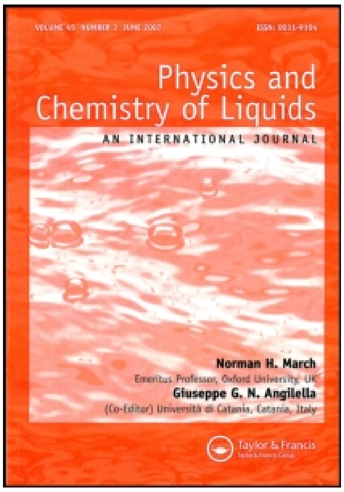

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OXIDATION OF *L*-ARGININE BY MANGANESE(VII) IN CONCENTRATED SULFURIC ACID MEDIUM

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Kinetics and mechanism of manganese(VII) oxidation of *L*-arginine has been studied in aqueous sulfuric acid medium. Various hypotheses for the mechanism of acid catalysis have been tested and it has been found that rate is related to the activity of water in accord with Bunnett's hypothesis. The energy and entropy of activation and frequency factor have been calculated using the Eyring and Arrhenius plots. Mechanisms in agreement with the observations are reported. The experimental rate law for the reaction was found to be

$$\frac{-d[\mathrm{Mn(VII)}]}{dt} = k_0[L\text{-Arginine}][\mathrm{Mn(VII)}]$$

The reaction appears to involve an acid catalysis and the data showed the role of water molecules in the rate-determining step facilitating proton transfer which satisfies Bunnett's theory.

Keywords: Oxidation; *L*-arginine; Manganese(VII); Bunnett's hypothesis

1. INTRODUCTION

The manganese(VII) oxidation of amino acids has received considerable attention in previous literature due to the importance of these compounds in biological systems. The oxidation has been widely studied in strong acidic media [1–8], where no noticeable auto-catalytic

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*Corresponding author.

effects were found. However, in neutral or weakly alkaline medium, the literature consulted agrees as to the appearance of the cited autocatalytic effect [9–13]. The purpose of this study is to analyze the manganese(VII) oxidation of *L*-arginine in sulfuric acid. The applicability of Bunnett's theory was also tested.

2. EXPERIMENTAL PROCEDURES AND TECHNIQUES

Materials All reagents used were of analytical grade from Merck, Sigma and Fluka. *L*-arginine was assayed for amino acid content by standard method [14]. The solutions were prepared in buffered medium with sulfuric acid and potassium sulfate, with triply distilled water which was deionized. The pH and the ionic strength of the medium were adjusted with the required concentrations of sulfuric acid and potassium sulfate to get the desired values and tested by the Vogel method [15]. Sulfuric acid, potassium sulfate, potassium pyrophosphate, and mercuric chloride were used without further purification.

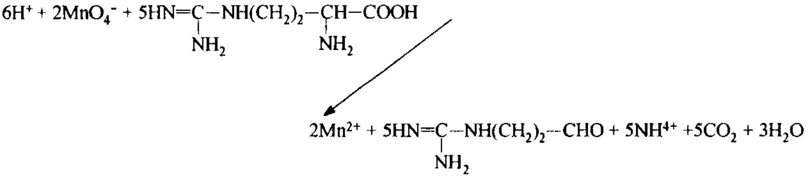
Kinetic measurements The course of reaction was followed by measuring the absorbance of unreacted permanganate from time to time at 525 nm using a fw-265 spectrophotometer, supplied with a conventional thermostatic bath (± 0.1 K). The reactions were carried out in the temperature range of 278–303 K.

The reaction was usually followed up to 50% completion, and products of the reaction were identified as ammonia, carbon dioxide, and the corresponding aldehyde [16]. Addition of mercuric chloride to the reaction system did not induce the precipitation of mercurous chloride, indicating that no free radicals are produced in the system [17].

2.1. Stoichiometry

The stoichiometry of the reaction was determined by following the reaction for one hour and estimating both permanganate and aldehyde before and after half an hour. Permanganate was estimated by quenching a known amount of the reaction mixture in a known excess of iron(II) and titrating the unreacted iron(II) against standard cerium(IV). The aldehyde was estimated colorimetrically using chromotropic acid.

