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Mechanistic Study on Oxidation of Hydroxylamine Monosulfonate (HAMS) by a Metal Bound Bridging Superoxide Ligand in Aqueous Acetate Buffer Medium

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A B S T R A C T

In aqueous acetate buffer medium (pH = 3.42 - 4.8) hydroxylamine monosulfonate, ($HONHSO_3^-$) reduces the one electron oxidant, bridging superoxo ligand in $[(dien)(en)Co^{III}(O_2)Co^{III}(en)(dien)](ClO_4)_5$ (**1**) to the corresponding hydroperoxo complex, $[(en)(dien)Co^{III}(HO_2)Co^{III}(en)(dien)]^{5+}$ (**2**) and itself gets oxidised to N_2O gas and SO_4^{2-}/ HSO_4^- following both proton coupled electron transfer (PCET) path and an electron – transfer reaction. The kinetics, stoichiometry and reaction mechanism clearly indicate that oxidation of $HONHSO_3^-$ occurs through the formation of an intermediate aminoxyl ($^-O_3SHNO^\cdot$) radical. In the presence of excess $HONHSO_3^-$ over **1**, the reaction obeys first-order kinetics and rate of the reaction increases with $[HONHSO_3^-]$. The reaction rate, however, decreases with increase in $[H^+]$ and the plot of $1/k_o$ with $[H^+]$ is linear with a small but significant intercept. The reaction rate also decreases with increase in ionic strength of the medium as expected for the two oppositely charged reactants. The decrease of reaction rate with $[H^+]$ is most likely due to the protonation of the superoxo complex **1**, which leads to a kinetic dead-end product. It is also noticed that the reaction rate significantly decreases with increasing proportion of D_2O replacing H_2O in the solvent. Therefore, an H-atom transfer (HAT) from the reducing species to the bridging superoxide in **1** seems reasonable at the rate determining step.

Key words: Hydroxylamine monosulfonat, Superoxo, Kinetics, Mechanisms, Oxidation-reduction

Hydroxylamines are industrial compounds used as intermediates in chemical synthesis and are known to produce radical intermediates, the pure material is a white, unstable crystalline, hygroscopic compound (Greenwood and Earnshaw 1997). However, hydroxylamine is almost always provided and used as an aqueous solution and it is produced as a result of interaction between SO_2 and NO_x in solution (Oblath *et al*. 1982, Zhang *et al*. 2015). Hydroxylamine and sulphur dioxide react in aqueous solution to form either sulfamic acid or ammonium bisulphate (Oblath *et al*. 1982, Chang *et al*. 1985). Therefore, the reactions between hydroxylamine and bisulfite is essential to understand the importance of SO_2 and NO_x interaction in atmospheric aqueous droplets in terms of acid rain formation (Zhang *et al*. 2015) and to develop a flue gas wet simultaneous desulfurization and denitrification processa (Zhao *et al*. 2011). In the recent years hydroxylamine gets impetus because it is an intermediate in biological nitrification and also used to prepare important functional group such as oximes (Lawton *et al*. 2014). Moreover, hydroxylamine and its various derivatives has also been used by biologists to introduce random mutations by switching base pairs in the probe functional areas of genes to elucidate what happens if their functions are broken (Ryszard *et al*. 1987). Hydroxylamine can also be used as an alternative method for the industrial synthesis of paracetamol developed by Hoechst–Celanese involves the conversion of ketone to a ketoxime

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(Jean and Vanden 2016). Some non-chemical uses of hydroxylamines include removal of hair from animal hides and photographic developing solutions (Lide 2006). In the semiconductor industry, hydroxylamine is often a component in the "resist stripper", which removes photoresist after lithography (Patnaik 2003). The nitrate salt, hydroxyl ammonium nitrate, is being researched as a rocket propellant, both in water solution as a monopropellant and in its solid form as a solid propellant (Oommen and Jain 1999).

