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ISSN: 2278-1862

Journal of Applicable Chemistry

2018, 7 (3): 686-694

(International Peer Reviewed Journal)

Kinetics and Mechanism of Oxidation of Thiosemicarbazide by Waugh-type 9-Molybdomanganate(IV) in Aqueous Perchloric Acid

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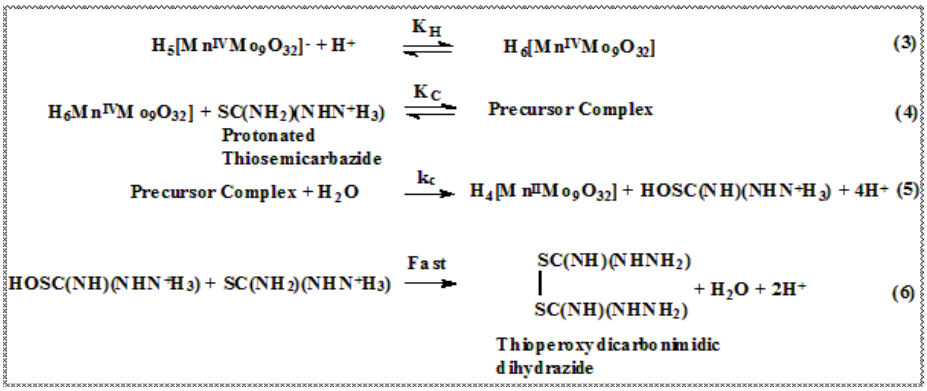
Accepted on 20th May 2018

ABSTRACT

Kinetics and mechanism of oxidation of thiosemicarbazide by Waugh-type polyoxometalate, 9-molybdomanganate (IV), was investigated under pseudo-first-order condition in aqueous perchloric acid. The stoichiometry was found to be 1 mole of $[Mn^{IV}Mo_9O_{32}]^{6-}$ *per two moles of thiosemicarbazide indicating thioperoxy dicarbonimidic dihydrazide as the product. The rate of reaction increases with increase in hydrogen ion, 9-molybdomanganate (IV) and thiosemicarbazide concentrations. The protonated forms of both the oxidant and thiosemicarbazide are active species. The thiosemicarbazide is in its protonated form and converted into a tautomeric form, with a negative charge on the sulfur atom and interact with the active form of the oxidant at the oxygen atoms of type-2 forming a precursor complex. The precursor complex formed decomposes with the formation of sulfenic acid as an intermediate. The results of effects of ionic strength, solvent polarity and the temperature also support the proposed mechanism.*

Graphical Abstract



Scheme 3

Keywords: Polyoxometalate oxidation, Reaction mechanism, 9-molybdomanganate, Thiosemicarbazide.

INTRODUCTION

The thiosemicarbazide is a simplest carbon and sulfur containing compound of thioamide family. These thiosemicarbazides are biologically active and used as antitumor [**1-3**], antibacterial [**4-5**], antiviral and anti-malarial agents [**6**]. Their biological activity is due to formation of coordination bonds to metal ions which may involve thiosemicarbazide as either a neutral ligand or as a deprotonated ligand [**7**]. Oxidation of these thiosemicarbazides by various oxidants like ferricyanide [**8**], ferric ion [**9**], n-chloro-3-methyl-2,6-diphenylpiperidin-4-one [**10**], bromated [**11**], manganese(III) [**12**], hydrogen peroxide [**13**] and by haloamines [**14-17**]. The major products of oxidation of thiosemicarbazide are carbon dioxide, nitrogen species and sulfate except in case of ferricyanide [**8**]. The product of oxidation of thiosemicarbazide by ferricyanide is reported to be the disulfide. The mechanism of oxidation by a metal ion generally involve formation of a coordination complex which further decompose in a rate determining step to give the final product[**12**]. The coordination chemistry of thiosemicarbazide has also received considerable attention as some of the coordination complexes are also having biological activity [**18**].

