ^b
3.60	0.01	5.0	1.22 ^a
3.62	0.01	5.0	1.05 ^b

^a I = 0.5 M (NaNO₃). ^b I = 0.1 M (NaNO₃).

[Mn⁴⁺] = (0.10 mM) at Temp = 25.0 °C, I = 1.0 M (NaNO₃). Values within the parenthesis are back calculated k_0 values using published rate constants of Table 2 in equation (9).

The observed k_0 vs. pH graph of the aforesaid reaction may be best illustrated and rationalized by strategy described below. Described proton dependent equilibrium in equation (2) and in equation (3) plays a major role for observed kinetics. Here RH signifies protonated form of reducing agent (NH₃OH⁺) and R⁻ represents NH₂OH.

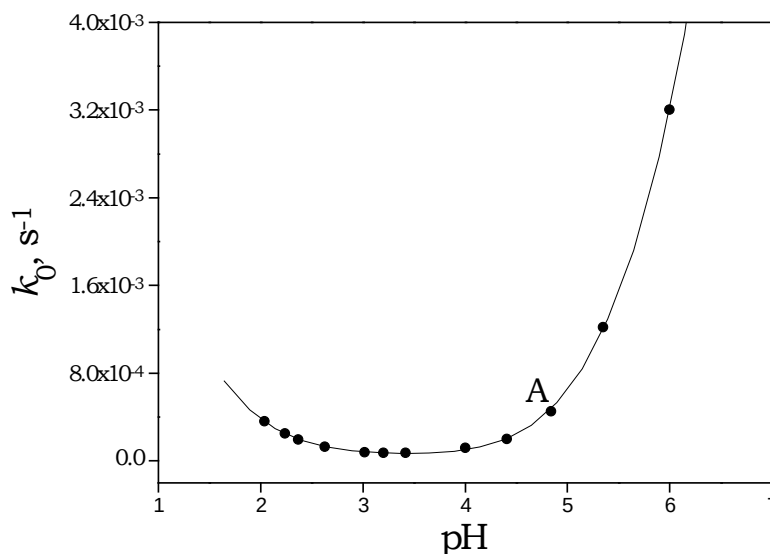


Figure 2: Plotting of k_0 versus $[H^+]$. $[Mn_4] = 0.10$ mM, Temp = 25.0 °C, $I = 1.0$ M (NaNO₃), $[bipy] = 3.0$ mM



Scheme 1

Scheme 1 Leads to the Rate Law Equation (8)

$$k_0(1 + K_1[H^+])(K_a + [H^+])/T_R = k_1K_1[H^+]^2 + (k_2K_1K_a + k_3)[H^+] + k_4K_a \quad (8)$$

K_1 is the protonation constant of complex **1**, the protonation occurs at the oxo-bridge of the oxidant. Several attempts have been made to evaluate the protonation constant of the title oxidant in our working pH range. Also, no pK_a value was obtained from the pH-meric titration of the complex solution, indicating very weak basic nature of the oxo-bridges in water solution. Available literature reports on study over a numerous multicore higher valent Mn complex (Thorp, 1989) suggest very weak basic nature of the oxo-bridges in aqueous medium. Hence, from all the above information we may assume that in our system $K_1[H^+] \ll 1$. The maximum concentration of H^+ used in our study is of order of 10^{-2} . Therefore, $(K_1)_{\max}10^{-2} \ll 1$, i.e., $(K_1)_{\max} \ll 10^2$, so $(K_1)_{\max} \leq 10$, i.e., upper limit of K_1 is nearly at 10. Now, applying the assumption $K_1[H^+] \ll 1$, the equation (8) is simplified and takes the form described in equation (9).

$$k_0(K_a + [H^+])/T_R = k_1K_1[H^+]^2 + (k_2K_1K_a + k_3)[H^+] + k_4K_a \quad (9)$$