It was found that one mole of permanganate oxidized 2.5 moles of aldehyde. The stoichiometry of the reaction is represented by the following equation:



$$6H^+ + 2MnO_4^- + 5HN{=}\underset{NH_2}{C}{-}NH(CH_2)_2{-}\underset{NH_2}{CH}{-}COOH \longrightarrow 2Mn^{2+} + 5HN{=}\underset{NH_2}{C}{-}NH(CH_2)_2{-}CHO + 5NH^{4+} + 5CO_2 + 3H_2O$$

3. RESULT AND DISCUSSION

Under the pseudo-first-order condition of [*L*-arginine] ≫ [KMnO4] in 3.2 M sulfuric acid, plots of log (absorbance) *vs.* time were linear, showing that the reaction is first-order in [KMnO4] (Fig. 1). This was further confirmed by varying [KMnO4], which did not show any change, in the pseudo-first-order of rate constants, k_0' (Tab. I). The reaction also exhibited a first-order dependence in [*L*-arginine] as could be seen from Figure 2 and Table II.

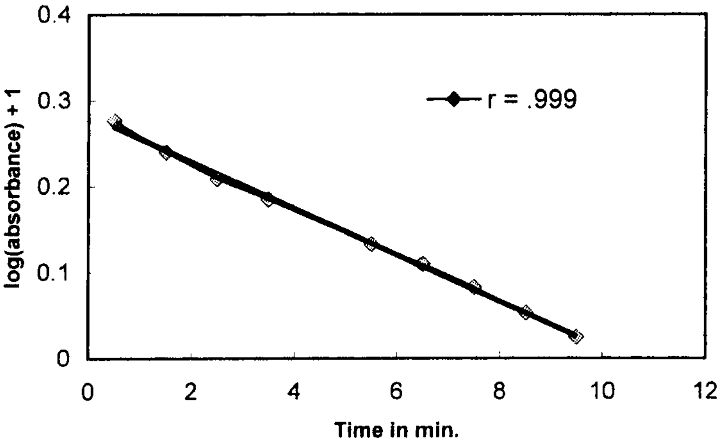


FIGURE 1 First-order plot for arginine–permanganate reaction.

TABLE I Effect of concentration of permanganate on the rate of oxidation in strong acid medium at 293 K[a]

$[KMnO_4]_0$ $(mol\ dm^{-3})$	$k'_0 \times 10^3$ (s^{-1})
1.50×10^{-4}	1.33
2.00×10^{-4}	1.35
2.50×10^{-4}	1.37
3.00×10^{-4}	1.38

[a] [*L*-Arginine]$_0 = 0.02\,mol\,dm^{-3}$ and $[H_2SO_4] = 3.2\,mol\,dm^{-3}$.

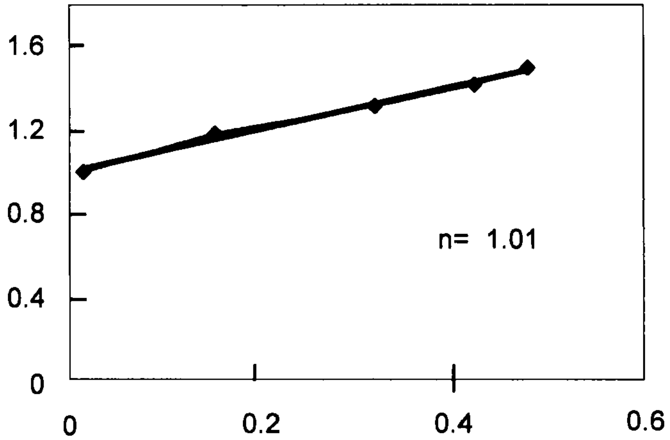


FIGURE 2 Order of [Arginine] in reaction, plot of $\log k'_0 + 3$ *vs.* log[Arginine] + 3.

TABLE II Effect of concentration of *L*-arginine on the rate of oxidation in strong acid medium at six different temperatures[a]

[*L* -*Arginine*]$_0$	$k'_0 \times 10^4 (s^{-1})$					
$(mol\ dm^{-3})$	278 *K*	283 *K*	288 *K*	293 *K*	298 *K*	303 *K*
0.01	2.45	4.57	6.85	9.30	10.38	14.62
0.015	3.47	5.12	9.53	10.50	14.24	18.13
0.02	4.26	9.70	15.63	13.84	20.90	27.51
0.025	5.94	10.06	19.75	20.18	26.57	39.16
0.03	8.62	14.23	20.14	26.51	30.18	42.27

[a] $[KMnO_4]_0 = 0.01$ [*L*-Arginine]$_0$ and $[H_2SO_4] = 3.2\ mol\ dm^{-3}$.

