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

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ABSTRACT
The kinetic of oxidation of 2,5-Diamino-1,2,3,-thiadiazole ferrate 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.

Keywords: Kinetics, Mechanism, Oxidation, 2,5-Diamino-1,2,3,-thiadiazole ferrate complex.

INTRODUCTION

Bioinorganic chemistry constitutes the discipline at the interface of the more classical areas of inorganic chemistry and biology. The ferrate 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 ferrate known as bioinorganic chemistry. Today however inorganic chemistry is beginning to have a major impact on modern medicine there important inorganic pharmaceuticals are cisplatin[1] an anticancer drug.
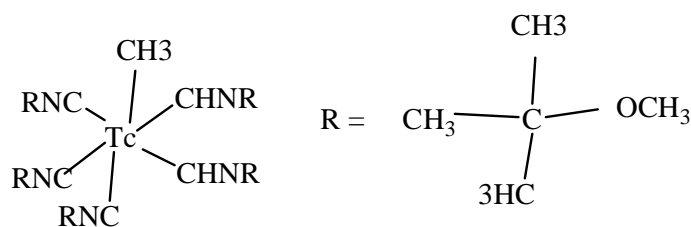
Cardiolyte, a heart imaging agent

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 ferrate ions. $M-OH_2$ bonds are very labile breaking and reforming as fast as billion times per second. The labilities of ferrate-ligand bonds for the ferrate complexes[2]. In general ligand exchange rates are faster for the less highly charged M^{+2} than for highly M^{+3} ferrate ions very[3]. The fast ferrate-ligand exchange rates of first row transition ferrate ions such as Fe^{+2}, Cr^{+3}, Co^{+3}[4].

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 ferrate complex attractive substrate in terms of their availability and easy to oxiditive property. This compound readily undergoes oxidation with various oxidant. Kinetic studies constitute important source of mechanistic information about reaction.

During the oxidation by permanganate it is evident that the Mn(VII) in permanganate is reduced to various oxidation states in acid, alkaline and neutral media. The mechanism by which this multivalent oxidant oxidize 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) this slowly develops yellow turbidity[5].

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 oxidizing agent like potassium dichromate Cr (VI) [6-8] The update literature survey shows that, though the considerable amount of work has been done on the oxidation of organic compounds[9to17] by potassium permanganate, but only a few studies is found on the kinetics of oxidation of organic compounds by potassium permagnate[18,19]. 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 ferrate complex occurs by two ways, hydrolysis followed by the oxidation of amino group, direct oxidation of ferrate complex. But no conclusive evidence was provided in support of either of the two pathways; hence it is decided to undertake the systematic investigation of kinetics of

2,5-Diamino-1,2,3,-thiadiazole ferrate complex. the kinetic of oxidation of 2,5-Diamino-1,2,3,-thiadiazole ferrate complex by potassium permanganate in moderately concentrate sulphuric and medium has been investigated. The above said ferrate complex is biologically active[20].

MATERIAL AND METHODS
All the chemicals used were of AR grade, specially potassium permanganate used were of AR grade and was prepared and estimated by standard method. Ferrate 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 ferrate 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 Spectrophotomer. The reaction were followed up to 70 to 85% completion and the product were identified as 2,5-Dinitro-1,2,3,-thiadiazole ferrate complex and detected by test of nitro group i.e. product is treated with FeSo$_4$ solution and NaOH solution and boiled, Radish-brown ppt is obtained, product is 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[21].

RESULTS AND DISCUSSION
Under the conditions [2,5-Diamino-1,2,3,-thiadiazole ferrate complex] > [KMnO$_4$] in 3.20 M. H$_2$SO$_4$. The plot of log absorbance (O.D.) Vs time were linear indicating the first order dependence of rate on [KMnO$_4$]. (Fig. has not shown) A Oxidation of 2,5-Diamino-1,2,3,-thiadiazole ferrate 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 ferrate 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[22].
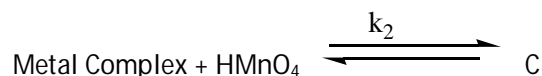
$$H^+ + MnO_4^- \longrightarrow HMnO_4$$

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 *HMnO₄* 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

