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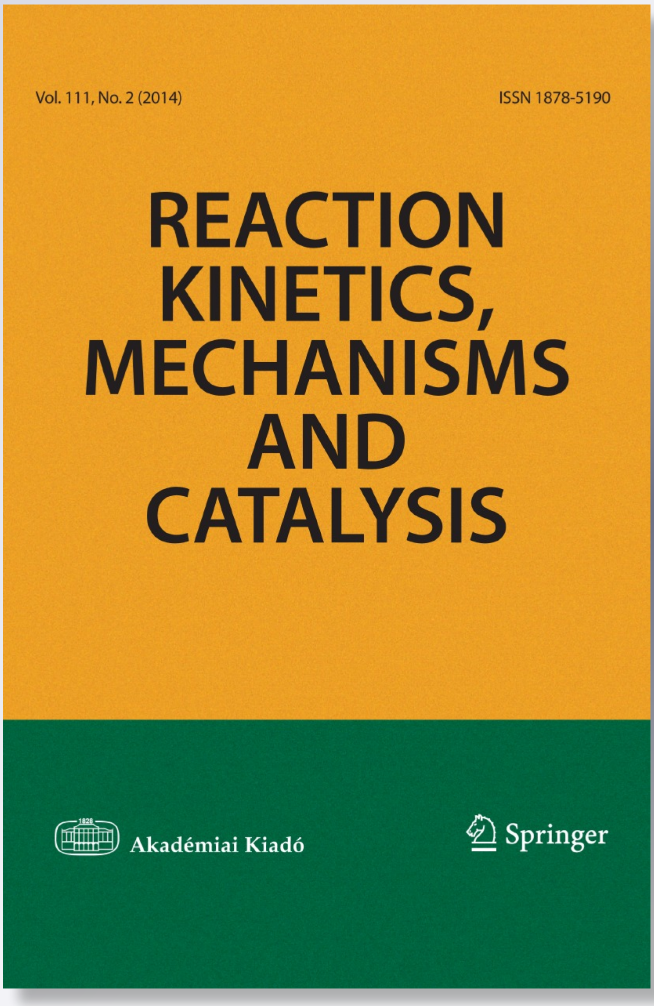

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Base-catalyzed oxidation of L-asparagine by alkaline permanganate and the effect of alkali metal ion catalysts: a kinetic and mechanistic approach

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Abstract Kinetic investigations on the oxidation of L-asparagine (Asn) by alkaline permanganate have been carried out spectrophotometrically at a constant ionic strength and temperature. The reaction is first order with respect to [MnO_4^-] and less than unit order with respect to both [Asn] and [alkali]. The influence of pH indicated that the oxidation is base catalyzed. The reaction rate was found to increase with increasing ionic strength and temperature. The addition of alkali metal ion catalysts accelerates the oxidation rate. The proposed reaction mechanism involves the formation of a 1:1 intermediate complex between L-asparagine and an alkali-permanganate species in a pre-equilibrium step, which was confirmed by both spectral and kinetic evidence. The complex decomposes slowly in a rate determining step, resulting in the formation of a free radical. The latter reacts again with another alkali-permanganate species in a subsequent fast step to yield the final reaction products which were identified as aldehyde (α-formyl acetamide), ammonia, manganate(VI) and carbon dioxide. The appropriate rate laws are deduced. The reaction constants involved in the mechanism were evaluated. The activation and thermodynamic parameters were determined and discussed.

Keywords L-Asparagine · Permanganate · Base-catalyzed oxidation · Kinetics · Mechanism

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Introduction

At present, large numbers of kinetic investigations on the oxidation of amino acids are being carried out using various oxidants under different experimental conditions [1–4] because of their biological significance, selectivity towards the oxidants and to understanding the mechanism of such biological redox reactions. In many cases, it was reported that amino acids undergo oxidative decarboxylation and deamination.

L-Asparagine is considered to be the first amino acid to be isolated from asparagus juice and creates in the liver to help feed the nervous system. It occurs in relatively high concentrations in plant tissues. Its role in the metabolism is crucial. It finds extensive applications in the production of pharmaceuticals and medicine. The oxidation of L-asparagine in alkaline medium has been previously studied by sodium *N*-chloro-*p*-toluene sulfonamide catalyzed by copper(II) [3] and by diperiodatonickelate(IV) complex [4].

Permanganate ion is one of the most important, eco-friendly and powerful multi-electron oxidants, which can exist in various oxidation states, among which +7 is its highest oxidation state, which occurs in the oxo-compounds like MnO_4^-, Mn_2O_7, MnO_3F. Among these, MnO_4^- is the most commonly used well known oxidant species to carry out kinetic studies in acidic, neutral and alkaline media [5]. The kinetics of oxidative deamination and decarboxylation of L-asparagine by aqueous alkaline permanganate has been investigated [6]. It was reported that the reaction exhibits first order kinetics with respect to $[MnO_4^-]$ and fractional order dependences with respect to [Asn] and [alkali]. Initially added products such as aldehyde, ammonia and manganate ion have no significant effect on the rate of reaction. An increase in ionic strength was found to increase the rate. Similar results were obtained [7] in the oxidation of L-proline by alkaline permanganate. The oxidation process [6] in alkaline medium was shown to proceed via two paths: one a substrate-dependent path, the other a substrate-independent path. Although permanganate ion in alkaline media has been used as a potent oxidant for many amino acids [8–12], no reports are available in the literature on the extensive kinetic and mechanistic studies on formation and decomposition of the probable intermediate complex throughout oxidation of L-asparagine by this oxidant. In view of the above aspects and the potential importance of L-asparagine, there was a need to investigate the title reaction in detail.