The different derivatives of hydroxylamine have also become important as intermediates for synthesizing complex nitrogen-containing compounds, especially natural products and their analogues (Khlestkin and Mazhukin 2003), e.g., N, N – diethyl hydroxylamine is used an antioxidant (Quan *et al*. 2019).

In addition to these all hydroxylamines were found to depend on the presence and accessibility of oxyhemoglobin to exert their toxicity. The interaction of some hydroxylamines with oxyhemoglobin is known to lead to the formation of radical intermediates and in some cases secondary product are formed and concomitantly generate the superoxide (O_2^-) and H_2O_2 (Spooren Anita and Evelo Chris 2000). At the same time all living organism contains superoxide and high concentration of superoxide is biologically highly toxic (Hiroko *et al*. 2015). So, study of reaction mechanism between superoxide and hydroxylamines is very essential. In the present work we represent the reaction kinetics and mechanism between a Co^{III}- bound superoxide ligand and hydroxylamine monosulfonate in aqueous acetate buffer medium.

MATERIALS AND METHODS

The superoxo complex, μ_2-superoxo [bis (ethylenediamine) bis (diethylenetriamime) cobalt (III)] perchlorate, $[(en)(dien)Co^{III}(O_2)Co^{III}(en)(dien)](ClO_4)_5$ was synthesized by the literature procedure (Duffy *et al*. 1969) and recrystallized from 0.3 M $HClO_4$. Its purity was checked by measuring absorbance at 708nm [ε^{708} mol^{-1} dm^3 cm^{-1}: found 1186; reported (Duffy *et al*. 1969):1210 ± 5%]. Hydroxylamine monosulfonate, HO-NH(SO_3K). H_2O was prepared as reported (Ackermann and Powell 1966), and the purity was checked by H, N microanalyses (From Anal. Calc. H, 2.36; N, 8.28. Found: H, 2.29; N, 8.37%). 2, 6-pyridinedicarboxylic acid (dipicolinic acid, Aldrich) was used as received. $NaClO_4$ was prepared by neutralizing $HClO_4$ with $NaHCO_3$ and subsequently concentrating the neutral solution. All other solutions were of the reagent grade and used without further purification.

Physical measurements and kinetics

Absorbances and UV-VIS spectra were recorded with a SIMADZOO 1800 spectrophotometer using 1.00 cm quartz cell. Reactions were conducted *in situ* in the thermostatted (25 ± 0.1ºC) cell housing of the spectrophotometer and in acetate buffer (pH, 3.42 - 4.8; T_{OAc} = 0.20 M) using excess [$HONHSO_3^-$] over [**1**] at an ionic strength 0.5 M ($NaClO_4$). The kinetics was monitored at 708 nm, the visible absorption maxima of the dicobalt complex (**1**). Under these conditions, the reactions obeyed excellent first-order kinetics at least up to 95% completion of reaction and the first order rate constants (k_o) were evaluated by non-linear least squares fitting of the decay of the absorbance (A_t) with time (t) data to standard first-order exponential decay equation. Furthermore, dipicolinic acid (dpa, $C_7H_5NO_4$) was added to sequester the ubiquitous metal ions (*vide infra*) present in the reaction media. A pH meter (Gold-533) with electrodes calibrated with standard buffer solutions was used for pH measurements, while reporting pH values in D_2O media the relation, pD = pH + 0.4 was used (Gain *et al*. 2012, Glasoe and Long 1960). All solutions were prepared in doubly distilled and then freshly boiled water.

Stoichiometry

The equilibrium absorbance of a mixture of $HONHSO_3^-$ with 4-5 times of **1** was measured after ~ 5h at 708 nm and the concentration of unused **1** in such a product mixture was determined spectrophotometrically at 708.