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

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

$$C \overset{k}{\longrightarrow} \text{Product}$$

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

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

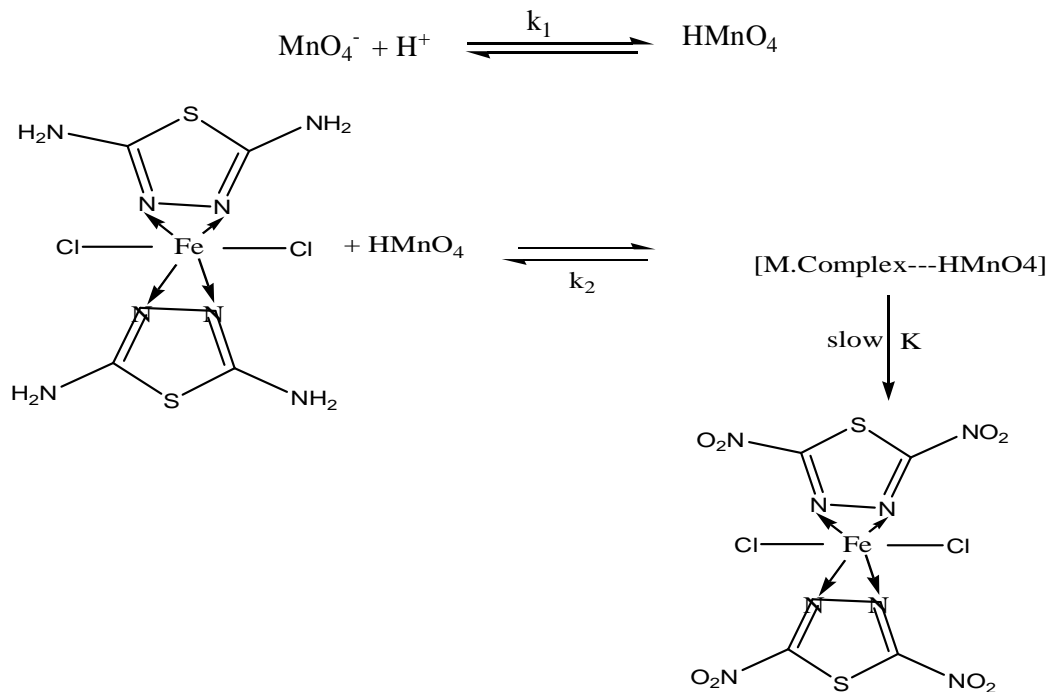$$= [MnO_4^-] \{[1 + k_1 [H^+]$$

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

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

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

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

Mechanism of oxidation of ferrate complexes

$$MnO_4^- + H^+ \xrightleftharpoons{k_1} HMnO_4$$

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[23].

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 HMnO₄ attacks on the ferrate 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 ferrate complex and the rate of reaction is more though there is presence of electron with drawing group $C\bar{l}$.

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^{0}C,
λ Max = 520 nm

S. No.	[Oxidant]x10^3 mol dm^{-3}	K$_{Obs}$ x 10^2 min.$^{-1}$
I	3.62	1.48
II	2.92	1.42
III	2.54	1.36
IV	2.17	1.42
V	1.48	1.28
VI	1.06	1.26

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

S.No.	[Metal complex]x10^{-3}	Log [Sub]	K$_{Obs}$ x 10^2 min.$^{-1}$	Log K^1
I	0.90	-2.522	0.9231	-2.055
II	1.82	-2.516	1.041	-1.827
III	2.12	-2.482	1.082	-1.781
IV	2.62	-2.388	1.101	-1.713
V	4.20	-2.210	1.182	-1.621
VI	4.51	-2.212	1.272	-1.602

Table 3: Effect of Variation of Concentration of Acid [H$_2$SO$_4$] on
Oxidation of 2,5-Diamino-1,3,4-thiadiazole metal complex
(KMno$_4$) =4.7× 10^{-4}m,   [H$_2$SO$_4$] = 0.857m
Temperature = 30$^{.c}$ max 520nm

S.No.	Acid [H$_2$SO$_4$]	Log [acid]	Log aw	Ho	Kx10^{-2}/min	logk	H$_0$+Log K
I	2.8	-3.5529	0.0621	0.65	1.6	-3.620	-3.074
II	3.0	-3.5229	0.0601	0.58	1.8	-3.520	-3.628
III	3.3	-3.4815	0.0426	-0.23	2.1	-3.506	-3.832
IV	3.5	-3.4560	0.0325	-0.034	2.8	-3.420	-3.454
V	3.8	-3.4203	0.0211	-0.27	3.2	-3.321	-2.591
VI	4.0	-3.3980	0.0112	0.02	3.8	-3.291	-2.311

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	4.86 x10^{-3}	26216	24160	80112	-164
298	3.36 x10^{-3}	1.02	-1.987	4.81x x10^{-3}	26216	24020	80227	-162
303	3.30 x10^{-3}	1.48	-1.823	5.2 x 10^{-3}	26216	23810	82116	-154
308	3.25x10^{-3}	1.72	-1.756	4.12 x10^{-3}	26216	23760	82810	-142
318	3.14 x10^{-3}	1.99	-1.699	3.92 x10^{-3}	26216	23720	83242	-162
323	3.10 x10^{-3}	2.30	-1.634	4.26 x10^{-3}	26216	23680	85240	-160

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