WORLD JOURNAL OF PHARMACEUTICAL RESEARCH
SJIF Impact Factor 8.074
Volume 7, Issue 5, 1895-1907. Research Article ISSN 2277– 7105

"STUDY OF HYPOTHESIS FOR ACIDITY FUCTIONS IN MICELLER CATALYZED OXIDATIVE DEAMINATION AND DECARBOXYLATION OF L-ALANINE BY ACIDIC PERMANGANATE"

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Article Received on
22 Jan. 2018,
Revised on 12 Feb. 2018,
Accepted on 04 March 2018
DOI: 10.20959/wjpr20185-10995

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ABSTRACT

A Kinetic investigation of oxidation of L isomers of amino acids by acidic permanganate in presence of surfactant as catalyst has been carried out spectrophotometrically. The reaction is double process in which first stage is followed by second fast stage process. The rate shows a first order dependence on each oxidant and substrate. Zucker-Hammett Hypothesis and Bunnett Hypothesis and Bunnett-Olsen Hypothesis has been discussed and verified. Plots of different hypothesis were also been drawn to verified the reaction. L-Isomers of amino acids i.e., L-alanine were taken for the study.

KEYWORDS: Catalysis, Hypothesis, L-isomers, Surfactant.

INTRODUCION

Homogeneous Acid Catalysis

The present investigation is being carried in the presence of moderating concentrated acidic medium. It is case of homogeneous acid catalysis. A detailed review on the same has been covered by Verma.[1] A brief description related with the work is given here. Lewis[2] suggested that acids accept and bases donate, electron pairs with the formation of covalent bonds. Therefore acids are proton donars and bases are proton acceptors. The reaction involved in the catalysis is the transfer of proton between the catalyst and the substrate as studied by Lowery[3] and Swain et al.[4,5] It showed that catalyst not only increase the rate of reaction but also played important role in the reaction mechanism.

It shows that the substrate in a catalytic reaction must behave as an acid or a base and the reaction involved in catalysis is a typical acid-base or protolytic reaction.[6] Species like H_3O^+,NH_4^+,CH_3COOH etc acts as acid catalyst while species like OH^-,CH_3COO^-,NH_3 etc acts as base catalyst. The rate of the reaction depends upon increasing hydrogen ion concentration or concentration and strength of the acid which is displacing protons from the water. In acid catalysis there is a increase of positive ion concentration.

It has been observed that in acid base equilibria, the solvent often plays an important role. The nature and the quantity of the catalytic species present will often be affected by the nature of the solvent. In the strong acidic solution, reactions are catalysed by the hydronium ion[7] and the rate expression is given by

$$\text{Rate} = k_{H+} [H_3O^+][S] \qquad (1)$$

k_{H+} is the catalytic constant for the ions which is determined by measuring rates in acid solutions at various concentration of H_3O^+ and S.

There are two stages involved in acid catalysis in aqueous solution, first involves proton transfer to the substrate(S) and the second involves proton transfer from the protonated substrate(SH^+). The initial proton transfer can be from a hydronium ion H_3O^+ or from some other acidic species present in the solution, this species is usually represented as BH^+. In the second stage, the proton transfer from SH^+ may be to a water molecule or to some basic species B, present in the solution. The species that transfer the proton to the substrate in the initial stage is not of primary importance so far as kinetic laws are concerned. The species to which SH^+ transfers the proton in the second stage have great importance. If the transfer is to a solvent molecule i.e. if the process is,

$$SH^+ + H_2O \rightarrow S + H_3O^+ \qquad (2)$$

The mechanism is said to be protolytic one.[7(b)] If on the other hand, the proton transfer in the second stage is to a solute molecule, the mechanism is prototropic.

$$SH^+ + B \rightarrow S + BH^+ \qquad (3)$$

In the later case the catalysis is general where as in the case of a protolytic mechanism, the catalysis may be specific or general according to the circumstances.

