Kinetic Studies on the Mechanism of Surfactant catalysed Oxidation of Alanine by Permanganate Ion in Moderately Concentrated Acidic Media in the Light of various Effects

D. S. GAUR

School of Studies in Chemistry, Vikram University Ujjain-456 010

The kinetic investigations of oxidation of DL-alanine by potassium permanganate in the presence of anionic surfactant sodium dodecyl sulphate (NaDS) have been conducted at 303 K in moderately concentrated acidic media of sulphuric acid. The rate shows a first order dependence on each, the oxidant and the substrate. A pertinent mechanism has been suggested and discussed from various view points.

A great deal of work has been done on the oxidation of organic and inorganic compounds by permanganate ion in varieties of media under different conditions[1]. However, a survey of the literature reveals that the surfactant-catalysed oxidative decarboxylation by MnO_4^- in acidic media has not received any attention. Therefore, the oxidative decarboxylation of DL-alanine by potassium permanganate in moderately concentrated acidic media has been discussed here.

Results and Discussion

Dependence of rate on [Oxidant] and [Substrate] : When alanine is in large excess, the plots of log $(a-x)$ vs time (t) were found to be linear indicating the first order dependence of the rate on permanganate. Similarly, the linear plot between log k vs log [Alanine] indicates the first order dependence of reaction rate on substrate alanine. This has been further confirmed by plotting $1/k$ vs $1/C$ (Michaelis-Menten) plot which also gave straight-line passing through the origin. This also indicates that there was no intermediate complex formation between the oxidant, permanganate and the substrate, alanine and if it was so than its formation constant should have been negligible.

Dependence of the rate on the surfactant concentration : The reaction was studied at different concentrations of the anionic surfactant sodium dodecyl sulphate [NaDS] in the range 1×10^{-4} to 6×10^{-4} mol dm^{-3}. The plot k_{obs} vs [Surfactant] was found linear showing the catalytic effect of the surfactant in the given range over the reaction rate (Table 1). The linear plot of log $(k_\psi - k_o)/(k_m - k_\psi)$ vs log [D] with the slope value of 2.00 indicates positive co-operativity[2]. This means that the substrate promotes the micellisation of the surfactant even before or below the cmc value, where k_o is the rate of reaction without surfactant, k_m the rate with maximum amount of surfactant concentration within the given range, k_ψ the rate with any given amount of surfactant concentration within the given range and [D] is the surfactant concentration for the rate, k_ψ.

Also there are extensive evidences from other systems which show that (i) external agents can promote micellisation, (ii) some aggregation of detergent is present below cmc and (iii) these small aggregates catalyse the reaction.

TABLE 1–VARIATION OF SURFACTANT CONCENTRATION

Temp. = 303 K, [Alanine] = 0.40 M, [KMnO₄] = 1×10^{-3} M, [H₂SO₄] = 5.0 M

Sl. no.	[NaDS] $\times 10^4$ mol dm^{-3}	k $\times 10^2$ mm^{-1}
1.	0.0	1.00
2.	1.0	1.54
3.	2.0	2.06
4.	3.0	2.84
5.	4.0	3.44
6.	5.0	4.09
7.	6.0	4.50
8.	7.0	5.53

Temperature effect and activation parameters : The reaction was studied at various temperatures to evaluate the activation parameters. Arrhenius plot (log k vs $1/T$) was found linear.

Effect of change in acid concentration and acid catalysis : In general, the amino acids exist predominantly as the protonated species in the concentrated acidic media[4,5]. Increase in the acid concentration also increases the rate of oxidation of alanine (Table 2). The reaction was studied at various concentrations of sulphuric acid in the presence of the surfactant and the rate of oxidative decarboxylation of alanine was correlated with the acid concentrations and different hypotheses for the mechanism of acid catalysis were tested. The Zucker-Hammett[6] plots (log k vs $-H_o$) and (log k vs log [Acid]) were found linear. This shows that the reaction was acid-catalysed even in the presence of another catalyst, the surfactant. However, none of the plots produced the ideal slope value of unity and this leads to study the acid catalysis in the light of Bunnett's hypothesis[7] by plotting respective graphs. The linear plots were obtained between log $k + H_o$ against $-$ log a_{H_2O}, log k

$-\log$ [Acid] vs $-\log a_{H_2O}$ and $\log k - \log$ [Acid] $-$ [H_0] vs $-\log a_{H_2O}$ with slope values of -3.19, 1.71 and 9.5 respectively. Thus as the plots were found linear and looking to the respective slope values, according to Bunnett's hypothesis the water molecule should act as proton-abstracting agent in the rate-determining stage.