Experimental and methods

Materials

All reagents were from Merck or Sigma. A stock solution of L-asparagine (E. Merck) was prepared afresh by dissolving the appropriate amount of asparagine sample in the required volume of distilled water. Solutions of potassium permanganate were prepared and standardized as reported earlier [13]. Other chemicals were of analytical grade and their solutions were prepared by dissolving requisite amounts of the samples in double-distilled water. Sodium hydroxide solution was used to provide the required alkalinity. The ionic strength (I) was maintained constant (0.2 mol dm^{-3}) using $NaClO_4$ as an inert electrolyte. The reaction temperature was controlled within ±0.1 °C.

Kinetic measurements

Kinetic runs were performed under pseudo-first order conditions where L-asparagine was present in a large excess over that of permanganate concentration at a constant ionic strength. However, some experiments were conducted under second order conditions of $[\mathrm{Asn}] \leq [\mathrm{MnO_4}^-]$ in order to check the data obtained from the pseudo-first order kinetics. The results obtained were found to be in a good agreement with each other within the experimental errors indicating the reproducibility of the measurements.

The absorbance measurements were made in a thermostated cell compartment at the desired temperature on a Shimadzu UV-1800 PC automatic scanning double-beam spectrophotometer fitted with a program controller using cells of path-length 1 cm. The course of reactions was followed up to not less than two half-lives of the reaction completion by recording the decrease in the absorbance of permanganate ion at $\lambda = 526$ nm, its absorption maximum, for the intermediate formation and at $\lambda = 606$ nm, the absorption maximum of the intermediate, for the intermediate decomposition as functions of time. It was verified that there is no interference from other reagents at these wavelengths. All experiments were carried out in triplet and the rate constants were found to be reproducible within ±3 %.

Results

Stoichiometry and product analysis

Reaction mixtures containing different ratios of the reactants were mixed in the presence of 0.05 mol dm^{-3} sodium hydroxide and were equilibrated in dark for about 24 h. The residual $[\mathrm{MnO_4}^-]$ in each case was determined periodically by both titrimetric and spectrophotometric techniques. Estimation of unreacted $[\mathrm{MnO_4}^-]$ revealed that 2 ± 0.13 mol of permanganate ion consumed 1.0 mol of L-asparagine. This result confirms to the following stoichiometric equation

$$\begin{aligned} &\mathrm{H_2N-COCH_2-CH\ (NH_2)COOH + 2MnO_4^- + 2OH^-} \\ &\quad \mathrm{= H_2N-COCH_2-CHO + 2MnO_4^{2-} + NH_3 + CO_2 + H_2O.} \end{aligned} \qquad (1)$$

The above stoichiometric equation is consistent with the results of product analysis. The products were identified as the corresponding aldehyde (α-formyl acetamide) by spot test [14], intermediate manganate(VI) by its visible spectrum, ammonia by Nessler's reagent [15] and carbon dioxide by lime water. The product, α-formyl acetamide was also estimated quantitatively as its 2,4-DNP derivative [15]. Similar oxidation products have been also reported earlier [8–12].

Spectral changes

Spectral changes during the oxidation of L-asparagine by permanganate ion are shown in Fig. 1 while spectral scans during formation and decomposition of the intermediate complex are shown in Figs. 2a, b.

Fig. 1 shows a gradual disappearance of MnO_4^- band at $\lambda = 526$ nm, its absorption maximum, with a simultaneous appearance of new bands at wavelengths of 606, 434 and 351 nm. The 606 nm band corresponds to the transient manganate(VI) species which absorb in the visible region [16]. A careful examination of the spectral scans confirms the formation of such intermediate by

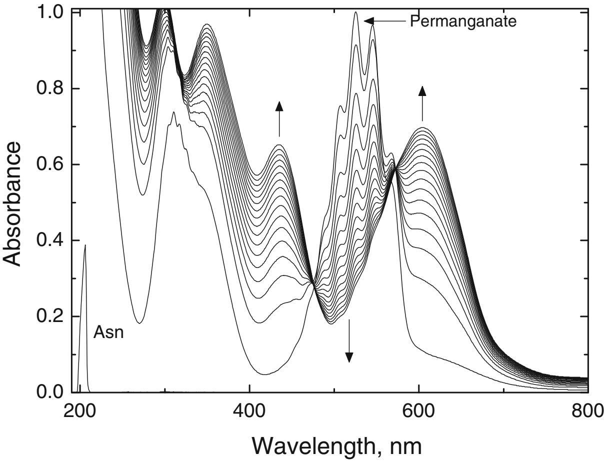


Fig. 1 Spectral changes for the oxidation of asparagine by alkaline permanganate. [Asn] $= 4 \times 10^{-3}$, $[MnO_4^-] = 4 \times 10^{-4}$ and $[OH^-] = 0.05$ mol dm^{-3}. Scanning time intervals = 4 min

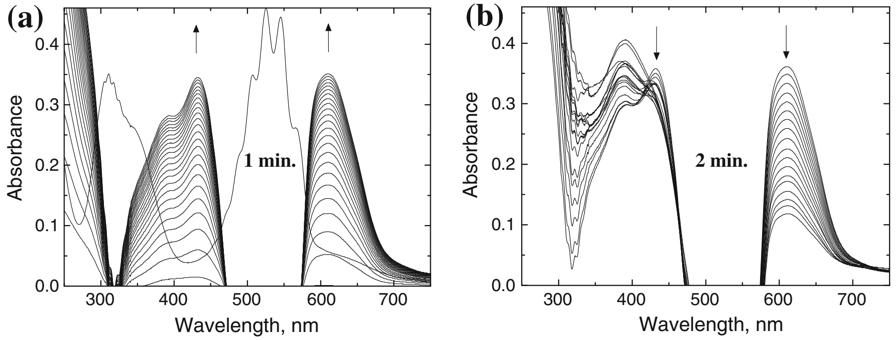


Fig. 2 Spectral changes (250–750 nm) for: **a** formation and **b** decomposition of the intermediate complex formed throughout oxidation of asparagine by alkaline permanganate. [Asn] $= 4 \times 10^{-3}$, $[MnO_4^-] = 4 \times 10^{-4}$ and $[OH^-] = 0.03$ mol dm^{-3}. Reference cell (MnO_4^- and OH^- of the same reaction mixture concentration)