RESULTS AND DISCUSSION

Stoichiometry and reaction products

Each mole of hydroxylamine monosulfonate (HAMS), $HONHSO_3^-$ consumed (Table 1) very nearly 2 moles of the superoxo complex **1**. Moreover, we also observed that the final spectrum is closely similar in shape and peak positions (Fig 1) to those determined for the hydroperoxo analogues of (**1**) (Hoffman and Taube 1968, Gain *et al*. 2011).

Table 1 Stoichiometric results for the oxidation of $HONHSO_3^-$ by **1** at T_{OAc} = 0.2M, *I* = 0.5 M ($NaClO_4$). T = 25.0°C

[**1**] /mM	[$HONHSO_3^-$] / mM	[**1**]left / mM	Δ[**1**] / Δ[$HONHSO_3^-$]
9.5	3.5	2.65	1.96[a]
14.0	4.5	5.11	1.98[b]
20	5.0	10.2	1.96[c]

[a]pH 4.12, [b]pH 4.0, [c]pH 4.1.

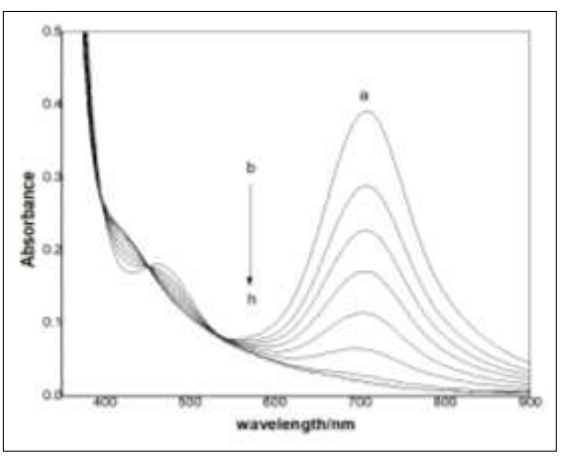


Fig 1 Time resolved spectra of 0.50 mM of **1** reacting with 7.0 mM HAMS. pH = 3.42 in acetate buffer, T_{OAc} = 0.2 M, *I* = 0.5 M, [dpa] = 2.0 mM, T = 25.0 ºC. (a) Spectrum of the pure complex, (b)-(h) spectra of reaction mixture at time intervals 60, 120, 365, 450, 610, 710 and 1800 second respectively

A clean conversion of the superoxo complex **1** to the hydroperoxo complex **2** is therefore anticipated (Eq 1). The observed stoichiometric ratios also establish N_2O and SO_4^{2-}/ HSO_4^- are the oxidation products for oxidations of HAMS.

$$4[(en)(dien)Co^{III}(O_2)\ CoIII(en)(dien)]^{5+} + 2HO\text{-}NHSO_3^- + H_2O \rightarrow 4[(en)(dien)Co^{III}(O_2H)\ Co^{III}(en)(dien)]^{5+} + N_2O + 2HSO_4^- \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Hydroxylamine monosulfonate ($HONHSO_3^-$) is a well-known reductant and depending upon the reaction conditions it may yield different products (Barge and Gkavi 2017) such as N_2, N_2O, NO_2^-, or NO_3^- and HSO_4^-/ SO_4^{2-}. When oxidation of hydroxylamine is initiated by a one electron oxidant or a H-atom abstractor, an intermediate of the oxidation number N (0) is formed, which may be $H_2NO\cdot$ (Aminoxyl radical) or its isomer, NHOH. Several quantum mechanical calculation and electron paramagnetic resonance (EPR) investigations predict that $NH_2O\cdot$ is thermodynamically more stable than NHOH (Schwarz and Dodson 1984). However, formation of nitroxyl radial was also reported by Zhang and Liu (2000), when mono and di-N- substituted hydroxyl amine is oxidised by a metal ion, such as neptunium (VI) (Zhang and Liu 2000). Similarly for HAMS we presumed and later one stablished that the product of one electron oxidation (or H-atom abtraction) of HAMS, was the sulfonate derivative of aminoxyl radical ($\cdot ONHSO_3^-$). $\cdot ONHSO_3^-$ is a weak acid which immediately reacted with the second mole of superoxo complex (**1**) in an electron transfer reaction to yield nitroxyl (HNO) and sulfate (following an electron transfer path). The nitroxyl (HNO), decomposed very rapidly to form nitrous oxide (N_2O), which was confirmed by chemical test (Housecroft and Sharp 2008) and the sulfate was detected by the barium chloride test. In this connection it is worthy to mention that oxidation of hydroxyl amine in acid medium by one electron reductant is already reported and the dehydrative dimerization rate constant of HNO is reported to be very high, $(1.8\text{-}7.2) \times 10^9\ M^{-1}$ (Richard *et al*. 1994).

