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Research Article

KINETICS AND MECHANISM OF OXIDATION OF 2,5-DIAMINO-1,3,4-THIADIAZOLE METAL COMPLEX IN ACID MEDIUM

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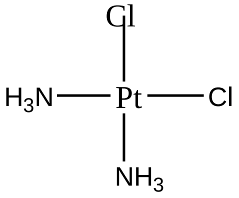
ABSTRACT

The kinetic of oxidation of 2,5-Diamino-1,2,3,-thiadiazole metal complex by potassium permagnate has been studied in the presence of acidic medium. The reaction is first order with respect to ester concentration. The reaction rate has been determined at different temperature and different thermodynamic parameters have been calculated which shows with increase in temperature reaction rate increases. With increase in the concentration of acid the reaction rate increase. A suitable mechanism has been proposed.

Key Words: *Kinetics, Mechanism, Oxidation, 2,5-Diamino-1,2,3,-thiadiazole metal complex, thermodynamic parameters etc.*

INTRODUCTION

Bioinorganic chemistry constitutes the discipline at the interface of the more classical areas of inorganic chemistry and biology. The metal containing compounds have been used not only as biological probes but also diagnostic and therapeutic pharmaceuticals. The mechanism of action of platinum anticancer drugs, gold antiazthratic agent and technetium radio pharmaceutical some currently active topic of investigation in bioinorganic chemistry. The study of naturally occurring inorganic elements in biology i.e., when compound or complex containing biologically active metal known as bioinorganic chemistry. Today however inorganic chemistry is beginning to have a major impact on modern medicine. The important inorganic pharmaceuticals include *Cisplatin* (Lippad and Berg, 2005) an anticancer drug.



Cisplatin

Quranofin an oral rheumatoid arthritis drug and cardiolyte a heart imaging agent. In bioinorganic compounds the kinetic aspects are very good. The water exchange rates for many essential metal ions. M-OH_2 bonds are very labile breaking and reforming as fast as billion times per second. The labilities of metal-ligand bonds for the metal complexes (Williams, 1990). In general ligand exchange rates are faster for the less highly charged M^{+2} than for highly M^{+3} metal ions (Ibers and Holm, 1980). The fast metal-ligand exchange rates of first row transition metal ions such as Fe^{+2}, Cr^{+3}, Co^{+3} (Karlin, 1993)

The paramagnet ion (MnO^-_4) oxidize a great variety of substances and it find extensive applications in organic synthesis. Among the various organic compounds employed in oxidative studies 2,5-Diamino-1,2,3,-thiadiazole metal complex attractive substrate in terms of their availability and easy to oxiditive property. These compounds readily undergoes oxidation with various oxidant. Kinetic studies constitute important source of mechanistic information about reaction.

During the oxidation by permangnate it is evident that the Mn(VII) in permagnate is reduced to various oxidation states in acid, alkaline and neutral media. The mechanism by which this multivalent oxidant oxidise a substrate depends not only on the substrate but also on medium used for the study in strongly alkaline medium the stable reduction product is the magnate ion, MnO_4^{-2} requires a pH range 12-13 below which the system becomes distributed and the reaction will proceed. Further to give a reduced product of oxidant as Mn (IV) which slowly develops yellow turbidity (Mulla, 2004).

Oxidation reactions by Potassium permanganate are of considerable academic and technological importance because of variable oxidation state of potassium.

The Kinetics provides the useful information about the mechanism and rate of chemical reaction, which helps to run a Oxidation of organic compound carried out by oxidising agent like potassium dichromate Cr (VI) (Sheik, 2010; Firouzabadi, 1992; and Mathiyalagan, 2010). The update literature survey shows that, though the considerable amount of work has been done on the oxidation of organic compounds by potassium permanganate (Panday, 2009; Kothari, 2007, 2000, 2002, 2000; Subbarao, 1971; and Sayyed Hussain, 2012, 2011, 2011, 2011). The object of present investigation is to formulate the reaction mechanism from the date gathered from kinetic measurement. It is found that the oxidation of 2,5-Diamino-1,2,3,-thiadiazole metal complex occurs by two ways, hydrolysis followed by the oxidation of alcohol, direct oxidation of esters. But no conclusive evidence was provided in support of either of the two pathways; hence it is decided to undertake the systematic investigation kinetic of 2,5-Diamino-1,2,3,-thiadiazole metal complex. the kinetic of oxidation of 2,5-Diamino-1,2,3,-thiadiazole metal complex by potassium permagnet in moderately concentrate sulphuric and medium has been investigated. The above said metal complex is biologically active (Rao, 1979).