the detection of the new peak located at 606 nm as shown in Fig. 2a. The appearance of two isosbestic points at $\lambda = 574$ and 474 nm suggests that an equilibrium is established between MnO_4^- and $Mn^{VI}O_4^{2-}$ [17, 18]. The formation of manganate(VI) and/or hypomanganate(V) short-lived intermediates was also confirmed by the change in the color of the solution mixture as the reaction proceeded from purple-pink (Mn^{VII}) to blue (Mn^{V}) to green (Mn^{VI}). As the reaction proceeds, a yellow turbidity slowly develops and on prolonged standing, the solution turns to colorless with a brown colloidal precipitate, $Mn^{IV}O_2$. The failure to detect the hypomanganate(V) intermediate, which was provided by absence of an absorption maximum around $\lambda = 700$ nm may be interpreted by its extreme short lifetime which undergoes a rapid disproportionation and this is autocatalytic in the presence of Mn^{IV} [19, 20]. When the concentration of the manganate(VI) intermediate builds up, a slow decay of the intermediate takes place, Fig. 2b, to give rise to the oxidation products.

Reaction-time curves

The reaction time curves which describe the double-stage time courses representing the growth and decay of the intermediate absorbance at a wavelength of 606 nm during the oxidation of L-asparagine by alkaline permanganate are illustrated in Fig. 3. These curves show that the oxidation reaction proceeds via two stages. The initial stage was found to be relatively fast involving formation of an intermediate complex, followed by a slow one corresponding to decomposition of such complex at the final stage of reaction to give rise to the oxidation products. This behavior confirms the spectral changes illustrated in Fig. 2a, b.

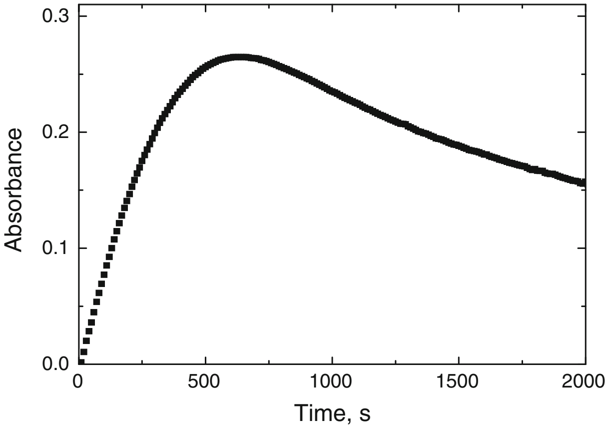


Fig. 3 Double-stage time courses representing the growth and decay of the intermediate absorbance at a wavelength of 606 nm in the oxidation of asparagine by alkaline permanganate. [Asn] = 1×10^{-2}, $[MnO_4^-] = 4 \times 10^{-4}$ and $[OH^-] = 0.03$ mol dm^{-3}

Table 1 Influence of $[MnO_4^-]$ and [Asn] on the first order rate constant in the oxidation of asparagine by alkaline permanganate. $[OH^-] = 0.05$ mol dm^{-3}

10^4 $[MnO_4^-]$ mol dm^{-3}	10^3 [Asn] mol dm^{-3}	10^5 k_{obs} s^{-1}
1.0	4.0	64.03
2.0	4.0	64.97
3.0	4.0	66.85
4.0	4.0	65.00
6.0	4.0	65.74
8.0	4.0	64.59
4.0	1.0	19.92
4.0	2.0	35.07
4.0	3.0	52.19
4.0	4.0	65.00
4.0	6.0	94.89
4.0	8.0	123.11

Experimental error ± 3 %

Order of reaction

It was observed that the first order rate constant plots (ln Abs. vs. time plots) for the formation and decomposition of the intermediate complex are linear up to about 90 % of the reaction completion. The linearity indicates that the formation and decomposition reactions are first order with respect to $[MnO_4^-]$ and intermediate concentration. The first order dependence of the formation reaction on $[MnO_4^-]$ was also confirmed by the non-variation of the observed first order rate constant (k_{obs}) at various $[MnO_4^-]_0$ ranging from 1.0×10^{-4} to 8.0×10^{-4} mol dm^{-3} while keeping others constant as listed in Table 1.

The reaction order with respect to asparagine was determined by studying the oxidation reaction at different concentrations of asparagine but at constants of $[OH^-]$, $[MnO_4^-]$, ionic strength and temperature. It was found that the rate of reaction increased with increasing the concentration of asparagine substrate as listed in Table 1. The plot of log k_{obs} against log [Asn] (figure not shown) gave a straight line with a slope of 0.83, which confirmed that the formation reaction is fractional first order with respect to the amino acid.

The influence of alkali on the rate of reaction was studied at various $[OH^-]$ keeping all other reactants concentration constant. The rate constant increased with the increase in alkali suggesting that the oxidation reaction is base-catalyzed. Plots of the observed first order rate constants of formation (k_{obs}) and decomposition (k_{dec}) of the intermediate complex versus $[OH^-]$ were found to be linear with non-zero intercepts as illustrated in Fig. 4 suggesting that such reactions are fractional first orders with respect to $[OH^-]$.