TABLE 2–VARIATION OF SULPHURIC ACID CONCENTRATION

Temp. = 303 K, [Alanine] = 0.40 M, [NaDS] = 6.0 $\times$ 10^{-4}mol dm^{-3}, [KMnO$_4$] = 1.0×10^{-3} M

Sl. no.	[H$_2$SO$_4$] M	$k \times 10^3$min^{-1}	$-H_0$	$-\log a_{H_2O}$
1.	3.5	2.13	1.62	0.111
2.	4.0	2.82	1.85	0.145
3.	4.5	3.64	2.06	0.176
4.	5.0	4.50	2.28	0.219

Effect of added neutral salts : If the reacting molecular species of the activated complex formed were either charged or dipolar in nature, a specific influence of the added cations and the anions on the reaction velocity may be observed depending on their charge, size, complexing tendency and general nature[5]. In order to investigate the effect of cations and anions at higher concentrations of their respective salts and in presence of the surfactant on reaction velocity, the anions of respective sodium salts and cations of sulphate salts were added. In the presence of surfactant most salts did not show any noticeable effect over the reaction rate. However, some did show their effect on the reaction rate. The pertaining results are presented in Table 3. This inconsistancy of the effect can be interpreted in the light of the structure of alanine molecule and also the properties of the Stern region of the micelle formed by NaDS molecules.
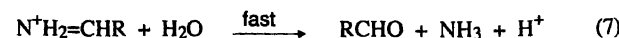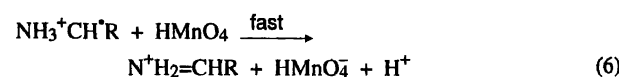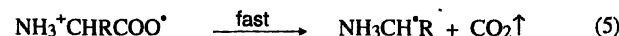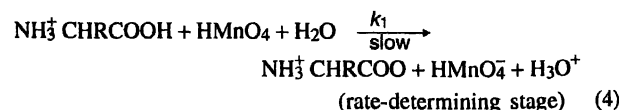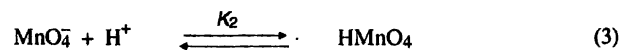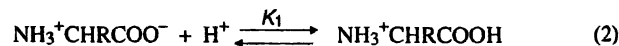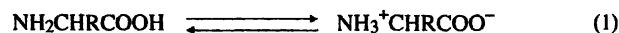
TABLE 3–EFFECT OF ADDED NEUTRAL SALT

[H$_2$SO$_4$] = 5.0 M, [Alanine] = 0.05 M, [NaDS] = 6.0 $\times$ 10^{-4} mol dm^{-3}, Temp. = 303 K, [KMnO$_4$] = 1.0×10^{-3} M

Rate constant without any added salt = 3.17×10^{-2} min^{-1}.

Sl. no.	Salt	Concn.	$k \times 10^2$
1.	MgSO$_4$	0.1	3.93
		0.2	4.55
		0.3	5.36
		0.4	6.00
2.	Na$_2$SO$_4$	0.1	3.54
		0.2	3.91
		0.3	4.15
		0.4	4.57
3.	NaOAc	0.1	2.79
		0.2	2.33
		0.3	1.93
		0.4	1.51
		0.3	2.16
4.	Al$_2$(SO$_4$)$_3$	· 0.025	5.43
		0.050	7.45
		0.075	9.43
		0.10	11.77

On the basis of the experimental results, the following probable mechanism and the rate law can be proposed. In this case the oxidative decarboxylation of DL-alanine proceeds by two paths : (i) in the absence and (ii) in the presence of the surfactant.

