Research Article

Kinetics and Mechanism of Electron Transfer to Heptavalent Manganese by *DL*-Aspartic Acid in Alkaline Aqueous and Micellar Media

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The kinetics and mechanism of the electron transfer of *DL*-Aspartic acid (Asp) by Mn(VII) in alkaline medium has been studied spectrophotometrically over the range $2.0 \leq 10^3[\text{Asp}] \leq 5.0 \text{ mol dm}^{-3}$; $0.01 \leq [\text{OH}^-] \leq 0.05 \text{ mol dm}^{-3}$; $298 \leq T \leq 318 \text{ K}$ and $I = 0.05 \text{ mol dm}^{-3}$ (KNO_3). The reaction exhibits first-order dependence in $[\text{MnO}_4^-]_T$ but shows fractional-order dependence in both $[\text{Asp}]_T$ and $[\text{OH}^-]_T$. The reaction was studied in the presence of sodium dodecyl sulfate (SDS); an increase in the rate with the increase in the micellar concentration was observed. The products were characterized by spectral analysis. A mechanism involving free radicals is proposed. Asp binds MnO_4^- to form a complex that subsequently decomposes to products. Activation parameters $\Delta H^\ddagger$ (kJ mol^{-1}) and $\Delta S^\ddagger$ ($\text{J K}^{-1} \text{ mol}^{-1}$) for the reaction are 5.62 ± 0.35 and -227.65 ± 1.1 , respectively. The negative value of $\Delta S^\ddagger$ indicates that oxidation occurs via inner sphere mechanism.

1. Introduction

Study of oxidation of amino acids has received considerable attention due to the importance of degradation of these compounds in biological systems. The Aspartic acid is a nonessential amino acid which is found abundantly in plant proteins especially in sprouting seeds. This can be manufactured in the body from oxaloacetic acid. It is of paramount importance in the metabolism during construction of amino acids and biochemicals in the citric acid cycle [1]. Among the biochemicals that are synthesized from aspartic acid are asparagine, arginine, lysine, methionine, threonine, isoleucine, and several nucleotides.

Although the kinetics of oxidation of aspartic acid has been studied using different oxidants [2–9], the current work is an attempt to understand the redox chemistry of permanganate oxidation in alkaline media as well as in micellar media and to derive a plausible mechanism.

2. Experimental

All chemicals used were of reagent grade. Double distilled water was used throughout the work. Stock solution of *DL*-Aspartic acid (SRL Chemicals) was prepared by dissolving the appropriate amount of the sample in double distilled water. The stock solution of KMnO_4 (Merck) was prepared by using double distilled water and was stored in a dark place. It was standardized against oxalic acid by following the literature method [10]. NaOH and KNO_3 were used to maintain the required alkalinity and ionic strength, respectively. The solution of sodium dodecyl sulfate was prepared by dissolving calculated amount of SDS (Merck) in double distilled water.

During kinetic investigation, the pH was maintained using a SYSTRONICS μ pH system-361 equipped with a combination of glass $\text{Ag}/\text{AgCl}/\text{Cl}^-$ (3 M NaCl) electrode. It was calibrated with standard buffers of pH 4.0, 7.0, and 9.0.

(Merck). Absorbance was recorded with a Cecil CE-7200 UV-visible spectrophotometer equipped with a CE-2024 thermo-electric controller. Ten-millimeter quartz Suprasil cuvettes were used. IR spectra were taken in Varian FTIR spectrophotometer (USA).

3. Kinetic Measurements

The oxidation of *DL*-Aspartic acid by KMnO_4 was followed under pseudo-first-order conditions where *DL*-Aspartic acid was taken excess over MnO_4^- at $25^\circ\text{C} \pm 0.1^\circ\text{C}$. The reaction was initiated by mixing the required quantities of previously thermostated solutions of MnO_4^- and *DL*-Aspartic acid, which also contained definite quantities of NaOH and KNO_3 to maintain required ionic strength. The progress of the reaction was followed by measuring the decrease in absorbance at 525 nm with time using a conventional mixing technique. A_∞ was measured after the completion of the reaction (approximately after 24 hours of mixing) when the absorbance became almost constant. The plot of $\ln(A_t - A_\infty)$ versus t was found to be linear as indicated in the following equation:

$$\ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - k_{\text{obs}}t, \quad (1)$$

where A_t and A_∞ are absorbance of the reaction mixture at time, t , and at equilibrium, respectively. The correlation coefficients (R^2) of the plots used to determine k_{obs} were found to be 0.99. The pseudo-first-order rate constant (k_{obs}) was calculated by the least squares method from the above relationship. The redox reactions were followed for about 3 half lives. The reported rate data represented as an average duplicate runs were reproducible to within $\pm 3\%$.