Dependence of reaction rate on ionic strength

In order to get more insight concerning the reactive species and, hence, on the mechanism of the intermediate formation, kinetic runs were performed at constant concentration of alkali, asparagine and permanganate as the $NaClO_4$ concentration

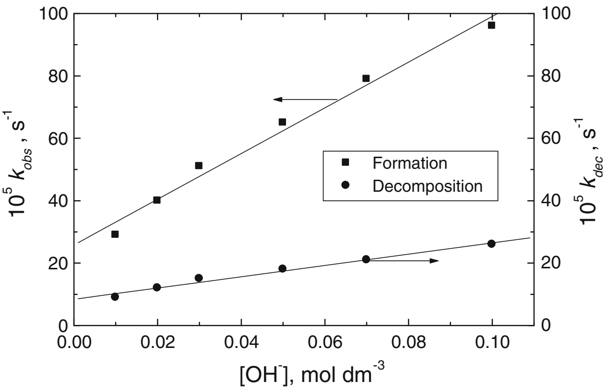


Fig. 4 Plots of first order rate constants (k_{obs} and k_{dec}) versus [OH$^-$] for the formation and decomposition of the intermediate complex in the oxidation of asparagine by alkaline permanganate. [Asn] = 4×10^{-3} and [MnO_4^-] = 4×10^{-4} mol dm^{-3}

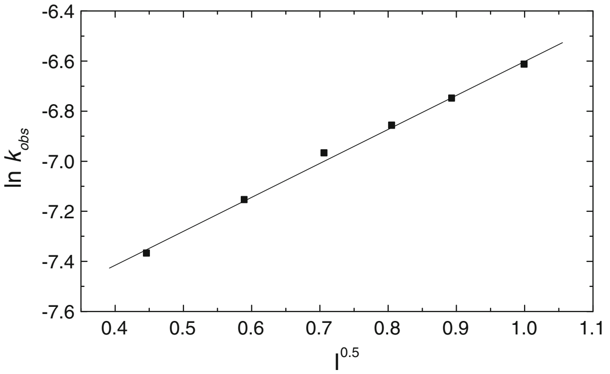


Fig. 5 Debye–Hückel plot for the oxidation of asparagine by alkaline permanganate. [Asn] = 4×10^{-3}, [MnO_4^-] = 4×10^{-4} and [OH$^-$] = 0.05 mol dm^{-3}

was increased. The Debye-Hückel plot (ln k_{obs} vs. $I^{0.5}$) was found to straight with a positive slope as shown in Fig. 5.

Effect of alkali metal ion catalysts

If the reactive species or activated complex formed are either charged or dipolar in nature, a specific influence of added metal ions on the reaction velocity may be expected, depending upon their charge, size, complexing tendency and general nature [21]. Therefore, chlorides of alkali metal ions such as Li^+, Na^+ and K^+ were added to the reaction medium at identical concentrations. The experimental observations show that the presence of such metal ions accelerates the reaction rate. The order of effectiveness of such ions is $Li^+ > Na^+ > K^+$. A plot of k_{obs} versus

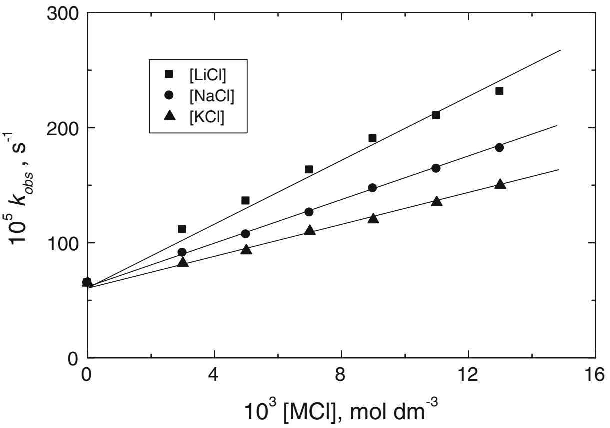


Fig. 6 Influence of alkali metal ion catalysts on the first order rate constant in the oxidation of asparagine by alkaline permanganate. [Asn] = 4×10^{-3}, [MnO_4^-] = 4×10^{-4} and [OH^-] = 0.05 mol dm^{-3}

electrolyte concentration exhibits a non-zero rate at zero electrolyte concentration as shown in Fig. 6.

Effect of temperature

To determine the activation and thermodynamic parameters, the reaction was studied at four temperatures namely 25, 30, 35 and 40 °C with varying concentrations of asparagine and alkali keeping other conditions constant. The temperature dependence was found to fit the Eyring equation.

Test for free radical intermediate

The reaction mixture, to which a known quantity of acrylonitrile scavenger had been added initially, was kept for 24 h in an inert atmosphere. On dilution with methanol, a white precipitate was formed, indicating the intervention of free radicals in the reaction. The blank experiments of either MnO_4^- or asparagine alone with acrylonitrile did not induce polymerization under the same conditions as those induce with reaction mixtures. This behavior was observed in earlier works [8–12].

Discussion

It was reported [22, 23] for permanganate ion in aqueous alkaline medium that the alkali first combines with permanganate ion to form an alkali-permanganate species $[MnO_4{\cdot}OH]^{2-}$ in a pre-equilibrium step as described by the following equilibrium

$$MnO_4^- + OH^- \overset{K_1}{\rightleftharpoons} [MnO_4 \cdot OH]^{2-} \qquad (2)$$

where K_1 is the equilibrium constant for formation of alkaline species of the oxidant.

This may be deduced from the apparent order of less than unity in OH^-. The formation of $[MnO_4{\cdot}OH]^{2-}$ species in alkaline medium further supported by the Michaelis–Menten plot ($1/k_{obs}$ vs. $1/[OH^-]$), which is linear with a positive intercept (Fig. 8).