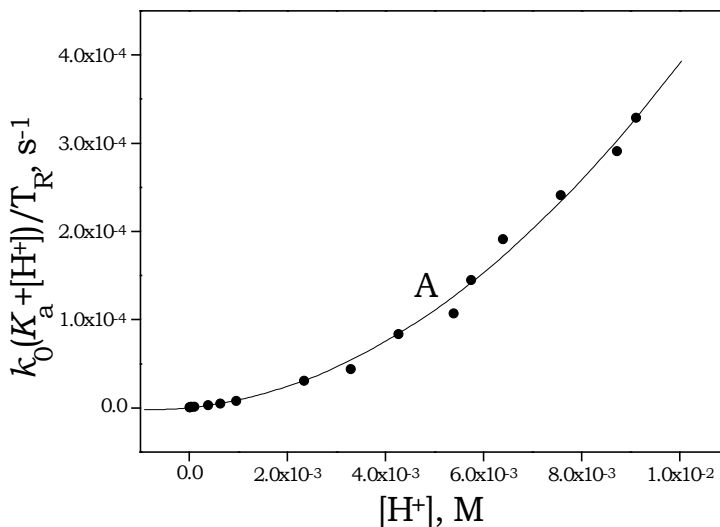


Figure 3: LHS of eqn. (9) vs. $[H^+]$. $[Mn_4] = 0.10$ mM, Temp=25.0 °C, $I=1.0$ M($NaNO_3$), $[bipy]=3.0$ mM

LHS of eqn. 9 is drawn on y-axis of a graph w.r.t. Hydrogen ion concentration on x-axis ended up with a nicely fitted polynomial curve representing the title kinetics (Figure 3, $r > 0.98$). Solving the fit composite or single rate constants is reported (Table 2). Recalculation of first order rate constants is executed with the data exhibited in Table 2. Recalculated values have very small deviations (within 7%) from the values noted experimentally. Similar treatments are pursued with the first order rate constants acquired when the kinetics are carried in D_2O medium and enlisted in Table 2.

Table 2: Representation of Rate Parameters for the Title Reaction

Reaction Path	k_1K_1 ($M^{-2} s^{-1}$)	$(k_2K_1K_a + k_3)$ ($M^{-1} s^{-1}$)	k_4 ($M^{-1} s^{-1}$)
H₂O medium	3.43 ± 0.20	$(4.4 \pm 0.3) \times 10^{-3}$	$(6.6 \pm 0.4) \times 10^{-1}$
95% D₂O medium	0.65 ± 0.04	$(1.9 \pm 0.1) \times 10^{-4}$	$(5.5 \pm 0.3) \times 10^{-2}$

Note: Conditions are similar like Table 1

For hydroxylamine reaction, k_4 pathway was found to be significant above a pH about 4. k_4 path effectively contributes to the observed first-order rate constants as judged by the relative contributions of the $k_1K_1[H^+]^2$ and $(k_2K_1K_a + k_3)[H^+]$ and k_4K_a values towards the noticed rate and at pH greater than or equal to 5.3, only k_4 path is enough to describe the overall kinetics. So, at higher pH ($pH \geq 5.3$) the right-hand side of the equation (9) contains only k_4K_a term and rearranges accordingly to give equation (10).

$$k_0(K_a + [H^+])/T_R = k_4K_a$$

$$T_R/k_0 = 1/k_4 + [H^+]/k_4K_a \quad (10)$$

A plot of T_R/k_0 versus $[H^+]$ was found to be a good straight line (Figure 4) whence the value of k_4 was evaluated from the slope [$k_4 = 1/(K_a \cdot \text{slope})$] and the intercept ($k_4 = 1/\text{intercept}$) of the graphical plotting depicted in Figure 4 and are listed in Table 3, which match well with the values reported in Table 2.

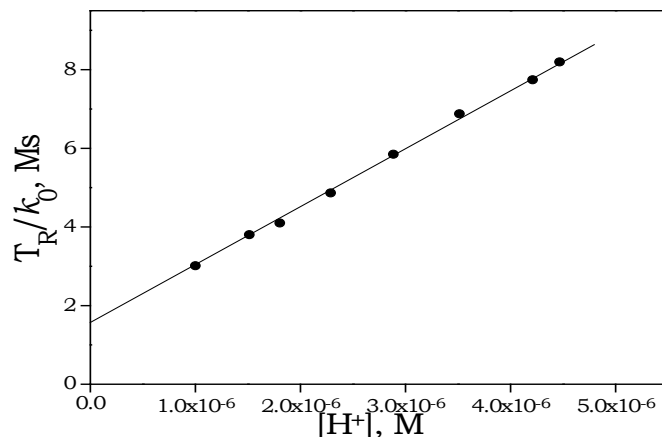


Figure 4: Plot of T_R/k_0 versus $[H^+]$. $[1] = 0.10$ mM, Temp = 25.0 °C, $I = 1.0$ M (NaNO₃)