The spectra of the reaction mixture recorded after ~ 24 hours matched with that of the same concentration of cobalt (II) chloride hexahydrate at the same conditions. Therefore, it can be said that the hydroperoxo species of **1** is not stable in the reaction media for a long time and ultimately self-decomposes to Co(II) and other products. Nevertheless, this self-decomposition of **2** is negligible during the reaction course and does not affect the stoichiometric studies.

Kinetics

In aqueous acetate buffer media **1** suffered no appreciable loss in absorbance over a long period of time indicating its stability against self-decomposition. Excess hydroxylamine monosulfonate (HAMS), however consumed **1** and the peak absorbance (at 708 nm) dropped gradually essentially to zero. The process followed excellent first-order kinetics (Fig 2). The first-order rate constants (k_o) increased linearly with [$HONHSO_3^-$] (Fig 3, Table 2). The reaction rates were found to be strongly influenced by the media acidity and a plot of $1/k_o$*vs* [H^+] was linear with a small but significant intercept (Fig 4, Table 3). But the reaction rate decreased significantly with increase of ionic strength of the media, as expected for two oppositely charged reactants.

Table 2 Variation of k_o with [HAMS], [**1**] = 0.50 mM, pH = 3.42, [dpa] = 2.0 mM, T_{OAc} = 0.2 M, I = 0.5 M, T = 25.0ºC

[HAMS] mM	5.0	7.0	9.0	11.0	13.0	15.0	17.0
10^2 x k_{obs} /s	2.3	2.9	4.3	5.01	6.02	7.6	8.8

Table 3 Variation of k_o with pH of the medium, [**1**] = 0.50 mM, [HAMS] = 6.0 mM, [dpa] = 2.0, T_{OAc} = 0.2 M, I = 0.5 M, T = 25.0ºC

pH	3.42	3.64	3.83	4.0	4.2	4.4	4.6	4.8
1/ k_{obs} , s	35.0	25.01	20.02	14.98	12.01	9.02	7.01	5.0

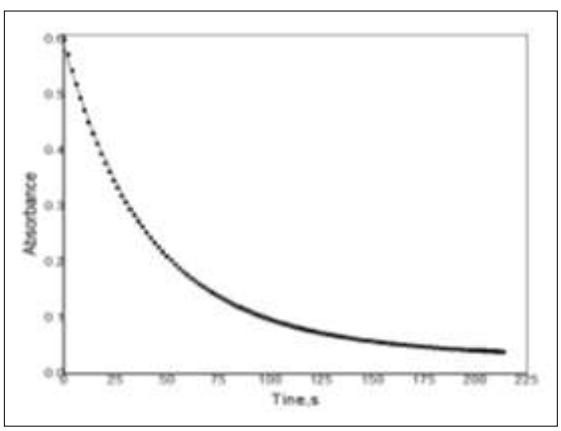


Fig 2 Decrease in absorbance (points shown in black circles) of **1** with time at 708 nm in its reaction with HAMS gives an excellent fit (solid line) to the first-order exponential decay equation. [**1**] = 0.50 mM, [HAMS] = 7.0 mM, pH = 3.42, T_{OAc} = 0.2 M, I = 0.5M ($NaClO_4$), [dpa] = 2.0 mM, T = 25.0ºC