On the other hand, amino acid in aqueous solution is known to exist as zwitterion [24], whereas in aqueous alkaline medium it exists as anion according to the following equilibria:

$$\underset{\text{Amino acid}}{RCH(NH_2)COOH} \overset{\text{Aq.}}{\rightleftharpoons} \underset{\text{Zwitterion}}{RCH(\overset{+}{N}H_3)COO^-} \overset{OH^-}{\rightleftharpoons} \underset{\text{Anionic form}}{RCH(NH_2)COO^- + H_2O}$$

Many investigators [8–11, 16, 23] suggested that most of the oxidation reactions by permanganate ion in neutral and alkaline media proceed through intermediate complex formation between oxidant and substrate. The spectral evidence for the complex formation between the oxidant and substrate obtained from UV–Vis spectra (Figs. 1 and 2), as well as obeying the [Asn] dependence of the rate constant to the Michaelis–Menten kinetics [25] for the formation of the intermediate complex ($1/k_{obs}$ vs. 1/[Asn] plot) as shown in Fig. 7, suggest the formation of an intermediate complex. On the other hand, the increasing rate of formation as the ionic strength increases refers to the fact that the formation process occurs between ions of similar charges sign [17, 26, 27].

In view of the above arguments, the following reaction mechanism may be suggested which involve attack of the active species of permanganate, $[MnO_4{\cdot}OH]^{2-}$, on asparagine leading to the formation of a complex (C) in a prior equilibrium step

$$Asn^- + [MnO_4 \cdot OH]^{2-} \overset{K_2}{\rightleftharpoons} [Asn - Mn^{VI}O_4 \cdot OH]^{3-}(C) \tag{3}$$

where K_2 is the formation constant of the complex.

This is confirmed by the two isosbestic points observed for this reaction as shown in Fig. 1 indicating the presence of an equilibrium before the slow (rate determining) step of the mechanism [24, 28]. In the complex, one electron is transferred from asparagine to permanganate ion. The cleavage of such complex leads to the formation of a free radical intermediate of asparagine and manganate(VI)

$$[Asn - Mn^{VI}O_4 \cdot OH]^{3-}(C) \xrightarrow[\text{slow}]{k_1} Asn^{\cdot} + MnO_4^{2-} + OH^- \tag{4}$$

followed by the decarboxylation of asparagine free radical forming a new radical intermediate ($X^{\cdot}$)

$$Asn^{\cdot} \xrightarrow{\text{fast}} X^{\cdot} + CO_2 \tag{5}$$

This intermediate ($X^{\cdot}$) is rapidly attacked by the active species of the oxidant to yield the final oxidation products

$$X^{\cdot} + [MnO_4 \cdot OH]^{2-} \xrightarrow{\text{fast}} \text{Aldehyde } (\alpha - \text{formyl acetamide}) + NH_3 + Mn^{VI}O_4^{2-} \tag{6}$$

According to the above-mentioned mechanism, the rate of disappearance of permanganate ion or formation of the intermediate complex can be expressed by the following rate law:

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = \frac{+d[\text{Asn} - \text{Mn}^{\text{VI}}\text{O}_4 \cdot \text{OH}^{3-}]}{dt} = k_1\left[\text{Asn} - \text{Mn}^{\text{VI}}\text{O}_4 \cdot \text{OH}^{3-}\right] \tag{7}$$

The change in the rate of complex formation with the change in substrate, hydroxyl ion and oxidant concentrations can be deduced (see Appendix 1 in Electronic Supplementary Material) to give the following equation

$$\text{Rate} = \frac{k_1K_1K_2[\text{Asn}][\text{OH}^-][\text{MnO}_4^-]}{1 + K_1[\text{OH}^-] + K_1K_2[\text{Asn}][\text{OH}^-]} \tag{8}$$

Under pseudo-first order conditions, in the presence of a large excess of substrate over MnO_4^-, the rate law can be expressed by Eq. 9:

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = k_{obs}\left[\text{MnO}_4^-\right] \tag{9}$$

After comparing and re-arranging Eqs. 8 and 9, one concludes that

$$\frac{1}{k_{obs}} = \left(\frac{1 + \text{K}_1[\text{OH}^-]}{k_1K_1K_2[\text{OH}^-]}\right)\frac{1}{[\text{Asn}]} + \frac{1}{k_1} \tag{10}$$

According to Eq. 10, the relationship between $1/k_{obs}$ and 1/[Asn] at constant $[\text{OH}^-]$ should be linear with a positive intercept on $1/k_{obs}$ axis. The experimental results satisfied this requirement, at different temperature, as shown in Fig. 7, from the intercepts of such plots values of the rate constant of the slow step (k_1) are evaluated and are listed in Table 3.

Eq. 10 can be rearranged to be

$$\frac{1}{k_{obs}} = \left(\frac{1}{k_1K_1K_2[\text{Asn}]}\right)\frac{1}{[\text{OH}^-]} + \left(\frac{1}{k_1K_2}\frac{1}{[\text{Asn}]} + \frac{1}{k_1}\right) \tag{11}$$

Inspection of Eq. 11, plots of $1/k_{obs}$ against $1/[\text{OH}^-]$ at constant [Asn] should also give straight lines with positive intercepts on $1/k_{obs}$ axes as was experimentally observed, Fig. 8. Values of the first and second equilibrium constants, K_1 and K_2 at different temperatures could be calculated from the slopes and intercepts of Fig. 8 (and the obtained k_1 values) and are also listed in Table 2. The values of K_1 are in a good agreement with those reported in earlier works [8, 29].

The activation parameters of the rate constant of the slow step (k_1) are calculated using Eyring plot (Fig. 9) and Arrhenius plot (figure not shown) as given in Table 3. Furthermore, thermodynamic parameters of the equilibrium constants, K_1 and K_2, are calculated using van't Hoff's plot and are also listed in Table 3.