At constant $[KMnO_4]_0$, [*L*-arginine]$_0$, and temperature an increase in $[H_2SO_4]$ increased the rate constant k'_0 from $6.92 \times 10^{-4} s^{-1}$ ($2.09\,mol\,dm^{-3}$ H_2SO_4) to $44.37 \times 10^{-4} s^{-1}$ ($4.5\,mol\,dm^{-3}\,H_2SO_4$)

(Tab. III). The addition of sulfate and pyrophosphate ions caused no significant effect on the rate (Tab. IV).

Activation parameters are calculated using the Eyring equation $k=(\mathrm{R}T/\mathrm{Nh})\exp((-\Delta H^{\neq}+T\Delta S^{\neq})/(\mathrm{R}T))$ plots of $\ln k_0/T$ *vs.* $1/T$ should be linear. From the intercept and slope values of entropy $\Delta S^{\neq}$ and enthalpy $\Delta H^{\neq}$ of activation were evaluated, respectively, and results are given in Table V. Frequency factor, A and

TABLE III Effect of concentration of sulfuric acid on the rate of oxidation at 293 K[a]

$[H_2SO_4]$ ($mol\ dm^{-3}$)	$k'_0 \times 10^4$ (s^{-1})
2.09	6.92
2.52	8.15
2.80	10.33
3.2	13.84
3.5	21.78
4.1	31.92
4.5	44.37

[a] [*L*-Arginine]$_0$ = 0.02 mol dm^{-3} and $[KMnO_4]_0 \cong 0.01$ [*L*-Arginine]$_0$.

TABLE IV Effect of concentration of sulfate and pyrophosphate ions on the rate of oxidation at 293 K[a]

Concentration ($mol\ dm^{-3}$)	$k'_0 \times 10^3$ (s^{-1})
$[SO_4^{2-}]=0.02$	1.83
$[P_2O_7^{4-}]=0.02$	1.74

[a] [*L*-Arginine]$_0$ = 0.02 mol dm^{-3}, $[H_2SO_4]$ = 3.2 mol dm^{-3} and $[KMnO_4]_0$ = 0.01 [*L*-Arginine]$_0$.

TABLE V Activation parameters on the oxidation of *L*-arginine by permanganate in strong acid medium at six different temperature[a]

Temp. (*K*)	$k_0 \times 10^6$ ($mol^{-1} dm^3 s^{-1}$)	$\Delta S^{\neq}$ ($J mol^{-1} K^{-1}$)	$\Delta H^{\neq}$ ($kJ mol^{-1}$)	E_{expt} ($kJ mol^{-1}$)	*Log A*
278	25.85	−187.16	40.09	42.72	3.48
283	42.69	−187.16	40.09	42.72	3.48
288	60.42	−187.16	40.09	42.72	3.48
293	79.53	−187.16	40.09	42.72	3.48
298	90.54	−187.16	40.09	42.72	3.48
303	128.1	−187.16	40.09	42.72	3.48

[a] $[KMnO_4]_0$ = 0.0001 mol dm^{-3} and $[H_2SO_4]$ = 3.2 mol dm^{-3}.

experimental energy, E_{exp} were also estimated by using Arrhenius plots of k_0 *vs.* $1/T$ Table V. In agreement with the experimental behavior, mechanisms is proposed to interpret the reaction pathways.

The expected species on permanganate oxidation in acid solution are manganese(III), manganese(IV), and manganese(VII) [18]. If manganese(III) or manganese(IV) were to be the reactive species, the addition of complexing agents like sulfate and pyrophosphate ions should have decreased the rate. In fact there is no effect of these ions on the rate [19], showing that only manganese(VII) is the most probable reactive species.

With increasing $[H^+]$, the rate enhances due to protonation of the oxidant resulting in the formation of a more powerful oxidant, namely, acid permanganate by the following equilibrium:

$$H^+MnO_4^- \Leftrightarrow HMn0_4$$

The same explanation has also been given in the oxidation of alcohols [18] and esters [20] by acid permanganate.

Plots of $\log k_0'$ *vs.* $\log[H_2SO_4]$ and $\log k_0'$ *vs.* H_0' were found to be linear, indicating that the reaction is acid catalyzed, but none of the above plots gave an ideal slope of unity. In view of the departure from the ideal behavior, the applicability of Bunnett's theory [21] was tested. A plot of $\log k_0' - \log[H_2SO_4]$ *vs.* $\log a_{H_2O}$ was linear Figure 3, and the slope was found to be -1.83. According to Bunnett's theory if the slope of such a plot is greater than -2, it will indicate the