Acidity Functions

The expression of tendency of given solution to transfer proton to a base under conditions where acid concentrations are too high, so that pH or hydrogen ion concentration loose their significance was first studied by Hammett et al.[8,9] They had reported a function called Acidity Function as;-

$$H_0 = -\log\left(\frac{a_H^+ . f_B}{f_{BH}^+}\right) \qquad (1)$$

Where a_{H+} is the total activity of the hydrogen ion in the solution.(f_B/f_{BH}^+) is the ratio of the activity coefficient of a neutral base B and its conjugate acid BH^+.

Acidity function H_0 is a property of the solvent and is independent of the base.[10] It has been also expressed as dissociation constant pk_a with the following equation ;-

$$H_0 = pk_a + \ log\frac{C_B}{C_{BH}^+} \qquad (2)$$

Where $\frac{C_B}{C_{BH}^+}$ is the ratio of the concentrations of the indicator in its basic and acidic form, which can be directly measured by spectrophotometer for a given solution. k $_{BH+}$ is the thermodynamic ionisation constant of a conjugate acid BH^+. Acidity function H_0 is given by the equation,

$$H_0 = -\log h_0 \qquad (3)$$

Where h_0 is activity of hydrogen ion or hydronium ion in dilute aqueous solution.

The H_0 is used to describe the properties of strong acid solutions but also for the investigation of the reaction mechanism.[11,15]

The acidity function predicts a linear relationship between H_0 and rate constant for those acid catalysed reactions in which activated complex differs from the reactants only by the addition of a proton.

Different acidic functions have been defined, which are related to different types of equilibrium involving indicators, a relationship between a particular acidity function and a rate constant. It has been reviewed by different researchers.[16,21]

Other acidity functions

(1) *The H_o^{III} Acidity Function*

It was quoted by Liler[21] for the deviation of tertiary aromatic amines(N,N-dimethyl-2,4,6-trinitroaniline) bases from Hammett acidity function.

(2) *The H_A Acidity Function*

It was introduced for the protonation of primary amides and it is known as an amide acidity function and designated as H_A. Here the slopes less than unity in the plots of log I Vs H_0 were found[22], where I is ionisation ratio. The values have been measured in sulphuric acid[23] and hydrochloric acid[24] for several amides.[25] The values of this acidity function coincide with H_0 values up to about 15% sulphuric acid value, than diverge from H_0 values on increase in the concentration. The function has been evaluated for up to 81.8% sulphuric acid.[23]

(3) *The H_I Acidity Function*

It has been studied for Indoles. Indoles have proved to be a class of simple bases which bring out particularly clearly the limitations of the Hammett activity coefficient postulates. The values of H_I acidity function of sulphuric acid/water mixture at 25°C were reported by Hinman and Long[24] in 1964.

(4) *The H_+ Acidity Function*

The H_+ acidity function was introduced by Brand and Horning[26,27] and measured in oleum solutions using m-nitroanilinium ion as indicator in the limited acid concentration range of 30-55%. The H_0 *and* H_+ acidity functions are identical or differ by small constant value. Vetesnik, Bievsky and Vecera[28] have used a series of substituted 1,2-Phenylen-diamines and 2,3-dimethyl quinoxalines to determine the H_+ acidity function for upto 80% sulphuric acid at 25°C.

(5) *The H_ Acidity Function*

H_ acidity scale could only be established by means of strongly acidic indicators such as cyano carbon acids.[29] The anions of these acids show strongly electronic absorbtions which disappear on protonation and so their ionisation ratio could be established by ultraviolet and visible spectrophotometry.

(6) *The H_R Acidity Function*

Deno and coworkers[30] by means of a series of eighteen substituted arylmethanols have determined H_R acidity function. It is concentration and temperature dependent at a particular range. Up to 65% acid there is no change in H_R scale with temperature, but becomes progressively more negative with increasing temperature at higher concentrations.[31]

(7) *The $H_R^{\prime}$ Acidity Function*

With the help of the equation;

$H_R^{\prime} = H_R - \log a_{H_2O}$ the value of $H_R^{\prime}$ can be determined. The functions H_R and $H_R^{\prime}$ change with the solvent composition at approximately the same rate over most of the range of the acid concentration, which means that they are equally useful in kinetic data.