From Table 3, the observed large negative value of $\Delta S^{\neq}$ indicates interaction of reacting ions of similar charges to form compacted intermediate complex and such activated complex is more ordered than the reactants due to loss of degree of freedom. This is also supported by very small frequency factor A [30]. The experimental values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were both favorable for an electron transfer

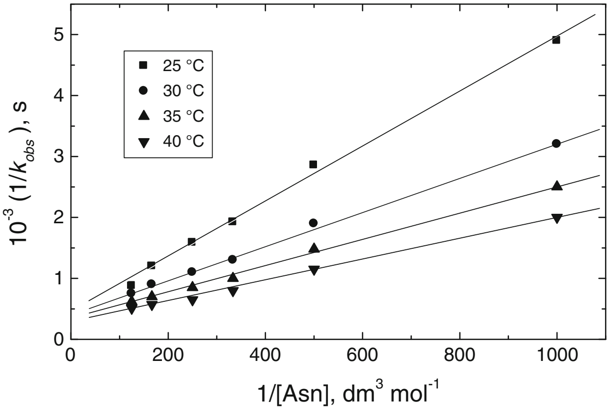


Fig. 7 1/k_{obs} versus 1/[Asn] plots in the oxidation of asparagine by alkaline permanganate at different temperatures. [MnO_4^-] = 4 × 10^{-4} and [OH^-] = 0.05 mol dm^{-3}

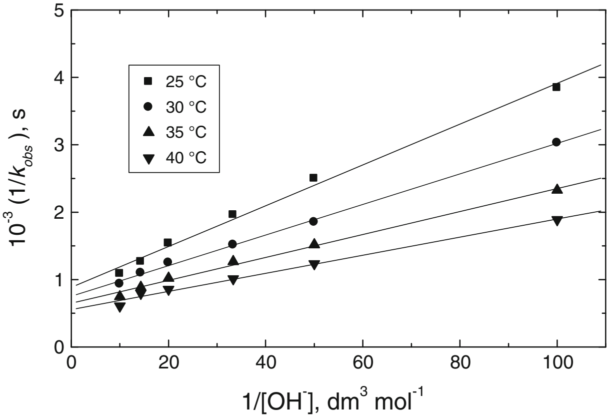


Fig. 8 1/k_{obs} versus 1/[OH^-] plots for in the oxidation of asparagine by alkaline permanganate at different temperatures. [Asn] = 4 × 10^{-3} and [MnO_4^-] = 4 × 10^{-4} mol dm^{-3}

process. Again, the positive values of both ΔH$^{\neq}$ and ΔG$^{\neq}$ indicate the endothermic formation of the intermediate and its non-spontaneity, respectively. This evidence accords with the suggested transition states which may confirm formation of an intermediate complex via inner-sphere electron transfer mechanism. This mechanism is supported by the proposition made by Stewart [26, 27] for ionic transition states in oxidation of many organic substrates by permanganate ion. They reported that the entropy of activation tends to be more positive for reactions of outer-sphere mechanisms, whereas it is more negative for reactions of inner-sphere type. Therefore, such agreement may be considered as evidence to support formation of an intermediate complex of inner-sphere nature for electron transfer mechanism with respect to the present redox reaction. The activation parameters for the

Table 2 Values of rate constant of the slow step (k_1) and the equilibrium constants (K_1 and K_2) in the oxidation of asparagine by alkaline permanganate at different temperatures

Constant	Temperature (°C)			
	25	30	35	40
$10^3\ k_1$, s^{-1}	2.34	2.51	2.86	3.37
K_1, $dm^3\ mol^{-1}$	14.23	15.46	17.99	19.18
K_2, $dm^3\ mol^{-1}$	231.12	259.31	278.95	288.54

Experimental error ± 4 %

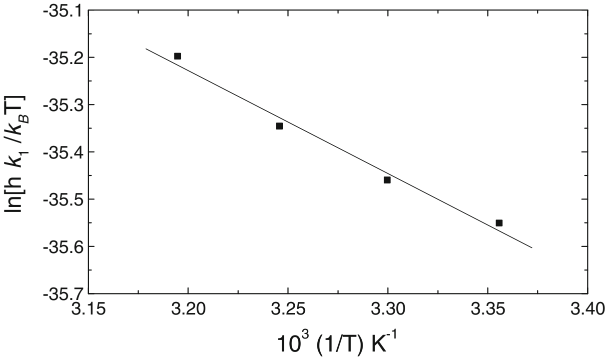


Fig. 9 Eyring plot for the rate constant of the slow step (k_1) in the oxidation of asparagine by alkaline permanganate. [Asn] = 4 × 10^{-3}, [MnO_4^-] = 4 × 10^{-4} [OH^-] = 0.05 and I = 0.2 mol dm^{-3}

oxidation reactions of some amino acids with alkaline permanganate having negative entropies of activation are summarized in Table 4. Leffler and Grunwald [31] have pointed out that many reactions show an isokinetic relationship, $\Delta H^{\neq} = \alpha + \beta\Delta S^{\neq}$, where β is called isokinetic temperature.