The molybdenum containing enzymes play important roles in metabolic activity of carbon, nitrogen and sulfur cycle and act as catalysts to bring about oxygen atom transfer between competent centres [**19**]. The examples of enzymes are sulphite oxidase, dimethyl sulfoxide reductase and nitrate reductases which catalyze the oxygen atom transfer reactions [**19**]. The polyoxometalates are also found to mimic the enzymes [**20**] and the oxidant used in the present study is a Waugh-type molybdenum containing polyoxometalate. The polyoxometalates are having wide variety applications in chemistry as outer-sphere transfer reagents as well as catalysts for redox as well as acid mediated organic transformations [**21**]. Therefore, since the compounds like thiosemicarbazide are considered as model compounds for investigation of biological mechanisms and polyoxometalates resemble enzymes, we thought it would be of interest to understand the interaction between the two. Therefore, in continuation of our earlier work [**21**], the present study of oxidation of thiosemicarbazide by 9-molybdomanganate(IV) was undertaken.

MATERIALS AND METHODS

All chemicals were of reagent grade and double-distilled water was used throughout the work. A solution of thiosemicarbazide (Koch Light Laboratories Ltd.) was freshly prepared by dissolving an appropriate amount of sample in double-distilled water. Standard solution of perchloric acid was prepared in double distilled water. The ammonium salt of Mn^{IV} complex, $(NH_4)_6[Mn^{IV}Mo_9O_{32}]$ was prepared by reported method [**22**]. The oxidant was characterized by FTIR and AAS analysis as reported earlier [**23-24**].

Kinetic measurements: Kinetic measurement was performed on Elico SL-177 spectrophotometer. The kinetics was followed under pseudo-first order conditions keeping large excess of [thiosemicarbazide] over [oxidant] at constant temperature 25 $\pm$ 0.1°C. The reaction was initiated by mixing the previously thermostated solutions of thiourea and $(NH_4)_6[Mn^{IV}Mo_9O_{32}]$ which also contained the required amount of perchloric acid and double distilled water. The progress of reaction was followed spectrophotometrically at 468 nm (ϵ = 360 $\pm$ 2 dm^3 $mole^{-1}cm^{-1}$) by monitoring the decrease in absorbance of oxidant. The pseudo-first order rate constants were determined form the log[oxidant] versus time plots and the rate constants were reproducible within $\pm$ 5% and reaction were studied up to 80 % completion.

Stoichiometry: The stoichiometry was studied by keeping concentration of $[Mn^{IV}Mo_9O_{32}]^{6-}$ constant at 2.0 x 10^{-3} mole dm^{-3} and varying concentration of thiosemicarbazide from 1.0 x 10^{-3} to 2.0 x 10^{-4} mole dm^{-3}. These reaction mixtures also contained required amount of perchloric acid. The concentration of unreacted $[Mn^{IV}Mo_9O_{32}]^{6-}$ was determined after 24 h spectrophotometrically. The stoichiometry was found to be one mole of $[Mn^{IV}Mo_9O_{32}]^{6-}$ per two moles of thiosemicarbazide.

Therefore, the product of the oxidation of thiosemicarbazide is thioperoxy dicarbonimidic dihydrazide. Such types of disulfide of thiosemicarbazides are formed when it is oxidized by a weak oxidant like ferric ion [9]. The stoichiometry of the reaction can be represented by equation (1).

$$[Mn^{IV}Mo_9O_{32}]^{6-} + 2NH_2NHCSNH_2 \longrightarrow [Mn^{II}Mo_9O_{32}]^{4-} + H_2N(HN)_2CSSC(NH)_2NH_2 + 2H^+ \quad (1)$$

RESULTS AND DISCUSSION

The reaction was also studied in presence of added acrylonitrile to understand the intervention of free radicals. There was no effect of added acrylonitrile on the reaction and also no precipitate due to the polymerization of the added acrylonitrile was observed thus confirming the absence of any free radical formation in the reaction.

The reaction was carried out under pseudo-first-order conditions, keeping large excess of thiosemicarbazide over that of the 9-molybdomanganate(IV). The plots of log [oxidant] against time were found to be linear in all the runs up to three half lives of the reaction and the values of pseudo-first-order rate constants between the range of [oxidant] of 2.0 x 10^{-4} to 2.0 x 10^{-3} mole dm^{-3} were constant (Table 1). Therefore the order in [oxidant] is unity. The pseudo-first-order rate constants were found to be increased (Table 1) as [thiosemicarbazide] increases from 5.0 x 10^{-3} to 5.0 x 10^{-2} mole dm^{-3} at constant [oxidant] of 1.0 x 10^{-3} mole dm^{-3}. The plot of k_{obs} against [thiosemicarbazide] was found to be linear without any intercept. Therefore, the order in thiosemicarbazide is unity.