4. Results

The electron transfer reaction between *DL*-Aspartic acid and alkaline Mn(VII) has been studied over the range $2.0 \leq 10^3[\text{Asp}] \leq 5.0 \text{ mol dm}^{-3}$; $0.01 \leq [\text{OH}^-] \leq 0.05 \text{ mol dm}^{-3}$; $298 \leq T \leq 318 \text{ K}$ and $I = 0.05 \text{ mol dm}^{-3}$ (KNO_3).

The reaction orders were determined using the slopes of $\log k_{\text{obs}}$ versus $\log[\text{MnO}_4^-]$ plots by varying the concentration of the reductant and OH^- while keeping other factors constant. With fixed concentrations of *DL*-Aspartic acid $1.0 \times 10^{-2} \text{ mol dm}^{-3}$, and alkali, $5.0 \times 10^{-2} \text{ mol dm}^{-3}$ at constant ionic strength, 0.05 mol dm^{-3} , the permanganate concentration varied from $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ to $3.0 \times 10^{-4} \text{ mol dm}^{-3}$. The linearity of plots of $\log(\text{absorbance})$ versus time, for different concentrations of permanganate, indicates that the order in $[\text{Mn(VII)}]$ is unity (Figure 1). The *DL*-Aspartic acid concentration was varied in the range of 2.0×10^{-3} to $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ at constant alkali and permanganate concentrations and constant ionic strength of 0.05 mol dm^{-3} at 298 K . The k_{obs} values increased with an increase in *DL*-Aspartic acid over the concentration range shown in Figure 3. At low concentration of *DL*-Aspartic acid, the reaction was of first order and at high concentration of *DL*-Aspartic acid, the reaction was independent of *DL*-Aspartic acid.

FIGURE 1: First-order plots of the oxidation of Aspartic acid by permanganate in aqueous alkaline medium. $[\text{Asp}] = 2 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{OH}^-] = 0.02 \text{ mol dm}^{-3}$, $I = 0.05 \text{ mol dm}^{-3}$. $10^4[\text{MnO}_4^-] \text{ mol dm}^{-3}$, $A = 2.5$, $B = 3.0$, $C = 2.5$, $D = 1.5$, and $E = 1.0$.

4.1. Effect of Alkali Concentration. The effect of alkali concentration on the reaction was studied at constant ionic strength of 0.05 mol dm^{-3} at 25°C . The $[\text{OH}^-]$ was varied in the range of 0.01 to 0.05 mol dm^{-3} . The rate constant increased with an increase in alkali concentration (Figure 4), indicating a fractional-order dependence of the rate on alkali concentration.

4.2. Effect of Ionic Strength. The effect of ionic strength was studied by varying the potassium nitrate concentration from 0.05 to 0.5 mol dm^{-3} at constant concentration of permanganate, *DL*-Aspartic acid, and alkali. Increasing ionic strength had no effect on the rate constant.

4.3. Effect of Temperature. The kinetics was also studied at five different temperatures with varying concentrations of *DL*-Aspartic acid and alkali, keeping other conditions constant. The rate constants were found to increase with the increase in temperature. The rate of the slow step was obtained from the slopes and intercepts of $1/k_{\text{obs}}$ versus $1/[\text{DL-Aspartic acid}]$ and $1/k_{\text{obs}}$ versus $1/[\text{OH}^-]$ plots at five different temperatures (298 – 318 K).

4.4. Test for Free Radical. To test for the involvement of free radicals, acrylonitrile was added to the reaction mixture, which was then kept for 24 h under nitrogen atmosphere. Addition of methanol, resulted in the precipitation of a polymer, suggesting the involvement of free radicals in the reaction. However, the blank experiments with reactants in presence of acrylonitrile did not respond to positive test for free radical formation. Initially added acrylonitrile decreased the rate of reaction [11].