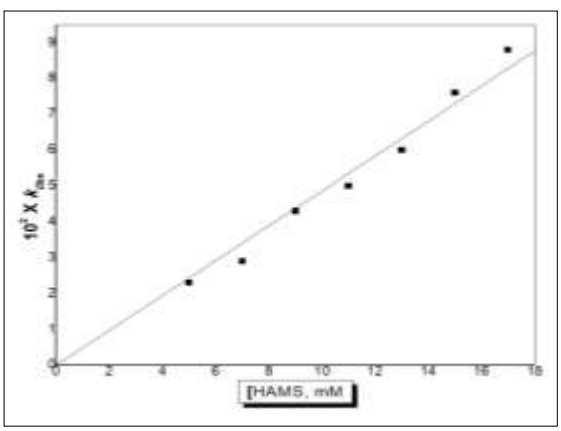


Fig 3 Linear variation of k_o for the reaction of [HAMS] with **1** (0.50 mM), at pH = 3.42, [dpa] = 2.0 mM, T_{OAc} = 0.2 M, I = 0.5M ($NaClO_4$), T = 25.0ºC.

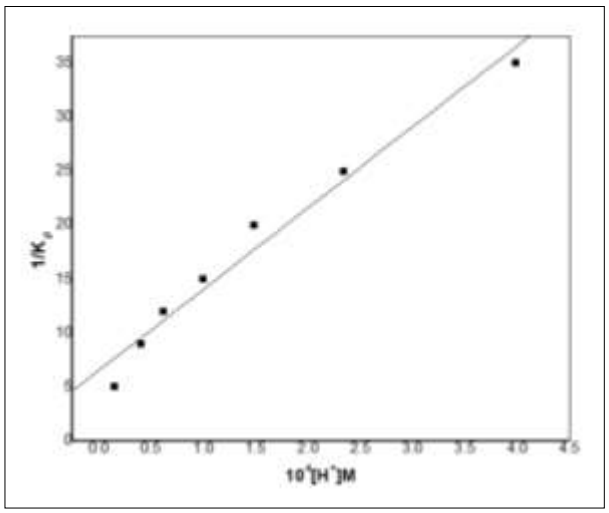


Fig 4 Plot of $1/k_o$ *vs* $[H^+]$. [**1**] = 0.50 mM, [HAMS] = 5.0 mM, T_{OAc} = 0.2 M, *I* = 0.5 M ($NaClO_4$), [dpa] = 2.0 mM, T = 25.0°C

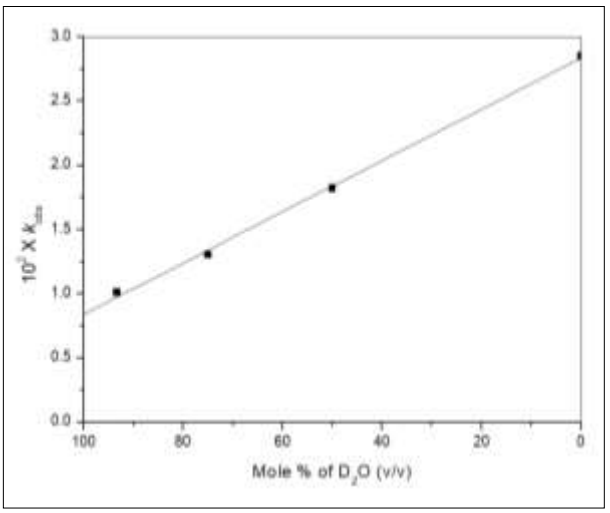
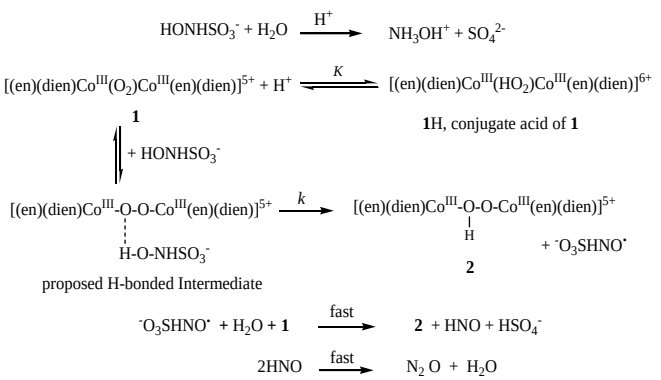