Table 1. Effect of concentration of oxidant, $[Mn^{IV}Mo_9O_{32}]^{6-}$, on the pseudo-first-order rate constant of oxidation of thiosemicarbazide by $[Mn^{IV}Mo_9O_{32}]^{6-}$ at 25°C dm^{-3}. $10^2[HClO_4]$ = 1.0 mole dm^{-3}, I = 0.1 mole dm^{-3}

$10^3[[Mn^{IV}Mo_9O_{32}]^{6-}]$ mole dm^{-3}	10^2[Thiosemicarbazide] mole dm^{-3}	10^4 k_{obs} s^{-1}
0.2	1.0	3.4
0.4	1.0	3.5
0.6	1.0	3.6
0.8	1.0	3.5
1.0	1.0	3.6
2.0	1.0	3.6
1.0	0.5	1.6
1.0	0.7	2.4
1.0	0.9	3.0
1.0	1.0	3.5
1.0	3.0	11
1.0	5.0	19
1.0	5.0	28.7

The effect $[H^+]$ on the reaction was studied by varying the perchloric acid concentration between 2.0 x 10^{-3} to 2.0 x 10^{-2} mole dm^{-3} at a constant ionic strength of 0.1 mole dm^{-3}. The rate of reaction is accelerated (Table 2) by increase in $[H^+]$ and the order in $[H^+]$ was found to be more than unity(1.10) as found from log k_{obs} against log $[H^+]$.

The effects of ionic strength and solvent polarity were studied keeping concentration of $[Mn^{IV}Mo_9O_{32}]^{6-}$, thiosemicarbazide and perchloric acid constant at 1.0 x 10^{-3} mole dm^{-3}, 0.01 mole dm^{-3} and 1.0 x 10^{-3} mole dm^{-3} respectively at 25°C. Sodium perchlorate was used to vary the ionic strength. The rate of the reaction was unaffected with varying ionic strength and the rate of reaction decreases as percentage of acetonitrile increases from 0 to 40% v/v and the plot of log k_{obs} versus (1/D) was linear with a negative slope. The activation parameters for the oxidation of thiosemicarbazide by $[Mn^{IV}Mo_9O_{32}]^{6-}$ were determined by studying the reaction at constant

concentration of $[Mn^{IV}Mo_9O_{32}]^6$, thiosemicarbazide and perchloric acid constant at 1.0 x 10^{-3} mole dm^{-3}, 0.01 mole dm^{-3} and 0.01 mole dm^{-3} respectively. The reaction was studied at 20, 25, 30, 35 and 40°C and the data are given in table 3.

Table 2. Effect of concentration of perchloric acid on the pseudo-first-order rate constant of oxidation of thiosemicarbazide by $[Mn^{IV}Mo_9O_{32}]^{6-}$ at 25°C.
$10^3[[Mn^{IV}Mo_9O_{32}]^{6-}]$ = 1.0 mole dm^{-3}, 10^2[thiosemicarbazide] = 1.0 mole dm^{-3}, I = 0.1 mole dm^{-3}.