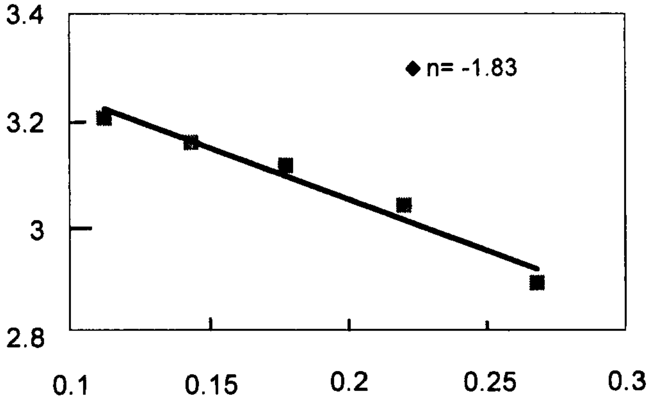
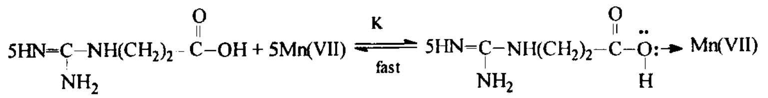


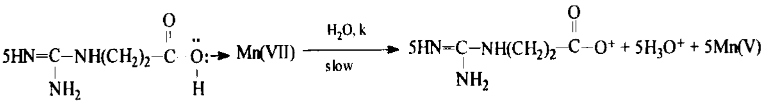
FIGURE 3 Bunnett's plot of $\log k_0' - \log[H_2SO_4]$ *vs.* $\log a_{H_2O}$.

involvement of a water molecule in the rate-determining step as a proton-abstracting base from the substrate. The values of Hammett's acidity function H_0' and $\log a_{H_2O}$ have been taken from the literature [22,23].

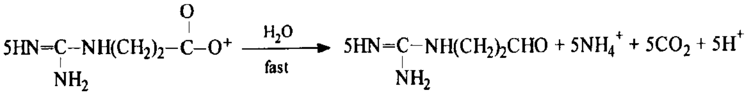
The mechanisms consistent with the observed kinetic data is as follows:



$$5HN{=}\underset{\displaystyle NH_2}{C}{-}NH(CH_2)_2{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OH + 5Mn(VII) \underset{fast}{\overset{K}{\rightleftharpoons}} 5HN{=}\underset{\displaystyle NH_2}{C}{-}NH(CH_2)_2{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\underset{\displaystyle H}{\ddot{O}}{:}\rightarrow Mn(VII) \quad (1)$$



$$5HN{=}\underset{\displaystyle NH_2}{C}{-}NH(CH_2)_2{-}\overset{\displaystyle O}{\overset{\|}{C}}\,\underset{\displaystyle H}{\ddot{O}}{:}\rightarrow Mn(VII) \xrightarrow[slow]{H_2O,\,k} 5HN{=}\underset{\displaystyle NH_2}{C}{-}NH(CH_2)_2{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O^+ + 5H_3O^+ + 5Mn(V) \quad (2)$$



$$5HN{=}\underset{\displaystyle NH_2}{C}{-}NH(CH_2)_2{-}\overset{\displaystyle O}{\overset{|}{C}}{-}O^+ \xrightarrow[fast]{H_2O} 5HN{=}\underset{\displaystyle NH_2}{C}{-}NH(CH_2)_2CHO + 5NH_4^+ + 5CO_2 + 5H^+ \quad (3)$$

$$4Mn(V) \xrightarrow[fast]{} 2Mn(VII) + 2Mn(III) \quad (4)$$

$$2Mn(III) \xrightarrow[fast]{} Mn(IV) + Mn(II) \quad (5)$$

$$Mn(V) + Mn(IV) \xrightarrow[fast]{} Mn(VII) + Mn(II) \quad (6)$$

The rate law for the above scheme comes out to be

$$\frac{-d[Mn(VII)]}{dt} = k_0[L\text{-Arginine}][Mn(VII)]$$

where

$$k_0 = Kk$$

From the bimolecular rate constants at different temperatures 278–303 K, activation parameters for reaction were evaluated (Tab. V).

Finally we concluded that the kinetic studies on the manganese(VII) oxidation of *L*-arginine in moderately acid medium could get an insight in to the mechanism. The order in both [*L*-arginine] and [$KMnO_4$] was found to be unity. The effect of complexing agents like sulfate and pyrophosphate ion was nil, from which manganese(VII) was confirmed to be the reactive species.

The slope of the linear plot $\log k'_0 - \log[H_2SO_4]$ *vs.* $\log a_{H_2O}$ (Bunnett's plot) was found to be -1.83, indicating that involvement of the water molecule in the rate-determining step is as a proton abstracting base from the substrate.

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