Recent Advances in Acid Catalysis and Different Hypothesis

Number of reactions have been found catalysed by mineral acids. The rate of acid catalysed reactions depend upon acid concentration in different ways. Some reactions accelerate more rapidly than others as the acid concentration is increased, some pass through a rate maximum at a particular acid concentration and some go steadily slower as the acid concentration is increased.[32]

To interpret the above phenomenon and to go inside the mechanism various hypothesis were presented. Few of them as Zucker-Hammett[33], Bunnett[32] and Bunnett-Olsen[34] are most widely in use.

Zucker- Hammett Hypothesis

For the reactions catalysed by mineral acid concentration that is 1M, Hammett postulated that when log k_1 was linear with H_0, transformation of the protonated substrate (SH^+) to transition state did not involve reaction with water and that when log k_1 was linear with $\log[H^+]$ transformation of (SH^+) to transition state required a molecule of water.

Zucker Hammett Hypothesis has sharply been criticised by number of workers[35,39] as several inconsistencies were noted. One of the limitations of Zucker Hammett Hypothesis is that few reactions fit the two categories perfectly. A perfect fit would be a straight line with slope unity, when graph between log k_1 and H_0 or log$[H^+]$. When plots were linear, slopes were lesser or greater than unity. Although Zucker Hammett Hypothesis was given some theoretical justification, it was basically empirical. In these circumstances Bunnett has been given new justification after reviewing the literature.

Bunnett Hypothesis

In the case of acid catalysed reactions in mineral acids of concentration 1M and greater, for most reactions plots of (log k_1 +H_0) verses log a_{H_2O} [32(a)] are linear or approximately so. The slope in such a plot constitutes a parameter ω, It has ranged from about -8 to +9, although most of them lies between -2 and +7.

Plotting (log k_1 + H_0) verses log a_{H_2O} amounts to considering the extent to which a plot of log k_1 verses- H_0 deviates from the ideal slope of unity, as a function of log a_{H_2O}. It is an empirical fact that the deviation is linear or approximately linear with the log a_{H_2O}. If the actual plot of log k_1 verses- H_0 lies above the ideal plot of slope unity, ω is negative, if the actual plot falls below the ideal, ω is positive and if the slope is unity, ω is zero.

Reaction giving linear plots of log k_1 against log $[H^+]$ with unit slope, usually have w values of +5 or higher.

Reactions of w about +3 to +4 fall in between Zucker Hammett categories.

Some dependence of ω on the mineral acids can been seen and no greater dependence of ω on temperature is evident.[32(b)]

Classification according to ω* values

Bunnett has reported that log$[H^+]$ may be used in place of - H_0 as a measure of acidity. The plot of (log k_1- log $[H^+]$) against log a_{H_2O} is linear. The slope of this plot gives another parameter ω*, which is an alternative representation of the response of the reaction to catalysis by strong acids. Further moderately basic or strongly basic substrates the plot, $[\log k_1 - \frac{[H^+]}{h_0 + k_{SH}^{+}}]$ or (log k_1-log$[H^+]$-H_0) verses log a_{H_2O} holds good in order to define ω* values.

Reaction which give some what curved plots of (log $k_1 + H_0$) often give straight plots of (log k_1- log $[H^+]$) against log a_{H_2O}. In such cases ω* is a more precise index of the response of the reaction to catalysis by concentrated acids since it is less dependent on the range of acid concentration used, ω* is thus a valuable complementary parameter.

Interpretation of ω and ω* values

Certain values of ω and ω* parameters are associated with characteristic modes of involvement of water molecule in the rate determining step. There is a distinction between substrates which in the reaction pathways are protonated on oxygen or nitrogen and those which are hydrocarbon like bases:

(1) ω is -2.5 to zero, showed water does not participated in the transformation of SH^+ to transition states.

(2) ω is 1.2 to 3.3 or ω* is less than -2, indicates water act as nucleophile.