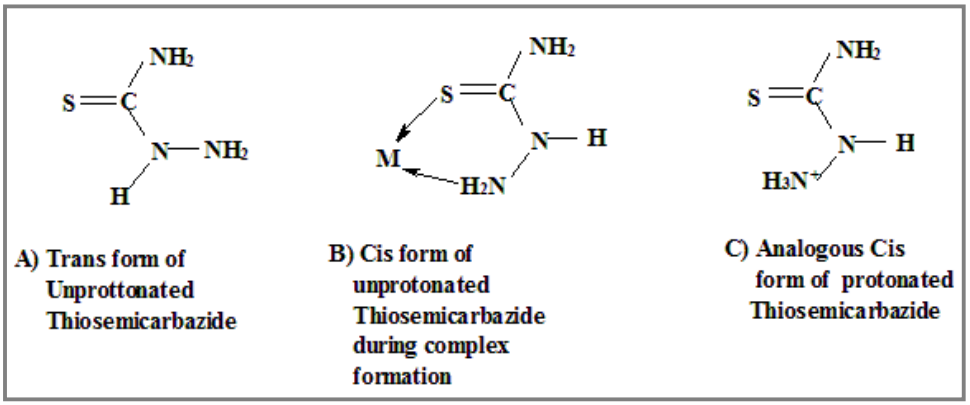
$10^2[HClO_4]$ mole dm^{-3}	$10^4 k_{obs}$ s^{-1}
0.1	0.62
0.3	0.81
0.5	1.7
0.7	2.4
0.9	3.1
1.0	3.5
2.0	6.6

Table 3. Effect of temperature on the pseudo-first-order rate constant of oxidation of thiosemicarbazide by $[Mn^{IV}Mo_9O_{32}]^{6-}$.$10^3[[Mn^{IV}Mo_9O_{32}]^{6-}]$ = 1.0 mole dm^{-3}, 10^2[Thiosemicarbazide] = 1.0 mole dm^{-3}, $10^2[HClO_4]$ = 2.0 mole dm^{-3}, I = 0.1 mole dm^{-3}.

T in K	$10^4 k_{obs}$ s^{-1}
293	2.4
298	2.9
303	3.5
308	4.0
313	5.2
Activation Parameters	
Ea kJ $mole^{-1}$	29.1 ± 0.5
$\Delta H^{\#}$ kJ $mole^{-1}$	27.05 ± 0.5
$\Delta S^{\#}$ J $mole^{-1}$ K^{-1}	-223.5 ± 4
$\Delta G^{\#}$ kJ $mole^{-1}$	94.8 ± 0.5

The energy of activation was determined form the plot of log k_{obs} against (1/T) while the enthalpy of activation was evaluated from the plot of log(k_{obs}/T) against (1/T). The activation parameters Ea, $\Delta H^{\#}$, $\Delta G^{\#}$ and $\Delta S^{\#}$ were found to be 29.1 kJ $mole^{-1}$, 27.05 kJ $mole^{-1}$, 94.8 kJ $mole^{-1}$ and -223.5 J $mole^{-1}$ K^{-1} respectively (Table 3). Thiosemicarbazide undergo protonation in acidic media as shown in equilibrium (2) and it has been found that only single protonation occurs at the terminal hydrazine group [25, 26]. The thiosemicarbazide in its unprotonated free crystalline state exists in the trans form as shown in structure A of Scheme 1. It will be converted into a trans form when it coordinates with the metal ions to form complexes [25]. In the protonated thiosemicarbazide also the cis form is retained. One of the reasons for retainment of the cis form in the protonated thiosemicarbazide is the steric effect. Apart from the steric effect the protonation at the terminal hydrazinic nitrogen causes a rotation around C-N(imine) bond thus converting it into a cis-conformation (structure C of Scheme 1) [25].

$$SC(NH)_2NH_2 + H^+ \underset{}{\overset{K_{TH}}{\rightleftharpoons}} SC(NH)_2NH_3^+ \qquad (2)$$



Scheme 1

The protonation constant of the thiosemicarbazide at different ionic strengths has also been determined [26] and its value is 18.0 x 10^{-3} dm^3 $mole^{-1}$ at an ionic strength of 0.10 mole dm^{-3}. Two types of oxygen are present in the 9-molybdomanganate (IV), the type-1 is the oxygen in MnO_6 octahedral and the type-2 is the oxygen associated with molybdenum [27] and are shown in figure 1.