MATERIAL AND METHODS

All the chemicals used were of AR grade, specially postassium permagnate used were of AR grade and was prepared and estimated by standard method. Metal complex is used as prepared in laborites, and the boiling point of it was confirmed. The acetic acid were always freshly distilled before used for the kinetic measurement, per magnate and sulphuric acid solution were taken in two different flasks and covered with black cloth and placed in a thermostat for 1 hour to attain constant temperature by both the flask. In order to prevent the hydrolysis, required volume of given metal complex was directly added to acid solution with micro pipette just before mixing it with permanganate solution. The course of reaction was followed by measuring the absorbance (optical density) of unreacted permanganate ions from time to time at 520 nm using systronics uv-visible Spectrophotometer. The reaction were followed up to 70 to 85% completion and the product were identified as 2,5-Dinitro-1,2,3,-thiadiazole metal complex and detected by test of nitro group i.e. product is treated with $FeSo_4$ solution and NaOH solution and boiled, Radish-brown precipitate is obtained, product was also analyzed by IR. The addition of actonitrile to reaction system did not induce the precipitation with acetonitrile showing that no free radicals are formed in the system (Gupta, 2012).

RESULTS AND DISCUSSION

Under the conditions [2,5-Diamino-1,2,3,-thiadiazole metal complex] > [$KMnO_4$] in 3.20 M. H_2SO_4. The plot of log absorbance (O.D.) Vs time were linear indicating the first order dependence of rate on [$KMnO_4$]) (Figure not shown) A Oxidation of 2,5-Diamino-1,2,3,-thiadiazole metal complex depends on the concentration of potassium per magnate. This was also confirmed by verifying [$KMnO_4$] which did not show any change in Pseudo First order constant (k^1) value (Table No.1). The reaction was also found to be first order in [2,5-Diamino-1,2,3,-thiadiazole metal complex] (Table 2). The rate of reaction increases with increases in [H_2SO_4]. (Table No.3)

The effect of temperature was also studied at different temperature like 293K, 298K, 308K, 318K, and 323K. It is shown in Table No.4. It is clear that as temperature increases rate constant increases (Table No. 4). Thermodynamic parameters such as $\Delta H^{\#}$, $\Delta S^{\#}$,$\Delta G^{\#,}$, E, ΔE and A i.e. frequency factor were studies and given in

The negative values of entropy of activation shows that the intermediate transition state is rigid the relatively small values of ΔH and ΔS are consistent with the reaction generally proceeds through highly ionized transition state (Narayan, 1979).

Table 1: Effect of variation of Oxidant ($KMnO_4$):-

[2,5-Diamino-1,3,4-thiadiazole metal complex] = 4.7 x 10^{-4}, Temperature: $30^{O}C$, λ Max = 520 nm

Sr.No.	*[Oxidant]x10^{3} mol dm^{-3}*	*K_{Obs} x 10^{2} $min.^{-1}$*
I	*3.62*	*1.660*
II	*2.92*	*1.620*
III	*2.54*	*1.584*
IV	*2.17*	*1.624*
V	*1.48*	*1.594*
VI	*1.06*	*1.636*

Table 2: Effect of variation of 2,5-Diamino-1,3,4-thiadiazole metal complex

Sr.No.	*[Metal complex]x10^{-3}*	*Log [Sub]*	*K_{Obs} x 10^{2} $min.^{-1}$*	*Log K^{1}*
I	*0.90*	*-2.7442*	*0.9872*	*-2.0652*
II	*1.82*	*-2.6570*	*1.0620*	*-1.9652*
III	*2.12*	*-2.5680*	*1.1521*	*-1.9362*
IV	*2.62*	*-2.4434*	*1.1820*	*-1.8820*
V	*4.20*	*-2.3984*	*1.2920*	*-1.8626*
VI	*4.51*	*-2.3960*	*1.4620*	*-1.8224*

Table 3: Effect of Variation of Concentration of Acid [H_2SO_4] on Oxidation of 2,5-Diamino-1,3,4-thiadiazole metal complex