In the absence of the surfactant : The whole mechanism and the rate law has already been studied[5], which is as follows :

$$NH_2CHRCOOH \rightleftharpoons NH_3^+CHRCOO^- \quad (1)$$

$$NH_3^+CHRCOO^- + H^+ \xrightleftharpoons{K_1} NH_3^+CHRCOOH \quad (2)$$

$$MnO_4^- + H^+ \xrightleftharpoons{K_2} HMnO_4 \quad (3)$$

$$NH_3^+ CHRCOOH + HMnO_4 + H_2O \xrightarrow[\text{slow}]{k_1}$$
$$NH_3^+ CHRCOO + HMnO_4^- + H_3O^+$$
$$\text{(rate-determining stage)} \quad (4)$$

$$NH_3^+CHRCOO^{\bullet} \xrightarrow{\text{fast}} NH_3CH^{\bullet}R + CO_2\uparrow \quad (5)$$

$$NH_3^+CH^{\bullet}R + HMnO_4 \xrightarrow{\text{fast}}$$
$$N^+H_2=CHR + HMnO_4^- + H^+ \quad (6)$$

$$N^+H_2=CHR + H_2O \xrightarrow{\text{fast}} RCHO + NH_3 + H^+ \quad (7)$$

where, R = CH_3 for DL-alanine. From equations (1) to (7), the rate expression can be derived as follows :

From equation (2),

$$K_1 = \frac{[NH_3^+CHRCOOH]}{[NH_3^+CHRCOO^-][H^+]}$$

or [NH$_3^+$CHRCOOH] = K_1 [NH$_3^+$CHRCOO$^-$] [H$^+$] (8)

From equation (3),

$$K_2 = \frac{[HMnO_4]}{[MnO_4^-][H^+]}$$

or
$$K_2 = \frac{[HMnO_4]}{[H^+]\{[MnO_4^-] - [HMnO_4]\}} \quad (9)$$

(This is because free [MnO$_4^-$] in the solution is equal to the initial [MnO$_4^-$]-[HMnO$_4$] formed).

or [HMnO$_4$] = K_2 [H$^+$] [MnO$_4^-$] $- K_2$ [H$^+$] [HMnO$_4$]

or
$$[HMnO_4] = \frac{K_2[H^+][MnO_4^-]}{1 + K_2[H^+]} \quad (10)$$

From equation (4),

$$\frac{-d[MnO_4^-]}{dt} = k_1 [NH_3^+CHRCOOH][HMnO_4][H_2O] \quad (11)$$

Substituting the values of [NH$_3^+$CHRCOOH][HMnO$_4$] from equations (8) and (10) respectively, in the equation (11), we have,
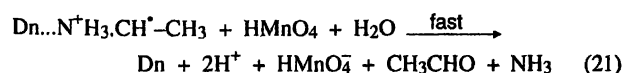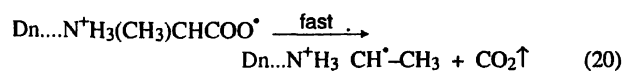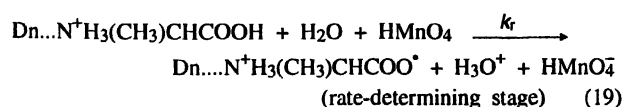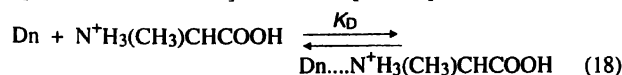
$$\frac{-d\,[MnO_4^-]}{dt} = \frac{k_1 K_1 K_2 [H^+]^2\,[H_2O]}{1 + K_2\,[H^+]}$$
$$[MnO_4^-]\,[NH_3^+CHRCOO^-] \quad (12)$$

Thus at the given concentration of acid,

$$\frac{-d\,[MnO_4]}{dt} = k\,[MnO_4^-]\,[Amino\ Acid] \quad (13)$$

with, $k = \dfrac{k_1 K_1 K_2 [H^+]^2\,[H_2O]}{1 + K_2\,[H^+]}$

In the presence of the surfactant :

$$NH_2(CH_3)CHCOOH \rightleftharpoons N^+H_3(CH_3)CHCOO^- \quad (14)$$

$$N^+H_3(CH_3)CHCOO^- + H^+ \xrightarrow{K_1} N^+H_3(CH_3)CHCOOH \quad (15)$$

$$MnO_4^- + H^+ \xrightarrow{K_2} HMnO_4 \quad (16)$$

$$nD \xrightarrow{K_s} Dn \quad (17)$$
$$[\text{Molecular surfactant}] \qquad [\text{micelle}]$$