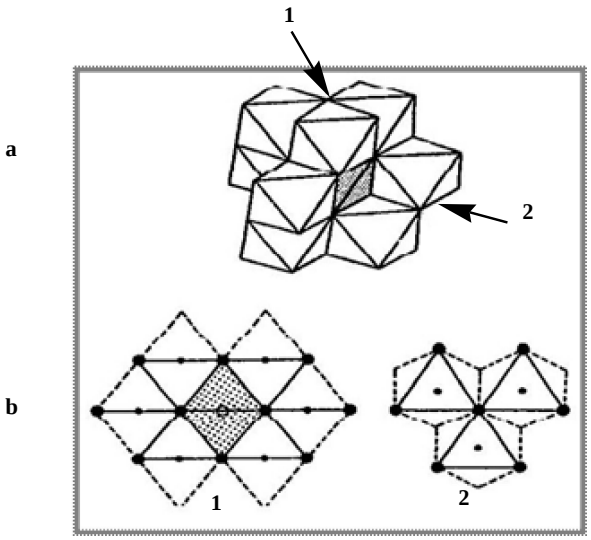
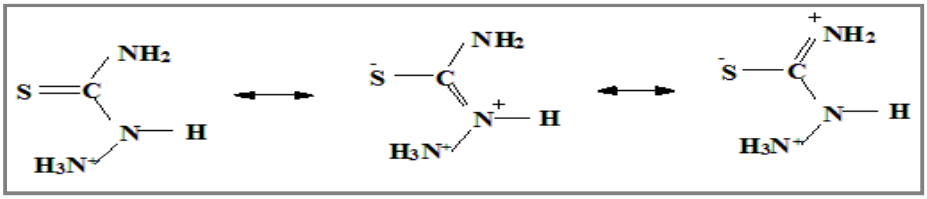


Figure 1. Arrangements of oxygen atoms in $[MnMo_9O_{32}]^{6-}$ [27].

a) Structure of the $[MnMo_9O_{32}]^{6-}$ anion. Shaded octahedron in (a) is MnO_6
b) Two arrays of oxygen atoms as the potential metal binding sites.
(large solid circles in (b) are oxygen atoms, small solid circles are Mo atoms and an open circle is a Mn atom).

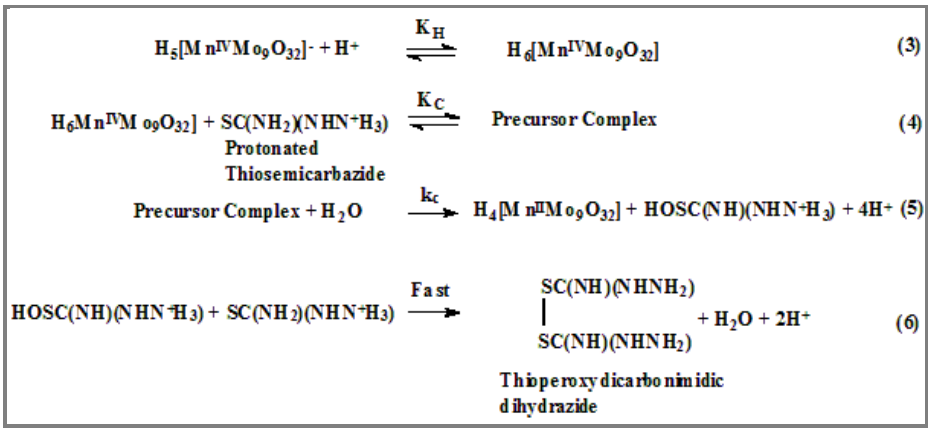
The protonation of the polyoxometalate also occurs at the type-1 oxygen atoms in acidic medium and completely protonated polyoxometalate resulting in change in its UV-visible spectrum with isosbestic points at around 438 and 522 nm. Replacement of these protons by a cation results in change in the environment of the oxygen atoms of type-1 and the isosbestic points will disappear. In the present study the UV-visible spectra of the 9-molybdomanganate (IV) ion in water, in presence of perchloric acid and in presence of both perchloric acid and thiosemicarbazide were examined. The UV-visible spectrum of 9-molybdomanganate (IV) ion in water shows absorption maxima at 468 nm while in perchloric acid two isosbestic points at 438 and 522 nm were obtained indicating protonation of the anion. To a solution containing 9-molybdomanganate(IV) ion in perchloric acid when thiosemicarbazide was added, the nature of spectrum did not change indicating that the added

thiosemicarbazide interact with the 9-molybdomanganate(IV) ion at oxygen atoms of type-2. Thiosemicarbazide in its protonated form undergoes tautomerism imparting negative charge at the sulfur atom as shown in scheme 2.



