

Micell (SLS) Catalyzed Oxidation Reactions of Butyric and Iso-butyric acid Hydrazides by Vanadium(V)

Yogiraj Vijapure¹ and Sanjeevan Gaikwad²

¹Shrikrishna College, Gunjoti, INDIA.

²Bhausaheb Birajdar Senior College, Balsur, INDIA.

²Corresponding Author: sanjivangaikwad123@gmail.com

ABSTRACT

The reaction between Butyric and Isobutyric acid hydrazide and Vanadium (V) is carried out in presence of a mixture of perchloric acid and sodium perchlorate. The reaction proceeds through formation of complex to give product. The various thermodynamic parameters were determined by studying the reaction at five different temperatures ranging from 30 to 50°C. Oxidation of butyric acid hydrazides by Vanadium (V) proceeds through complex formation between hydrazide and the oxidant. Free radical formation can be confirmed by effect of acrylonitrile. The activation parameters were also determined and the mechanism is predicted.

Keywords- Kinetics, Micell, Oxidation.

I. INTRODUCTION

Surface active molecules or surfactants are the substances which get preferentially adsorbed at air-water interfaces forming an oriented monolayer where the hydrophilic groups point towards aqueous phase and hydrocarbon part point towards air or oil phase.

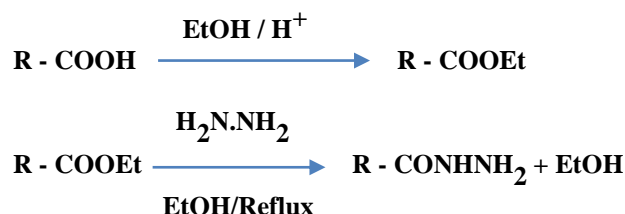
The ability of polar portion of surfactant molecule to increase the solubility of non-polar side chain can be used to estimate the contributions of solute and solvent to the observed bulk properties. The most characteristic property of a surfactant solution is the self-association of solute within a narrow concentration range in dilute solution to form high molecular weight aggregates known as MICELLES or ASSOCIATION COLLOIDS.

At extremely low concentration of surfactant, the true crystalline solutions are formed, but above a fairly distinct concentration, the solutions become colloidal due to aggregation of surfactant molecules.

Mild oxidising agent like ammonium metavanadate is used to oxidise organic substrates like hydrocarbons, ketones, aliphatic alcohols, aldehydes and aliphatic esters. The hydrazides selected for the kinetic study, belong to a homologous series, so that the effect of chain length on the reaction rate and on the mechanism of the reaction can be established. The hydrazides chosen for kinetic study are 1) n-Butyric acid hydrazide 2) iso-Butyric acid hydrazide.

II. EXPERIMENTAL

The experimental part includes preparation and purification of chemicals. The procedure followed for the synthesis of hydrazides is given below -



The pseudo first order reaction condition was used by keeping the concentration of hydrazide excess over that of oxidant. The progress of the reaction was followed at different time intervals by spectrophotometric measurement of absorbance due to complex formed between ammonium metavanadate and hydrazide in acid medium.

To study the oxidation of hydrazide, the reaction mixture was prepared by using requisite concentrations of ammonium metavanadate i.e. V(V), hydrazide, perchloric acid and sodium perchlorate in solution when and as required. The progress of reaction was followed by measuring optical density (O.D.) of the reaction mixture at 390 nm spectrophotometrically. λ_{max} was determined by varying wavelength, it was observed that maximum absorbance for both ammonium metavanadate and a mixture of hydrazide and ammonium metavanadate was obtained at 390 nm.

Standard Kinetic Run:

Preliminary experiments were carried out in order to decide the range of temperature, concentrations of ammonium metavanadate, hydrazide, perchloric acid and sodium perchlorate. It was found that the reaction proceeds with a measurable velocity at 35°C using 5.0×10^{-4} M ammonium metavanadate, 1.0×10^{-2} M hydrazide, 5.0×10^{-2} M perchloric acid and 5.0×10^{-2} M sodium perchlorate.

The observed rate constant (k) of the reaction was evaluated by graphical method.

It may be noted that the first order kinetics of reaction refers to change in concentration of V(V) and

observed rate constant (k) stands for first order rate constant, because the reaction was studied under pseudo-first order condition in which concentration of hydrazide was in excess as compared to that of ammonium metavanadate.

III. RESULTS AND DISCUSSION

Effect of V(V) Concentration:

To study the effect of varying concentration of V(V) on rate of reaction, the reaction was carried out with different initial concentrations of ammonium metavanadate at 35°C and constant ionic strength by keeping fixed concentrations of hydrazide and perchloric acid.

An examination of data and log O.D. versus time plots make it clear that, oxidation of hydrazide at different initial concentrations of V(V) follows the first order kinetics because the log O.D. versus time plot in each case is linear with positive slope and intercept on log O.D. axis. The constancy of k values at different initial [V(V)] indicate the pseudo-first order kinetic behaviour of reaction.