(KMno4) =4.7×10^{-4}m, [H_2SO_4] = 0.857m, Temperature = 30^{c} max 520nm

Sr. No.	Acid[H_2SO_4]	Log [acid]	Log aw	Ho	$Kx10^{-2}$/min	logk	H_O+Log K
I	2.8	-3.5529	0.0700	0.70	1.8	$^{-}3.744$	$^{-}3.044$
II	3.0	-3.5229	0.0550	0.65	2.0	$^{-}3.698$	$^{-}3.048$
III	3.3	-3.4815	0.0422	-0.10	2.4	$^{-}3.602$	$^{-}3.702$
IV	3.5	-3.4560	0.0320	-0.045	3.1	$^{-}3.522$	$^{-}3.972$
V	3.8	-3.4203	0.0200	-0.20	3.5	$^{-}3.455$	$^{-}2.655$
VI	4.0	-3.3980	0.0150	0.02	4.0	$^{-}3.397$	$^{-}2.312$

Table 4: Effect of variation of temperature on reaction rate

[$Kmno_4$] = $4.7x\ x10^{-4}$m, (2, 5-Diamino-1, 3, 4-thiadiazole metal complex) = $4.7x\ x10^{-3}$

Temp	$1/T\ x\ 10^{-3}$	$Kx10^{-2}$/min	logk	A	Ej/mole	ΔHJ/mole	ΔGJ/mole	ΔSJ/mole
293	$3.41x10^{-3}$	0.86	$^{-}2.060$	$5.13\ x10^{-3}$	26801	24380	80642	-192
298	$3.36\ x10^{-3}$	1.02	$^{-}1.987$	$5.10x\ x10^{-3}$	26801	24360	81590	-192
303	$3.30\ x10^{-3}$	1.48	$^{-}1.823$	$6.02\ x10^{-3}$	26801	24280	82110	-190
308	$3.25x10^{-3}$	1.72	$^{-}1.756$	$5.02x10^{-3}$	26801	24240	82012	-188
318	$3.14\ x10^{-3}$	1.99	$^{-}1.\ 699$	$4.90\ x10^{-3}$	26801	24150	85230	-191
323	$3.10\ x10^{-3}$	2.30	$^{-}1.634$	$4.85\ x10^{-3}$	26801	24110	86236	-190

$$H^{+} + Mno_4^{-} \longrightarrow HMno_4$$

This point has been also confirmed by previous researchers. Hence Mn (VII) could be considered as the reactive specie and this probably exists to a certain extent as $HMnO_4$.

As the acid concentration is increased the formation of $HMnO_4$ is favoured and hence increases the oxidation may be assumed to be taking place by Mn (VII) in the form of either MnO_4^- or $HMnO_4$ or both depending on the acid concentration. The linear plot of $10K^1$ Vs log [H_2SO_4] and $logK^1$ Vs Ho (fig has not shown) indicates that the reactions are acid catalyzed, but none of the above plots gives an ideal slope for unity. In view of the departure from the ideal behavior, applicability of Bunnett's hypothesis was tested. A plot of $logK^1$ Vs Ho Vs log H20 was linear (fig has not shown) and the slop was found to be -2.5 . This value indicates non-involvement of water molecule in the rate determining steps as per Bunnett's, while the hydrolysis rate was 3.2×10^{-5}liter mol^{-1} sec^{-1} under identical condition, from this it is

Derivation of Rate Law:-

$$MnO_4 + H^+ \overset{K_1}{\rightleftharpoons} HMnO_4$$

$$\text{Metal Complex} + HMnO_4 \overset{k_2}{\rightleftharpoons} C$$

$$C \xrightarrow{k} \text{Product}$$

$$[MnO_4^-] = \quad [MnO_4^-] + [\ HMnO_4]$$

$$= [MnO_4^-] + k_1\ [MnO_4^-]\ [H^+]$$

$$= [MnO_4^-]\ \ \{[1+k_1\ [H^+]$$

$$\text{Rate} \ = \frac{k\,k_2\,[MnO_4^-]\,[\text{ metal complex}]}{1+k_1\,[H^+]}$$