$$Dn + N^+H_3(CH_3)CHCOOH \xrightarrow{K_D}$$
$$Dn....N^+H_3(CH_3)CHCOOH \quad (18)$$

$$Dn...N^+H_3(CH_3)CHCOOH + H_2O + HMnO_4 \xrightarrow{k_r}$$
$$Dn....N^+H_3(CH_3)CHCOO^\bullet + H_3O^+ + HMnO_4^-$$
$$\text{(rate-determining stage)} \quad (19)$$

$$Dn....N^+H_3(CH_3)CHCOO^\bullet \xrightarrow{fast}$$
$$Dn...N^+H_3\ CH^\bullet{-}CH_3 + CO_2\uparrow \quad (20)$$

$$Dn...N^+H_3.CH^\bullet{-}CH_3 + HMnO_4 + H_2O \xrightarrow{fast}$$
$$Dn + 2H^+ + HMnO_4^- + CH_3CHO + NH_3 \quad (21)$$
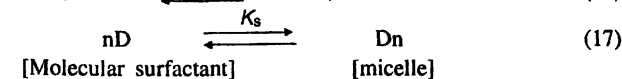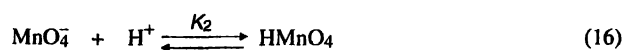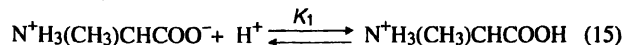
From equation (19), we have

$$\frac{-d\,[MnO_4^-]}{dt} = k_r[Dn...N^+H_3(CH_3)CHCOOH]$$
$$[H_2O][HMnO_4] \quad (22)$$

In the above equation, the values of $[HMnO_4]$ and $[Dn...N^+H_3(CH_3)CHCOOH]$ can be obtained by the application of the law of mass action to steps (16) and (18) of the mechanistic scheme after appropriate mathematical operations. Thus we have

$$\frac{-d\,[MnO_4^-]}{dt} =$$
$$\frac{k_r K_2 K_D\,[Dn]\,[N^+H_3(CH_3)CHCOOH][H_2O][H^+]\,[MnO_4^-]}{1 + K_2[H^+]} \quad (23)$$

The values of $[Dn]$ and $[N^+H_3(CH_3)CHCOOH]$ can be obtained by applying the law of mass action to steps (17) and (15) respectively. Thus the final rate expression will be

$$\frac{-d\,[MnO_4^-]}{dt} =$$
$$\frac{K_1 k_r K_2 K_D K_s\,[nD][H^+]^2[N^+H_3(CH_3)CHCOO^-][H_2O][MnO_4^-]}{1 + K_2[H^+]} \quad (24)$$

$$\frac{-d\,[MnO_4^-]}{dt} = k[N^+H_3(CH_3)CHCOO^-]\,[MnO_4^-] \quad (25)$$

$$k = \frac{k_1 k_r K_2 K_D K_s\,[nD][H^+]^2[[H_2O]}{1 + K_2[H^+]} \quad (26)$$

The above rate expression shows that the order of the reaction should be one each, with respect to the alanine and permanganate ion which is in accordance with the observed facts. Hence the scheme of the mechanism suggested above on the basis of which the rate expression has been derived is supported and therefore is valid. The presence of the term [nD] in equation (26) can be explained with the fact that in the experiments due to the adsorption or the attachment of $N^+H_3(CH_3)CHCOOH$ at the micelle surface its charge gets neutralised and thus the salt-effect and specific ionic effect are not exhibited appreciably. This observation in the highly concentrated acidic medium in the presence of surfactant leads to the mechanistic criterion regarding neutral molecule $HMnO_4$ and micelle absorbed charged species in the rate-determining stage. Linear Zucker-Hammett plots show that the reaction is acid-catalysed. Also the linear Bunnett plots show the involvement of water molecule in the rate-determining stage. The magnitudes of the activation parameters are also in conformity with the redox event in the rate-determining stages.

Experimental

All compounds used were of AnalaR grade. Requisite amounts of the solutions of subsrate, surfactant, acid and water (to maintain the total volume constant for all the runs) were taken in black painted stoppered glass bottles and thermostated at 303 K. A measured amount of permanganate solution at the same temperature was added to the reaction mixture and the progress of the reaction was followed by iodometric estimations of the aliquots taken out periodically.

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