Scheme 2.

Therefore, both the protonated species of thiosemicarbazide and the 9-molybdomanganate(IV) are the active species in the present reaction under the reaction conditions. The mechanism in terms of the protonated active species can be represented as in scheme 3. The order with respect to $[H^+]$ is found to be more than unity indicating two prior protonation equilibria. One of the protonation equilibria is due to the protonation of the oxidant 9-molybdomanganate(IV) ion which exists as an anion [27] and is shown in equilibrium (3) with pK_a 3.0 and another protonation equilibria is that of the thiosemicarbazide as shown in equilibria (2).



Scheme 3

The thiosemicarbazide is converted into a tautomeric form, with a negative charge on the sulfur atom, and interact with the active form of the oxidant at the oxygen atoms of type-2 forming a precursor complex. This precursor complex decomposes with the formation of sulfenic acid as an intermediate.

The intermediate, sulfenic acid, is proposed in oxidation of 4-methylthiosemicarbazide by bromated [11] and is formed as a result of electrophilic attack of the oxidant like bromine on sulfur which further hydrolyse in aqueous solution. The intermediate, sulfenic acid is unstable and it dimerizes quickly to generate thioperoxy dicarbonimidic dihydrazide as shown in equation (6) of scheme 3. Such types of products are formed in oxidation of thiosemicarbazide by mild oxidizing agents like $FeCl_3$ [28] during corrosion studies. The present oxidant also has redox potential of 1.0 V which can also be considered as a mild oxidizing agent. The rate law according to scheme 3 is derived. From equation (5) of scheme 3, the rate of reaction is given by equation (7) and by substituting equilibrium (4) for [Precursor Complex] we get equation (8). Then from equation (3) of scheme 1, the total $[H_5Mn^{IV}Mo_9O_{32}]^-$, $[H_5Mn^{IV}Mo_9O_{32}]^-_T$, in terms of free $[H_5Mn^{IV}Mo_9O_{32}]^-$, $[H_5Mn^{IV}Mo_9O_{32}]^-_F$ and $[H_6Mn^{IV}Mo_9O_{32}]$ can be obtained as in equation (10). Since K_H is very small (1.0×10^{-3} dm^3 $mole^{-1}$) and $[H^+]$ is also 1.0×10^{-2} mole dm^{-3}, the denominator of equation (10) can be neglected. Substituting the $[H_6Mn^{IV}Mo_9O_{32}]$ from equation (11) in equation (8) we get equation

(12). Similarly, considering the protonation of thiosemicarbazide as that of the oxidant according to equilibrium (2) the total thiosemicarbazide will be given by equation (13).

$$\text{Rate} = k_c[\text{Precursor Complex}] \quad (7)$$

$$\text{Rate} = k_c K_C\ [H_6Mn^{IV}Mo_9O_{32}]\ \ [\text{H Thiosemicarbazide}^+] \quad (8)$$

$$[H_5Mn^{IV}Mo_9O_{32}]^-_T = [H_5Mn^{IV}Mo_9O_{32}]^-_F + [H_6Mn^{IV}Mo_9O_{32}] \quad (9)$$

$$[H_5Mn^{IV}Mo_9O_{32}]^-_T = [H_5Mn^{IV}Mo_9O_{32}]^-_F + K_H[H^+]\ [H_5Mn^{IV}Mo_9O_{32}]^-_F$$

$$[H_5Mn^{IV}Mo_9O_{32}]^-_T = [H_5Mn^{IV}Mo_9O_{32}]^-_F\ (1+ K_H[H^+])$$

$$[H_5Mn^{IV}Mo_9O_{32}]^-_F = [H_5Mn^{IV}Mo_9O_{32}]^-_T / (1+ K_H[H^+])$$

$$[H_6Mn^{IV}Mo_9O_{32}] = K_H[H^+]\ [H_5Mn^{IV}Mo_9O_{32}]^-_F / (1+ K_H[H^+]) \quad (10)$$

$$[H_6Mn^{IV}Mo_9O_{32}] = K_H[H^+]\ [H_5Mn^{IV}Mo_9O_{32}]^- \quad (11)$$

$$\text{Rate} = k_c K_C K_H[H^+]\ \ [H_5Mn^{IV}Mo_9O_{32}]^-\ [\text{H Thiosemicarbazide}^+] \quad (12)$$