4.5. Effect of Ionic Surfactants. It is well established that most of the micellar reactions involving an ionic or neutral

reactants are believed to take place either inside the stern layer or at interface between the micellar surface and bulk solvent water [12, 13]. The effect of the ionic and nonionic micelles on the reaction rates of bimolecular reactions is due to the association through electrostatic/hydrophobic and hydrogen bonding interactions between the reactants within a small volume of the self-assemblies [14]. During the study, the concentration of sodium dodecyl sulfate (SDS) varied keeping the concentrations of *DL*-Aspartic acid, MnO_4^- , temperature and ionic strength constant (Table 3). With the increase in the concentration of SDS, the rate tends to attend a limiting value at high surfactant concentration indicating a micellar binding of the substrate. The equilibrium constant values for the formation of complex (C) with permanganate for *DL*-Aspartic acid and cysteine are comparable indicating equal probability of formation of the complex.

4.6. Stoichiometry and Product Analysis. The reaction between *DL*-Aspartic acid and MnO_4^- in alkaline medium has a stoichiometry of 1:4. The main reaction product is 3-oxopropanoic acid. It was treated with 2,4-DNP and kept in refrigerator for 24 hours, a yellow solid was separated and recrystallized with ethanol. It was characterized by FT-IR. The FT-IR spectra of *DL*-Aspartic acid and its product complex are similar. The C=N stretching band appears at 1619 cm^{-1} which is absent in *DL*-Aspartic acid. The other significant bands appear at 1411 cm^{-1} (for symmetric carboxylate stretching) 1520 cm^{-1} (N-H bending). The other reaction products are identified as ammonia (Nessler's reagent test), CO_2 (lime water test), and manganate (MnO_4^{2-}).

5. Discussion

Under the experimental conditions at $\text{pH} > 12$, the reduction product of Mn(VII), that is, Mn(VI), is stable, and no further reduction is initially observed [15]. During this reaction, color changes from violet Mn(VII) to dark green Mn(VI) through blue Mn(IV). It is clear from Figure 2 that the absorbance of MnO_4^- decreases at 525 nm, while increases at 630 and 430 nm are due to Mn(VI). As the reaction proceeds, a yellow turbidity slowly develops, and after keeping for a long time the solution decolorizes and forms a brown precipitate. This suggests that the initial products might have undergone further oxidation resulting in a lower oxidation state of manganese. It appears that the alkali combines with permanganate to give $[\text{MnO}_4 \cdot \text{OH}]^{2-}$ [16, 17]. In the second step, $[\text{MnO}_4 \cdot \text{OH}]^{2-}$ combines with *DL*-Aspartic to form an intermediate complex. The variable order with respect to *DL*-Aspartic is most probably due to the complex formation between oxidant and *DL*-Aspartic prior to the slow step. A plot of $1/k_{\text{obs}}$ versus $1/[\text{Asp}]$ (Figure 3) shows an intercept in agreement with complex formation. Further evidence for complex formation was obtained from the UV-vis spectra of reaction mixture. Two isosbestic point were observed for this reaction (Figure 2), indicating the presence of an equilibrium before the slow step of the mechanism [18, 19].

FIGURE 2: Spectral changes during the oxidation of *DL*-Aspartic acid by permanganate in alkaline medium at 303 K: $10^4[\text{MnO}_4^-] = 2.0\text{ mol dm}^{-3}$, $10^3[\text{Asp}] = 2.0\text{ mol dm}^{-3}$, and $10^2[\text{OH}^-] = 1.0\text{ mol dm}^{-3}$ and $I = 0.05\text{ mol dm}^{-3}$. 1: mixture immediately after mixing; 2, 3, 4, 5, and 6 after 5 min, 10 min, 15 min, 20 min, and 25 min, respectively.

In our proposed mechanism, in the complex one electron is transferred from aspartic acid to Mn(VII). The cleavage of this complex (C) is assigned as the slowest step, leading to the formation of an *DL*-Aspartic radical intermediate and Mn(VI). The radical intermediate reacts with another Mn(VII) species, $[\text{MnO}_4 \cdot \text{OH}]^{2-}$, to give the final products: Mn(VI), 3-oxopropanoic acid and NH_3 (Scheme 1). The effect of the ionic strength and dielectric constant on the rate is consistent with the involvement of a neutral molecule in the reaction. The suggested structure of complex (C) is given in Scheme 1.