Effect of Hydrazide Concentration:

The reaction at different initial concentrations of hydrazide substrate was investigated to study the effect of concentration of hydrazide on the rate of reaction. To achieve this, the concentration of hydrazide was varied from 2.5 to 10⁻³ M to 2.5 x 10⁻² M keeping temperature, ionic strength and concentrations of ammoniummeta vanadate and perchloric acid constant. The kinetic data of these runs and graphical presentations show that since the log O.D. against time plots are linear, the observed rate constant (k) were computed with respect to change in the concentration of hydrazide. The value of pseudo-first order rate constant (k) depends on initial concentration of hydrazide and it increases with increase in Hydrazide concentration. The order with respect to hydrazide is determined by plotting log dA/dt versus log concentration of hydrazide which is a straight line, the slope of which gives an order of reaction. It is found to be fractional.

Hydrazide	Order
n-butyric acid	0.56
iso-butyric acid	0.52

Effect of Perchloric Acid Concentration :

Keeping concentrations of ammonium metavanadate and hydrazide constant, the effect of varying HClO₄ concentration on the rate of oxidation of hydrazide was studied over a range of perchloric acid concentration 4.0 x 10⁻² M to 10.0 x 10⁻² M, from this data the log O.D. versus time graphs are plotted, from these plots it is observed that the values of rate constants remain almost constant between the range of hydrogen ion concentration studied.

Effect of Sodium Perchlorateconcentration:

The reaction was studied by changing the concentration of sodium perchlorate which was not assumed to give any secondary reactions and with assumption that it is completely dissociated. This can be done to investigate the effect of ionic strength on specific rate of reaction. The results of this kinetic study of oxidation of acid hydrazides showed that the specific rates of reactions are not influenced by increase in ionic strength. By varying the concentration of sodium perchlorate in the reaction mixture from 0.0 M to 5.0 x 10⁻² M the effect of ionic strength was studied and it was observed that for the rates of reactions were almost constant during this variation of ionic strength.

Effect of Temperature:

The present oxidation reaction was carried out at five different temperatures ranging from 30 to 50°C so as to investigate the effect of temperature on the rate of reaction.

The pseudo-first order rate constants were calculated from the graph of log O.D. against time.

The activation parameters energy of activation (E_a), Enthalpy of activation (ΔH[#]) were calculated by plotting log k versus 1/T and log k/T versus 1/T respectively. From the slope of the plot 1/T versus log k energy of activation was calculated as

$$E_a = - 2.303 \times R \times \text{slope.}$$

The slope of the plot 1/T versus log k/T is determined from which the enthalpy of activation for each hydrazide was calculated as

$$\Delta H^\# = - 2.303 \times R \times \text{slope.}$$

The entropy of activation ΔS[#] was calculated at each temperature by using the formula

$$\Delta S^\# = 4.576 (\log k - 10.573 - \log T + E_a / 4.576T)$$

From the values of ΔH[#] and ΔS[#] the free energy of activation ΔG[#] was computed using the relation ΔG[#] = ΔH[#] - T ΔS[#]. The values of temperature coefficient were calculated by taking the ratios of first order rate constants for rise in temperature by 10⁰C.

IV. TEMPERATURE COEFFICIENT

Hydrazide	K ₄₀ / k ₃₀	K ₄₅ / k ₃₅	K ₅₀ / k ₄₀	Mean Values
n-butyric acid	1.46	1.44	1.46	1.45
Iso-butyric acid	1.72	1.64	1.45	1.61

Hydrazide	Temp. Coefficient	Ea KJ/mol	ΔH^\ddagger KJ/mol	ΔS^\ddagger e.u.	ΔG^\ddagger KJ/mol
n-butyric acid	1.45	65.47	59.35	-28.77	96.42
Iso-butyric acid	1.6	70.07	69.5	-23.92	100.32

Test for Intervention of Free Radical:

The free radical mechanism was confirmed by testing the reaction mixture with acrylonitrile and mercuric chloride solution. Again its already confirmed that the order of the reaction with respect to V (V) is one.

Effect of H_2SO_4

$$[HYD] = 1.0 \times 10^{-2} \text{ M} \quad [NaClO_4] = 5.0 \times 10^{-2} \text{ M}$$