It has been asserted that apparently linear correlation of $\Delta H^{\neq}$ with $\Delta S^{\neq}$ are sometimes misleading and the evaluation of β by means of the above equation lacks statistical validity [32]. An alternative method have advocated by Exner [33] for the treatment of experimental data. If the rates of several reactions in a series have been measured at two temperatures and log k_1 (at T_2) is linearly related to log k_1 (at T_1) according to the following equation

$$\log k_{1\ (\mathrm{at\,T2})} = a + b\log k_{1\ (\mathrm{at\,T1})}, \tag{12}$$

then β can be evaluated from the equation

$$\beta\ =\ \mathrm{T_1T_2}(b-1)\,/\,(\mathrm{T_2}b-\ \mathrm{T_1}) \tag{13}$$

According to Eq. 12 a plot of log k_1 at 303 K versus log k_1 at 298 K for a series of amino acids was found to be linear with a slope of $b = 1.2$ as shown in Fig. 10. Replacement of the b value in Eq. 13 provided us a way to calculate β, where β = 275.4 K. The latter value (275.4 K) is smaller than the experimental temperature (298 K) suggesting that the oxidation rate is governed by the enthalpy of activation [34]. The value of β is supported by that obtained from the relationship between the

Table 3 Activation parameters of the rate constant of the slow step (k_1) and thermodynamic parameters of the equilibrium constants; K_1 and K_2 in the oxidation of asparagine by alkaline permanganate

Rate const.	Parameter					Eq. const.	Parameter		
	$\Delta S^{\neq}$ J mol^{-1}K^{-1}	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta G^{\neq}$ kJ mol^{-1}	$E_a^{\neq}$ kJ mol^{-1}	A mol^{-1} s^{-1}		ΔH^o kJ mol^{-1}	$\Delta G^o_{298\ \mathrm{K}}$ kJ mol^{-1}	ΔS^o J mol^{-1}K^{-1}
k_1	−68.5 ± 2.1	27.3 ± 0.6	47.7 ± 1.2	20.9 ± 0.8	10.1 ± 0.3	K_1	16.20 ± 0.5	−6.57 ± 0.1	76.41 ± 2.0
						K_2	12.10 ± 0.4	−13.48 ± 0.1	85.84 ± 1.7

Table 4 Kinetic parameters for the intermediate formation in the oxidation of some amino acids by alkaline permanganate

Amino acid	$10^2\ k_1$, s^{-1} at 298 K	$10^2\ k_{2,}$ s^{-1} at 303 K	$\Delta S^{\neq}$ J $mol^{-1}K^{-1}$	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta G^{\neq}_{298\ K}$ kJ mol^{-1}	Reference
R-Serine	10.00	28.00	−28 ± 2.4	49 ± 1	58 ± 3	[10]
L-Arginine	5.38	8.00	−31.1	29.4	33.4	[11]
Glutamic acid	4.00	6.13	−86 ± 4	45 ± 2.5	70.6 ± 1	[8]
L-Leucine	1.53	1.96	−62.0	30.7	49.2	[9]
L-Isoleucine	1.10	1.39	−71.0	28.8	49.3	[9]
L-Histidine	0.27	0.34	−49.7 ± 2.2	26.5 ± 1.3	41.5 ± 2	[8]
L-Asparagine	0.23	0.25	−68.5 ± 2.1	27.3 ± 0.6	47.7 ± 1.2	This work

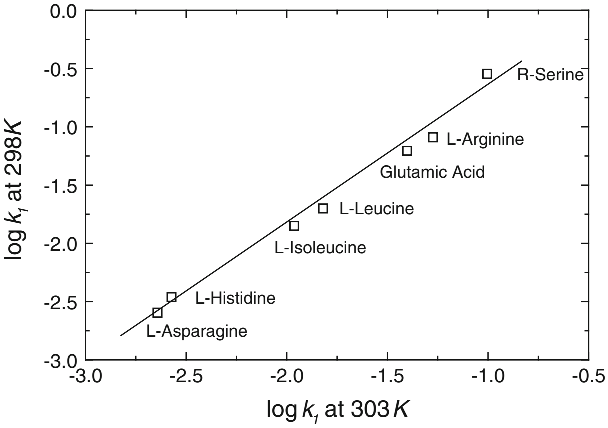


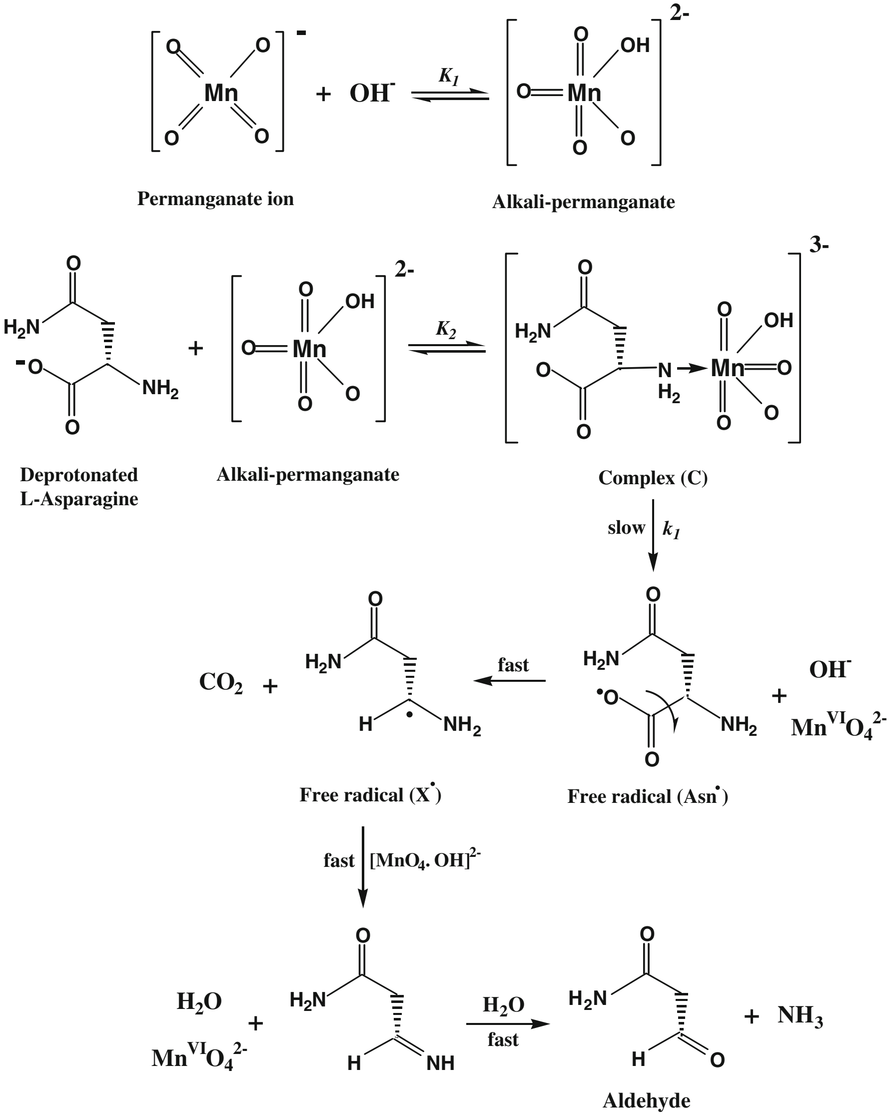
Fig. 10 Isokinetic plot for oxidation of some amino acids by alkaline permanganate