From Scheme 1, the rate law can be derived as follows:

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = kK_1K_2[\text{MnO}_4^-]_f[\text{Asp}]_f[\text{OH}^-]_f \quad (2)$$

The total $[\text{MnO}_4^-]$ can be written as

$$\begin{aligned} [\text{MnO}_4^-]_t &= [\text{MnO}_4^-]_f \\ &\times (1 + K_1[\text{OH}^-] + K_1K_2[\text{Asp}][\text{OH}^-]), \\ [\text{MnO}_4^-]_f &= \frac{[\text{MnO}_4^-]_t}{1 + K_1[\text{OH}^-] + K_1K_2[\text{Asp}][\text{OH}^-]}, \end{aligned} \quad (3)$$

TABLE 1: Effect of $[DL\text{-Aspartic acid}]$, $[MnO_4^-]$, and $[OH^-]$ on the oxidation of $DL\text{-Aspartic acid}$ by permanganate in aqueous alkaline medium at 298 K. $[MnO_4^-] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$ and $I = 0.05 \text{ mol dm}^{-3}$.

$[OH^-]$ (mol dm ⁻³)	$10^2 [DL\text{-Aspartic acid}]$ (mol dm ⁻³)	$10^3 k_{\text{obs}}$ (s ⁻¹)	R^2
0.01	0.2	0.13	0.99
0.01	0.3	0.18	0.98
0.01	0.4	0.24	0.98
0.01	0.5	0.29	0.97
0.02	0.2	0.25	0.99
0.02	0.3	0.31	0.98
0.02	0.4	0.38	0.99
0.02	0.5	0.44	0.97
0.03	0.2	0.35	0.98
0.03	0.3	0.42	0.98
0.03	0.4	0.47	0.99
0.03	0.5	0.54	0.99
0.04	0.2	0.44	0.97
0.04	0.3	0.50	0.99
0.04	0.4	0.56	0.98
0.04	0.5	0.63	0.98
0.05	0.2	0.53	0.99
0.05	0.3	0.60	0.99
0.05	0.4	0.67	0.97
0.05	0.5	0.76	0.98

TABLE 2: Activation and thermodynamic parameters for the oxidation of $DL\text{-Aspartic acid}$ by alkaline $KMnO_4$ with respect to the slow step of the reaction (Scheme 1).

Effect of temperature with respect to the slow step of Scheme 1 [OH [−]] = 0.01 mol dm ^{−3} , [Asp] = 0.004 mol dm ^{−3}		
Temperature (K)	10 ³ <i>k</i> (s ^{−1})	<i>R</i> ²
298	0.24	0.99
303	0.29	0.99
308	0.34	0.99
313	0.39	0.98
318	0.44	0.99
Activation parameters	Value	
<i>E</i> _a (kJ mol ^{−1})	23.8	
Δ <i>H</i> [#] (kJ mol ^{−1})	5.6 ± 0.3	
Δ <i>S</i> [#] (JK ^{−1} mol ^{−1})	−227.6 ± 1.1	
Δ <i>G</i> [#] (kJ mol ^{−1}) (298 K)	73.4	
Effect of temperature on equilibrium constants <i>K</i> ₁ and <i>K</i> ₂		
<i>T</i> (K)	10 ^{−2} <i>K</i> ₁ (dm ³ mol ^{−1})	10 ^{−3} <i>K</i> ₂ (dm ³ mol ^{−1})
298	1.3	1071.0
303	0.7	1139.5
308	3.2	978.9
313	11.1	955.7
318	20.2	891.1

where “ t ” and “ f ” stand for “total” and “free”, respectively. Similarly, total $[OH^-]$ can be calculated as

$$[OH^-]_t = [OH^-]_f + [MnO_4 \cdot OH]^{2-} + [\text{Complex C}], \quad (4)$$

$$[OH^-]_f = \frac{[OH^-]_t}{1 + K_1 [MnO_4^-] + K_1 K_2 [Asp] [MnO_4^-]}.$$

In view of the low concentration of MnO_4^- and $DL\text{-Aspartic acid}$ used in the experiment, in (3), the terms $K_1 [MnO_4^-]$ and $K_1 K_2 [Asp] [MnO_4^-]$ can be neglected.

Thus,

$$[OH^-]_f = [OH^-]_t. \quad (5)$$

TABLE 3: Effect of SDS on the oxidation of *DL*-Aspartic acid by permanganate in aqueous alkaline medium at 298 K, $[\text{MnO}_4^-] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{DL-Aspartic acid}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{OH}^-] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$, and $I = 0.05 \text{ mol dm}^{-3}$.