(3) ω is greater than +3.3 or ω* is greater than -2, showed that the water acts as a proton transfer agent.

(4) ω is about zero, is associated with the proton transfer agent in the mechanism of hydrocarbon like bases.

Linear free energy relationships

Linear free energy relationships is the relationship between logarithm of rate constants or equilibrium constant, i.e. free energy quantities.[39] These relations are formulated by using empirical constants and are linear with respect to at least one variable.

Bunnett-Olsen Hypothesis

For acid catalysed reactions, Bunnett and Olsen[40] made a linear relationship between ($\log k_1 + H_0$) against ($\log[H^+] + H_0$) for reactions of weakly basic substrates and log $k_1$against ($\log[H^+] + H_0$) for reactions of strongly basic substrates. They are called as Linear free energy relationships. Their slopes have represented by a new parameters ϕ which characterises the response of reaction rate to changing mineral acid concentration.

Values of ϕ for reactions of strongly basic substrates reflect only relationships between protonated substrate and transition state and may be related to reaction mechanism. ϕ values for reactions of weakly basic substrates reflect both equilibrium protonation of the substrate and transformation of protonated substrate to transition state and are therefore less directly related to the mechanism.

Three catagories of reaction mechanism with respect to ϕ values are:-

(1) ϕ is less than zero indicated that water molecule not involved in rate determining step.

(2) ϕ is +0.22 to 0.56 showed that water involved in rate determining step.

(3) ϕ is greater than 0.58 indicated water involved as proton transfer agent in the rate determining step.

Hammett Equation

Hammett proposed an equation which relates equilibrium and rate constants for the reaction of meta and para substituted benzene derivatives. It is usually expressed[30] in the forms,

$$\log k = \log k_0 + \sigma\rho \qquad (4)$$

Where k_0 is the rate constant for the parent and k for the substituted compound.

For equilibrium constant,

$$\log K = \log K_0 + \sigma\rho \qquad (5)$$

Of these two constant σ depends only on the substituent, while ρ is a reaction constant, varying with the reaction and the external conditions. Substituents with positive σ values are stronger electron attractors than hydrogen, substituents with negative σ values attract electrons more weakly (or repel electrons more strongly) than hydrogen. Reactions with positive σ values are aided by electron withdrawal from the benzene ring, while those with negative σ values are retarded by electron withdrawal.

The validity of the Hammett relationships is equivalent to the existence of linear relationships between the free energies (of reaction or activators) for different series of rections.

Experiment

1. Material and method

All reagents used were of AnalaR and G.R. grade. Permanganate solution was prepared and tested as given in literature. Doubly distilled water was used to prepare all the solutions.

Kinetic experiments were carried out in a thermostat in which the temperature is controlled within ± 0.1^0C. The reactions were usually followed upto 70% of completion. The reaction was initiated by adding requisite amount of pre equilibrated solution of permanganate to an equilibrated mixture of substrate(L-Alanine), surfactant and sulphuric acid solutions. The zero time of the reaction was noted when half of the permanganate solution was added. The total volume of the reaction mixture was always kept 50 ml.

All kinetic measurements were conducted under pseudo first order conditions where the amino acid was maintained in a large excess over the permanganate ion concentration. Kinetic studies was performed by using Systronics 106 spectrophotometer at 525 nm i.e.at absorbance maximum of permanganate. It was verified that there is no interference from other reagents at this wavelength. 2 ml of the aliquot of reaction mixtures were withdrawn at known intervals of time and the reaction was quenched by adding it to a known excess of ice-cold distilled water (temperature $<2^0$C) in the optic cell. The values of the absorbance due to unreacted permanganate at given times were read out directly from the spectrophotometer.

RESULT AND DISCUSSION

The experimental results obtained on varying the concentration of sulphuric acid at constant concentration of L-Alanine, permanganate and NaLS are summaried in the following table only for the surfactant catalysed reactions. The effect of variation of $[H^+]$ has been investigated between 2 mol dm^{-3} to 6 mol dm^{-3}(Table 1).