Fig 5 Effect of D_2O on k_o, [**1**] = 0.50 mM, [HAMS] = 5.0 mM, pH/pD = 3.82, T_{OAc} = 0.2 M, *I* = 0.5 M ($NaClO_4$), [dpa] = 2.0 mM, T = 25.0 °C

The rate-enhancement with pH seemed not accountable from deprotonation of $HONHSO_3^-$ as the species is weak acids and our experimental pH range was 3.4 - 4.6. Rather, a mechanism transferring hydrogen atom (or H^+ + e) to the coordinated superoxide (hydrogen atom transfer, HAT) seemed reasonable as superoxide was well-known to be a fairly strong base (Hoffman and Taube 1968, Gain *et al*. 2011). The observed proton-dependence on rate clearly establishes **1**H as a kinetically dead-end species. Increased proton concentration consumed more **1** from the solution forming more **1**H and consequently reaction rate dropped. **1**H, being already protonated species of **1** is a redox dead-end as it has no more room to accommodate a further proton following a HAT from the reducing species. In the rate determining step, **1** is reduced to its corresponding hydroperoxo complex (**2**). The Scheme 1 below represents a cartoon of the mechanism.



Scheme 1

We observed a significant retardation in k_o values when solvent H_2O was enriched with D_2O (k_{H2O} / k_{D2O} ~ 2.82). Moreover, the plots of k_o versus mole % of D_2O in the solvent media was found to be linear (Fig 5) indicating transfer of a single proton at the rate step (Albery and Davis 1972).

This supports an electroprotic HAT mechanism (H^+ + e). Proposed reaction scheme in abbreviated form is thus:

$$\mathbf{1} + H^+ \overset{K}{\rightleftharpoons} \mathbf{1}H \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (2)$$

$$\mathbf{1} + HO\text{-}NHSO_3^- \xrightarrow{k} \mathbf{2} + \cdot ONHSO_3^- \quad \ldots\ldots\ldots\ldots\ (3)$$

Equations (2) and (3) lead to the rate equation (4).

$$k_0 = k[HO\text{-}NHSO_3^-]/(1 + K[H^+]) \qquad (4)$$

Equation (4) may be rearranged to equation (5).

$$1/k_0 = 1/ (k[^-O_3SHNOH] + K[H^+]/ (k[^-O_3SHNOH]) \quad \ldots\ldots\ldots\ldots\ldots\ (5)$$

A plot of $1/k_o$ *versus* $[H^+]$ was found to follow excellent straight-line trajectory (Fig 4) as expected from equation (5) and yielded k = 19.05 (± 0.4) s^{-1} and K = 1.4 (± 0.3) × 10^2 M^{-1}. Free superoxide is a strong base (pK_a = 4.88) (Maan *et al*. 2016) and the presence of a residual basicity in a coordinated superoxide ligand is not unexpected but the basicity of the superoxide ligand due to coordination to two Co (III) centers in **1** is expectedly somewhat reduced. Again, hydrogen atom transfer mechanism is an established phenomenon for phenols as reducing agents (Alina and Willem 2007).

To verify the proposed mechanism, **1** was reacted with phenol and N, N di-methyl hydroxyl amine. Both reacted with **1** but neither phenyl methyl ether nor O-methyl hydroxylamine reacted under comparable conditions, substantiating the mechanistic proposal that the presence of O–H bond is absolutely essential in the reducing agent for the reaction to proceed.

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