$$[\text{Thiosemicarbazide}]_{\text{Total}} = [\text{Thiosemicarbazide}]_{\text{Free}} + [\ \text{H Thiosemicarbazide}^+] \quad (13)$$

$$[\text{Thiosemicarbazide}]_{\text{Total}} = [\text{Thiosemicarbazide}]_{\text{Free}} + K_{TH}[H^+]\ [\text{Thiosemicarbazide}]_{\text{Free}}$$

$$[\text{Thiosemicarbazide}]_{\text{Total}} = [\text{Thiosemicarbazide}]_{\text{Free}}\ (\ 1+ K_{TH}[H^+]) \quad (14)$$

$$[\text{Thiosemicarbazide}]_{\text{Free}} = [\text{Thiosemicarbazide}]_{\text{Total}} / (1 + K_{TH}[H^+]) \quad (15)$$

Then from equilibrium (2) the [HThiosemicarbazide$^+$] will be given by equation (16) and substituting for [Thiosemicarbazide]$_{Free}$ from equation (15) we get equation (17). Since KTH is of the order of 10^{-3} and [H+] is also of the order of 10^{-2} the denominator of equation (17) can be neglected and simplified to equation (18).

$$[\text{H Thiosemicarbazide}^+] = K_{TH}\ [H^+]\ [\text{Thiosemicarbazide}]_{\text{Free}} \quad (16)$$

$$[\text{H Thiosemicarbazide}^+] = K_{TH}\ [H^+]\ [\text{Thiosemicarbazide}]_{\text{Total}} / (1 + K_{TH}[H^+]) \quad (17)$$

$$[\text{H Thiosemicarbazide}^+] = K_{TH}\ [H^+]\ [\text{Thiosemicarbazide}]_{\text{Total}}$$

$$[\text{H Thiosemicarbazide}^+] = K_{TH}\ [H^+]\ [\text{Thiosemicarbazide}] \quad (18)$$

Then from equation (18) and (12) we get the final rate law (19) which can be rearranged to get the expression for the value of k_{obs} as in equation (20).

$$\text{Rate} = k_c K_C K_{TH} K_H[H^+]^2\ \ [H_5Mn^{IV}Mo_9O_{32}]^-\ \ [\text{Thiosemicarbazide}] \quad (19)$$

$$k_{obs} = \text{Rate} / [H_5Mn^{IV}Mo_9O_{32}]^-\ [\text{Thiosemicarbazide}] = k_c K_C K_{TH} K_H[H^+]^2 \quad (20)$$

The derived rate law (20) explains the order in [H^+] of more than unity and order of unity in both the reactants. The activation enthalpy of 27.05 $\pm$ 0.5 kJ mole^{-1} and activation free energy of 29.10 + 0.5 kJ mole^{-1} were favorable for electron transfer processes. The decrease in entropy of activation is due to the formation of a precursor complex between the reactants in which the interaction of negative

sulfur atom with the oxygen atoms of type-2 in the oxidant. The effect of ionic strength indicates that one of the reactant is neutral and decrease in the rate with decrease in the dielectric constant is in conformity with Amis concept for ion-dipole interactions [29].

CONCLUSIONS

The reaction between 9-molybdomanganate(IV) and thiosemicarbazide in aqueous perchloric acid was found to occur through formation of a precursor complex between the active protonated forms of both the reactants. The orders in both the reactants were found to be unity each while order in hydrogen ion concentration is slightly more than unity. The thiosemicarbazide under the experimental conditions remains both in unprotonated as well as protonated form while protonated form of 9-molybdomanganate(IV) is the active oxidant species thus making the reaction to be catalyzed by hydrogen ion concentration. The formation of precursor complex as a result of interaction with the sulfur atom of thiosemicarbazide with the protonated 9-molybdomanganate(IV) at the oxygen atoms of type-2. Slow electron transfer within the precursor complex led to its decomposition into sulfenic acid intermediate. The sulfenic acid further reacts in a fast step with another thiosemicarbazide to give the final product thioperoxy dicarbonimidic dihydrazide.

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