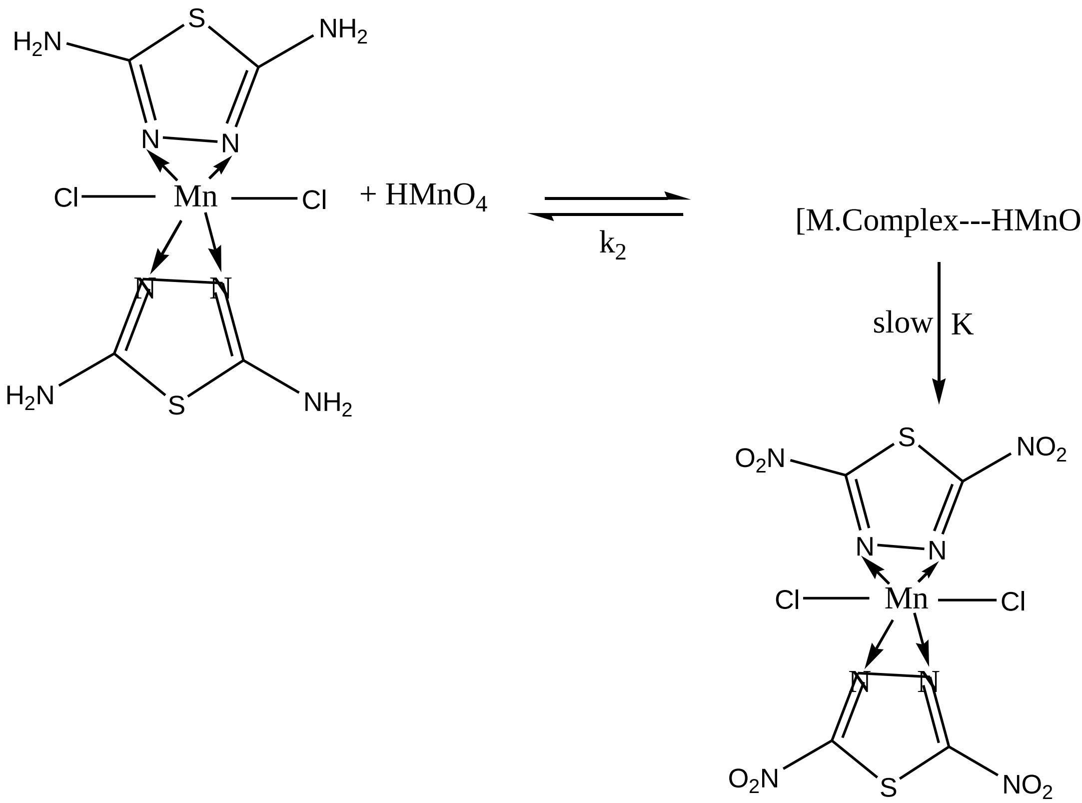
$$\frac{\text{Rate}}{[MnO_4]\ \ [\text{M.Complex}]} = \frac{kk_2}{1+K_1\ [H^+]}$$

$$\text{Kobs} = \frac{kk_2}{1+k_1\ [H^+]}$$

$$\frac{1}{k_{obs}} = \frac{1}{kk_2} + \frac{k_1[H^+]}{kk_2}$$

Mechanism of oxidation of metal complexes:-

$$MnO_4^- + H^+ \overset{k_1}{\rightleftharpoons} HMnO_4$$



Compound (III) being highly unstable disproportionate to give acetic acid and the corresponding aldehyde. The rate law can be expressed by equation (1)

$$\frac{-d[Mn(VII)]}{dt} = k(\text{Metal complex})[Mno_4]_{Total}$$

This type of hydride ion transfer process has been proposed in the oxidation of aldehyde, formic acid, ethers, alcohols etc. by permagnate in moderately concentrated acid solutions (Banerji, 1973).

The effect of temperature on reaction rate was studied which shows the increase in reaction rate with increase in temperature (table 2 and 3). The rate of oxidation in case of dimethyl phthalate, diethyl phthalate, and dibutylphthalate, the rate of reaction as the number of alkyl group increases there is decrease is clear that the direct oxidation is the only process occurring under the experimental conditions used.

A probable mechanism (scheme -1) in which MnO_4^- or $HMnO_4$ attacks on the metal complex is considered for explaining the observed kinetic result.

K value, due to steric effect In case of 2,5-Diamino-1,2,3,-thiadiazole metal complex and the rate of reaction is more though there is presence of electron with drawing group $\bar{Cl}$.

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