[SDS] (mol dm^{-3})	$10^4 k_{\text{obs}} (\text{s}^{-1})$
0.000	10.2
0.005	13.8
0.010	16.4
0.015	17.6
0.020	18.5
0.025	19.4
0.030	20.4
0.035	21.1
0.040	21.5

FIGURE 3: Plots of $1/k_{\text{obs}}$ versus $1/[\text{Asp}]$ at five different temperatures. $10^2 [\text{OH}^-]_T = 1.0 \text{ mol dm}^{-3}$, $10^4 [\text{MnO}_4^-]_T = 2.0 \text{ mol dm}^{-3}$, and $I = 0.05 \text{ mol dm}^{-3}$. $10^3 [\text{Asp}]_T$ varied from 2.0 to 5.0 mol dm^{-3} .

Similarly,

$$[\text{Asp}]_f = [\text{Asp}]_t. \quad (6)$$

Substituting (3), (5), and (6) in (2), we get

$$[\text{MnO}_4^-]_f = \frac{1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{Asp}] [\text{OH}^-]}{1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{Asp}] [\text{OH}^-]}, \quad (7)$$

$$\frac{\text{Rate}}{[\text{MnO}_4^-]} = k_{\text{obs}} = \frac{k K_1 K_2 [\text{Asp}] [\text{OH}^-]}{1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{Asp}] [\text{OH}^-]}. \quad (8)$$

Equation (8) is consistent with the observed orders with respect to different species, which can be verified by rearranging to (9)

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k K_1 K_2 [\text{Asp}] [\text{OH}^-]} + \frac{1}{k K_2 [\text{Asp}]} + \frac{1}{k}. \quad (9)$$

FIGURE 4: Plots of $1/k_{\text{obs}}$ versus $1/[\text{OH}^-]$ at five different temperatures. $10^3 [\text{Asp}]_T = 2.0 \text{ mol dm}^{-3}$, $10^4 [\text{MnO}_4^-]_T = 2.0 \text{ mol dm}^{-3}$, and $I = 0.05 \text{ mol dm}^{-3}$. $10^2 [\text{OH}^-]_T$ varied from 2.0 to 5.0 mol dm^{-3} .

According to (9), other conditions being constant, plots of $1/k_{\text{obs}}$ versus $1/[\text{Asp}]$ and $1/k_{\text{obs}}$ versus $1/[\text{OH}^-]$ should be linear (Figures 3 and 4). The slopes and intercepts of such plots lead to values of K_1 , K_2 , and k (Table 2). With these values, the rate constants were calculated under different experimental conditions. The thermodynamic quantities for the first and second equilibrium steps of Scheme 1 can be evaluated. The $[\text{DL-Aspartic acid}]$ and $[\text{OH}^-]$ (Table 1) were varied at five different temperatures. van't Hoff's plots of $\log K_1$ versus $1/T$ and $\log K_2$ versus $1/T$ gave the values of enthalpy of reaction ΔH° , entropy of reaction ΔS° , and free energy of reaction ΔG° , calculated for the first and second equilibrium steps (Table 2). A comparison of the later values (from K_2) with those obtained for the slow step of the reaction shows that they mainly refer to the rate-limiting step, supporting the fact that the reaction before the rate-determining step is fairly fast and involves low activation energy [20, 21]. The moderate values of ΔS° were both favorable for the electron transfer processes. The values of ΔS° , that is within the expected range for radical reactions, have been ascribed to the nature of electron pairing and unpairing processes and the loss of degrees of freedom formerly available to the reaction upon the formation of a rigid transition state [22]. The negative values of ΔS° indicate that the complex (C) is more ordered than the reactants [23, 24]. The enthalpy of activation and a relatively low value of entropy and a higher rate constant of the slow step indicate that the oxidation most probably occurs via inner-sphere mechanism [25, 26].

6. Conclusion

It is noteworthy that the oxidant species MnO_4^- required the pH 12, below which the system gets disturbed and the

SCHEME 1: Proposed mechanism for the oxidation of *DL*-Aspartic acid by alkaline MnO_4^- .

reaction proceeds further to give a more reduced state of Mn, that is, Mn(IV) which slowly develops yellow turbidity. In this reaction, the role of pH is crucial. The rate constant of the slowest step and other equilibrium constants involved in the mechanism were evaluated and activation parameters were calculated. The proposed mechanism is consistent with product, mechanistic, and kinetic studies.

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