Table 3: Comparison of the Value of the Second-Order Rate Constant (k_4).

k_4 from Slope ($M^{-1} s^{-1}$) pH ≥ 5.3	k_4 from Intercept ($M^{-1} s^{-1}$) pH ≥ 5.3	k_4 from Table 2 ($M^{-1} s^{-1}$) pH = 2.0 – 6.0
$(6.7 \pm 0.4) \times 10^{-1}$	$(6.6 \pm 0.4) \times 10^{-1}$	$(6.6 \pm 0.4) \times 10^{-1}$

Value obtained from non-identical situation for the reduction of **1** by N(-I) at [bipy]=5.0 mM, Temp=25.0°C, $I = 1.0$ M (NaNO₃).

Therefore, from Table 3, it can be concluded that the k_4 path alone is enough to guide effectively the overall reaction at pH ≥ 5.3 , as concluded from the relative contributions of the $k_1K_1[H^+]^2$, $(k_2K_1K_a + k_3)[H^+]$ and k_4K_a values towards the observed rate.

NH₃OH⁺ cation is the main prevalent form of NH₂OH at high acidic zones, like pH less than 3, whose oxidation by **1**H⁺ is electrostatically more unfavorable than the oxidation of NH₂OH. Oxidation of cationic NH₃OH⁺ requires higher concentrations of **1**H⁺, which are produced at much lower pH.

In title redox reactions, the rate of the redox process drops down noticeably with decrease of ionic strength of the reactive solution towards lower pH range, ca. at pH 2.1 or 3.6 where $[NH_3OH^+] \gg [NH_2OH]$ i.e., the reaction between similarly charged species. But the first-order rates are unchanged during ionic strength variation when the N(-I) oxidation reaction is carried out in higher pH (~ 5 - 6) region (where $[NH_2OH] > [NH_3OH^+]$).

From Table 2, it is concluded that highest limit for k_3 pathway (where form **1** reacts with acidic reductant) will be $4.4 \times 10^{-3} M^{-1} s^{-1}$ for N(-I) redox. For NH₂OH oxidation $(k_3)_{\max} \ll k_4$ indicating superior reactivity of NH₂OH as the reactivity goes up with increasing pH, only at very low pH (~ 2 – 3) the rate increases with increasing acidity due to high activity of the additional cationic oxidizing agent-**1**H⁺ over the **1**. To draw out the whole redox process, the formidable supremacy of **1**H⁺ is established. Initially it is assumed that $K_1[H^+]$ is lower in value than 1, and this puts up a higher value for the K_1 almost to 10. As it is considered that rate of diffusion-controlled reaction is $10^{11} M^{-1} s^{-1}$, then the minimum value of K_1 estimated from the k_1K_1 value tabulated in Table 2 is of the order of 10^{-9} .

Mechanism

Titile reaction process deals with altogether eight electronic transfers, but not through an individual process, rather through multistep electron transfer.

Oxidation of Hydroxylamine by Mn Complex

In spectral investigation no immediate changes in the pattern of reactants were observed in the reaction condition. Also, throughout the reaction, the rate constant, k_0 varies linearly with the total concentration of hydroxylamine, proposing the generation of a weak adduct between both the reagents. The electrochemistry of $[\text{Mn}_4(\mu\text{-O})_6(\text{bipy})_6]^{4+}$ has been comprehensively observed by Dunand-Sauthier *et al.* (1997, 1998, 1999). Complex **1** is electrochemically converted into a mixed valent binuclear $[\text{Mn}^{\text{III,IV}}_2(\mu\text{-O}_2)(\text{bipy})_4]^{3+}$ and uninuclear $[\text{Mn}^{\text{II}}(\text{bipy})_3]^{2+}$ systems and *vice versa*. A study in HNO_3 media at pH around 2 converted the compound electrochemically into divalent Manganese ion.