standard errors of the activation enthalpy and activation entropy: their ratio (285.6 K) gave the average temperature of the experiments [35]. The linearity and the slope of the plot obtained may confirm that the kinetics of these reactions follow similar reaction mechanism, free radical intervention, as shown in Scheme 1.

Inspection of the effect of alkali metal ion catalysts, a critical literature survey on salt effect shows that a generalized theory of the influence of salts in reaction velocity is not yet available. Many authors [36, 37] have interpreted specific effects of metal cations in terms of bridging which facilitates electron transfer in redox systems, while Wahl [38, 39] and his co-workers have interpreted specific effects in terms of complex formation. It was found that metal complexes can be more active than the free ligands, i.e. asparagine, and can exhibit bioactivities which are not shown by the free ligands.

Base-catalyzed decomposition of the intermediate complex

The observed base-catalytic behavior of the intermediate decomposition based on dependence of the rate of intermediate decomposition (k_{dec}) on [OH^-], Fig. 4,



Scheme 1 Mechanism of formation and decomposition of the intermediate complex in the oxidation of L-asparagine by alkaline permanganate

suggests that mechanism of intermediate decomposition can be visualized by a fast deprotonation of the intermediate prior to the transfer of electrons from amino acid to manganate(VI) in the rate-determining step as follows

$$\left[\mathrm{Asn}-\mathrm{Mn}^{\mathrm{VI}}\mathrm{O}_4\cdot\mathrm{OH}\right]^{3-}+\mathrm{OH}^- \overset{K_3}{\rightleftharpoons} \left[\mathrm{Asn}-\mathrm{Mn}^{\mathrm{VI}}\mathrm{O}_4\cdot\ \mathrm{OH}\right]^{4-}+\mathrm{H_2O} \qquad (14)$$

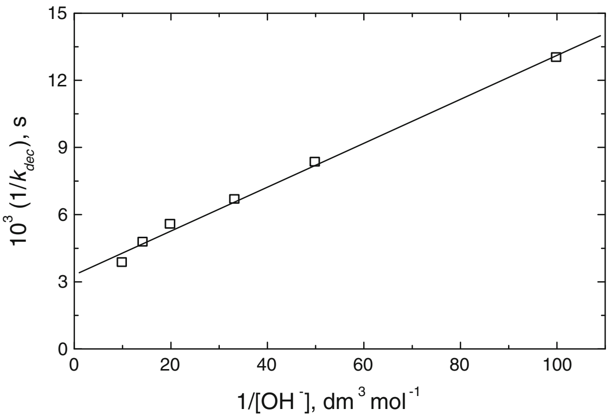


Fig. 11 $1/k_{dec}$ versus $1/[OH^-]$ plot for the decomposition of the intermediate complex in the oxidation of asparagine by alkaline permanganate. $[Asn] = 4 \times 10^{-3}$ and $[MnO_4^-] = 4 \times 10^{-4}$ mol dm^{-3}

$$\left[\mathrm{Asn} - \mathrm{Mn^{VI}O_4 \cdot OH}\right]^{4-} \xrightarrow[\text{slow}]{k_2} \text{products} \tag{15}$$

where K_3 is the dissociation constant of the intermediate.

The change of the rate of intermediate decomposition with the change in pH and intermediate concentration can be given by the rate law (16) (see Appendix 2 in Electronic Supplementary Material)

$$\text{Rate} = \frac{k_2 K_3 [\mathrm{Asn} - \mathrm{Mn^{VI}O_4 \cdot OH^{3-}}]_T [\mathrm{OH^-}]}{1 + K_3 [\mathrm{OH^-}]} \tag{16}$$

The rate of decomposition of the intermediate complex can be described by the following rate law:

$$\text{Rate} = \frac{-d[\mathrm{Asn} - \mathrm{Mn^{VI}O_4 \cdot OH^{3-}}]}{dt} = k_{dec}\left[\mathrm{Asn} - \mathrm{Mn^{VI}O_4 \cdot OH^{3-}}\right] \tag{17}$$

where k_{dec} is the decomposition rate constant.

Comparing Eqs. 16 and 17 and rearrangement yield

$$\frac{1}{k_{\mathrm{dec}}} = \frac{1}{k_2 K_3} \frac{1}{[\mathrm{OH^-}]} + \frac{1}{k_2} \tag{18}$$

Eq. 18 requires that a plot of $1/k_{dec}$ versus $1/[OH^-]$ to be linear with a positive intercept on $1/k_{dec}$ axis as is experimentally obtained (Fig. 11). The values of k_2 and K_3 can be determined from the slope and intercept of such plot at 25 °C as 30×10^{-5} s^{-1} and 33.74 dm^3 mol^{-1}, respectively.

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