To investigate the rate of H^+ ion on the oxidation reaction various hypotheses have been applied. The two Zucker-Hammett[4] relations i.e.
(a) The plot of logk against $-H_o$ (figure-2.1) and
(b) The plot of logk against log[acid](figure-2.2)

Show linear correlation of rate with the sulphuric acid concentration confirming that the reaction is acid catalysed too. However, no straight line of Zucker-Hammett plots produce ideal slope value of unity.[8,19,40]

Here $-H_o$ is a acidity function and a_{H_2O} is a activity of water and their values corresponding to the given sulphuric acid concentration have been collected from Paul and Long[16] and Bunnett[32] respectively. The result, have been reported for both the stages of oxidation reaction.

In view of the reported departures of the slope value from the ideal slope values from unity applicability of Bunnett[32] and Bunnett-Olsen[34] hypotheses were also tested. A summary of the slopes (ω and ω*) of two Bunnett plots i.e. (log k+ H_o) Vs (log a_{H_2O})(figure-2.3) and slope 'ϕ' of Bunnett-Olsen plot between (log k+ H_o) and (H_o+ log[H^+]) (Figure-2.4) have been reported in the Table-2. The slope values of all these plots confirms that in the acid catalysed reaction the water molecule should act as a proton abstracting agent in the rate determining step as per Bunnett and Bunnett-Olsen emperical observations.

Summary Table -1

Dependence of rate on sulphuric acid concentration [H^+]

[$KMnO_4$] = 1x10^{-3} mol dm^{-3} [L-Alanine]= 0.1mol dm^{-3}

[NaLS] = 1x10^{-4} mol dm^{-3} Temp. = 303K

[H^+] mol dm^{-3}	-Ho	-log a_{H_2O}	k_1 X 10^{-3} min^{-1}	k_1^1 X 10^{-3} min^{-1}
2.0	0.84	0.043	2.45	4.48
3.0	1.38	0.085	3.67	5.89
4.0	1.85	0.142	4.55	7.67
5.0	2.28	0.219	5.87	9.33
6.0	2.76	0.32	6.87	13.76

Summary Table -2

Slope values from plots of different of correlation

[L-Alanine] = 0.1mol dm $^{-3}$ [$KMnO_4$] = 1x10^{-3} mol dm^{-3}

[NaLS] = 1x10^{-4} mol dm^{-3} Temp. = 303K

correlation	figure	parameters	1^{st} stage (slope values)	2^{nd} stage (slope values)
Zucker-Hammett Plots				
log k Vs H_o	Figure- 2.1	slope	0.2320	0.2473
log k Vs log[H^+]	Figure-2.2	slope	0.9285	0.9632
Bunnett Plot				
(log k+ H_o)Vs(log a_{H_2O})	Figure-2.3	ω-slope	8.1761	8.3395
Bunnett-Olsen Plot				
(log k+ H_o)Vs (H_o+ log[H^+])	Figure-2.4	ϕ -slope	0.9857	0.9968