Isolation of the mono reduced form $[\text{Mn}^{\text{IV}}_3\text{Mn}^{\text{III}}(\mu\text{-O})_6(\text{bipy})_6]^{3+}$ by general inorganic reducing method is quite impossible. From the work of Blondin *et al.* (1997), the one electron reduced complex was accumulated with very high chemical reactivity by the method of cryogenic radiolytic reduction of mother complex. This single reduced form is even very much unstable at lower temperatures, like 190K. From the above discussion it can be concluded that the tetrameric complex is not a powerful oxidant. The overall process of reducing tetramer Mn^{IV} to Mn^{II} is a smooth transition, but initially mono electronic transfer to generate the mixed valent tetramer is not an energy-smooth active process. In the whole redox process (equations 4 – 7), assuming initial one electron donation process is the rate limiting step that generate the active internal form $[\text{Mn}^{\text{IV}}_3\text{Mn}^{\text{III}}(\mu\text{-O})_6(\text{bipy})_6]^{3+}$, it is again converted to ultimate format in a very fast process with help of extra reductant components or with the generated radicals at the RDS. No evidence of polymerization was noted during the studied reaction of tetramer and reductant when it was carried out in a 6% v/v acrylonitrile solution; still, it can't rule out the situation of radical production.

It may happen that generated radical reacts with the mono reduced Mn tetramer at a much faster rate compared to the polymerization reaction. The mono reduced components of oxidant or protonated oxidant will have oxo-bridges of highly basic nature, as a result, it immediately abstracts a proton from the reaction solution, and this removes thermodynamic or kinetic barricades for subsequent reduction to final state (Baldwin & Pecoraro, 1996; Vrettos *et al.*, 2001). It is one of the main characteristics involved in the reduction process of the Kok cycle in PS II (Renger, 2004).

Radicals generated after mono electronic oxidation of hydroxylamine, i.e., NH_2OH^+ are listed and its mechanistic approach leading to the production of nitrous oxide is well documented in nitrogen chemistry. Reaction of hydroxylamine is carried out in D_2O media (95%) and treated further in exactly the similar way to that in aqueous medium for further verification of the electron transfer procedure. Described redox is an outstanding example of kinetic isotope effect. The overall reaction rate for N(-I) oxidation decreases when it is executed in 95% D_2O medium compared to the rate observed in aqueous media. Electroprotic mechanism is established by diminishing of reaction rates in medium concentrated with D_2O . It was found that diminishing rates in $\text{H}_2\text{O}/\text{D}_2\text{O}$ mix medium are directly proportional ($r > 0.98$) with the amount of D_2O present, indicating the one electron movement of a proton at the slow RDS.

In practice it was observed that acidic power decreases in D_2O media (Wiberg, 1955; Ghosh *et al.*, 2002) and it is observed that pK_a 's of many reducing weak acids noticeably increased in D_2O medium, like glyoxylic, pyruvic (Das *et al.*, 2006), nitrous (Das & Mukhopadhyay, 2007) and hydroxylammonium cation. It can be concluded that for the oxidant the protonation constant (K_1) also increases in D_2O medium; it implies that concentration of 1H^+ is more in D_2O medium compared to H_2O medium in similar conditions. These redox reactions may be an example of a secondary isotope effect, as in the moment of isotope replacement, no oxygen bonded to H/D is formed or ruptured during RDS., suggesting a strong bonding association of isotopes via H-bond in the intermediate structure. This experimental fact again supports the existence of postulated hydrogen-bonding network in the OEC. In the observed oxidation, all the second order rate constants decrease in D_2O media. Decreased k_1 outweighs the increment of K_1 , hence slowing down the N(-I) redox. Numerical value of K_a in deuterated medium is reduced compared to its valuation in

H₂O and this again drops the value of combined rate constants ($k_2K_1K_a + k_3$) value in deuterated media. Both NH₂OH and NH₃OH⁺ are reacting with the title oxidizing agent.

The molecular mechanics generated organization of the oxygen-evolving complex points out well systematic array of hydrogen bonding frameworks in the vicinity of the OEC moiety (Jeans *et al.*, 2002); these title redox tries to provide a clear look on the transfer of proton and water in the active position.

Conclusion

Existence of a hydrogen cation in chosen reductant may be one of the reasons for the described redox activity. Also, HAT mechanism operated from the hydroxylamine to generate radical NHOH[•] and mono-reduced multivalent Mn^{IV}₃Mn^{III} tetramer attached with a proton on its oxo bridges. In general, protonated oxidant 1H⁺ is expected to be more kinetically reactive in oxidizing the hydroxylamine than 1. This higher oxidizing nature of 1H⁺ is predicted due to the very swift transaction of hydrogen or hydrogen ions throughout the structured H-bonding network created by combination of oxo-bridges in the center of the protonated metal core with the oxygen and hydrogen atoms of the reductant.

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