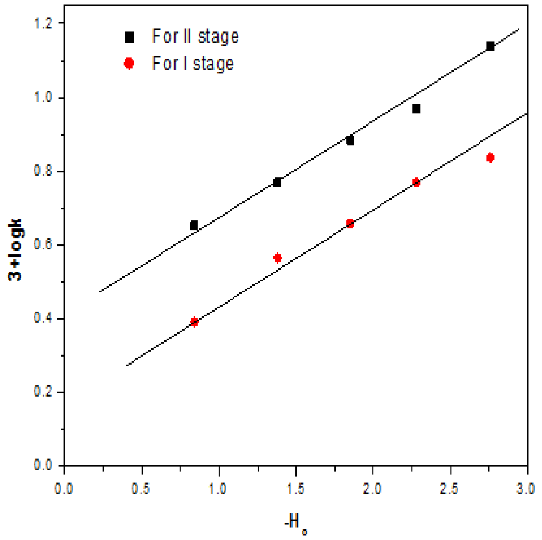

Figure 2.1:-Zucker-Hammett Plot-1

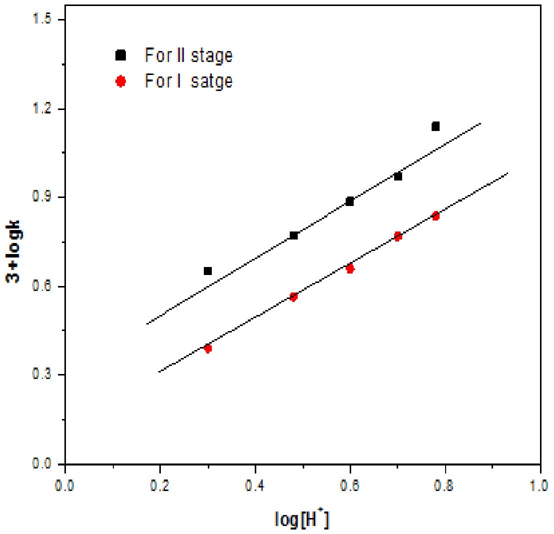

Figure 2.2:- Zucker-Hammett Plot-2

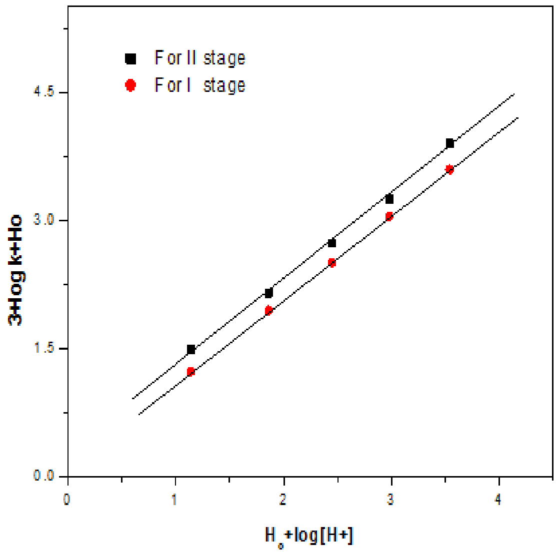

Figure 2.4:-Bunnett-Olsen Plot

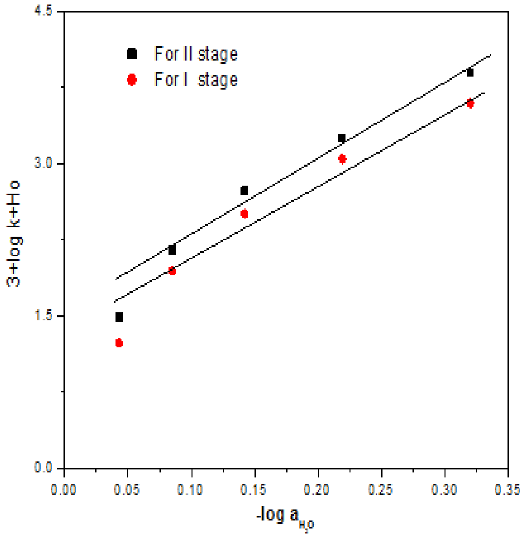

Figure 2.3:-Bunnett plot

CONCLUSION

On the basis of kinetic results and observations it has been confirmed that oxidation of L-Isomers of amino acids is catalysed by H^+ ion and the reaction rate also enhanced in the presence of micelles. A straight line with slope unity, when graph between log k_1 and H_0 or log$[H^+]$. When plots were linear, slopes were lesser or greater than unity in case of Zucker – Hammett Hypothesis. The slope values of all Bunnett plots confirms that in the acid catalysed reaction the water molecule should act as a proton abstracting agent in the rate determining step as per Bunnett and Bunnett-Olsen emperical observations. Through the values of acidity functions it has been suggest that the studied reaction comes under the category of slow reactions. The Zucker –Hammett Hypothesis confirmed the water act as a proton donar in the reaction.

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