$$[AMV] = 5.0 \times 10^{-4} \text{ M} \quad \text{Temp} = 35^\circ\text{C}$$

$$\lambda_{\text{max}} = 390 \text{ nm}$$

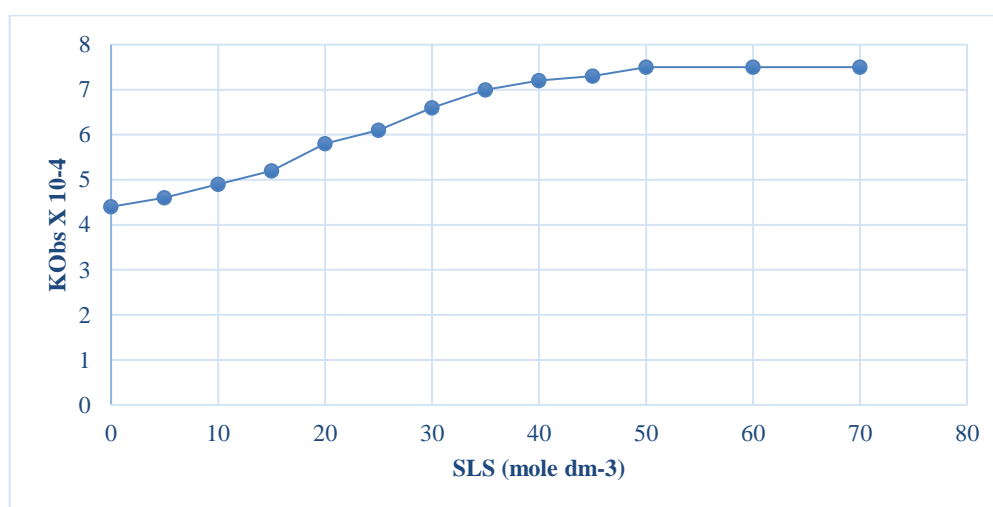
$[H_2SO_4] \times 10^2 \text{ N}$	n-butyric acid $k \times 10^5 \text{ sec}^{-1}$	Iso-butyric acid $k \times 10^5 \text{ sec}^{-1}$
1.0	4.39	8.2
2.5	12.3	23.6
5.0	14.2	27.2
7.5	17.0	33.4
10.0	20.3	40.8

Effect of Varying SLS Reaction conditions:

$$[V(V)] = 20.0 \times 10^{-3} \text{ mol dm}^{-3}, \quad [\text{Hydrazide}] = 50.0 \times 10^{-3} \text{ mol dm}^{-3},$$

$$[H_2SO_4] = 2.0 \times 10^{-3} \text{ mol dm}^{-3} \quad \text{Temperature} = 35^\circ\text{C}$$

[SLS] (mol dm ⁻³)	$k_{\text{obs}} \times 10^{-4} \text{ (s}^{-1}\text{)}$
0	4.4
5	4.6
10	4.9
15	5.2
20	5.8
25	6.1
30	6.6
35	7.0
40	7.2
45	7.3
50	7.5
60	7.5
70	7.5



V. CONCLUSION

Review of literature revealed that anionic species are stabilized by cationic micelles, cationic species by anionic micelles and neutral molecules by nonionic micelles exhibiting catalytic effect. Micelles may catalyze or inhibit a reaction. In this study we have used an anionic surfactant, SLS, which has a catalytic effect i.e. the rate of oxidation of aliphatic acid hydrazide by vanadium(V) in presence of SLS has been enhanced. In this experiment the micelle SLS catalyses the oxidation reaction at the surface level of both the reactant.

REFERENCES

- [1] Zhengzheng, P., and Martin, N., (2007). Kinetics and Mechanism of Oxidation Reactions of Porphyrin–Iron(IV)–Oxo Intermediates. *Inorg. Chem.*,46(16), 6767-6774
- [2] Donald, G., Huifa, G., (1993). Kinetics and mechanism of the oxidation of alcohol by ferrate ion. *Canadian journal of chem.*, 71, 1394-1400
- [3] Keerti, M.,N., Sharanappa, T.,N., (2012). Kinetics and mechanism of oxidation of L-leucine by alkaline diperiodatocuprate(III) - A free radical intervention,

deamination and decarboxylation. *Journ. of chemical sci.*, 124, 809-819

[4] Okoro, H., K., and Odebunmi, E., O., (2009). Kinetics and mechanism of oxidation of sugar and sugar alcohols by KMnO_4 . *Internation journ. of phy. Sci.*, 4(9), 471-476

[5] Hina, H., Hiran, B., L., Joshi, S., N., (2015). Kinetics and mechanism of oxidation of primary alcohols by pyridinium dichromate. *Chem. Sci. Trans.*, 4(1), 49-58

[6] Agarwal, A., Gupta, B., and Sharma, P., D., (2012). The Kinetics and Mechanism for the Oxidation of Nicotinic Acid by Peroxomonosulfate in Acidic Aqueous Medium. *Journal of the Korean chemical society*, 56 (2), 212-216.

[7] Mamman, S., Iyun, J., F., (2004). Kinetics and mechanism of the redox reaction between catechol and trisoxalatocobaltate (III) ion in aqueous acid medium. *Nigerian journ. of chem. Research.*, 9, 35-39.

[8] Aghamammadova, S., Negieva, Gasanova, L., and Negiev, T., (2016). Kinetics and Mechanism of the Reaction of Coherently Synchronized Oxidation and Dehydrogenation of Cyclohexane by Hydrogen Peroxide. *ICCCP.*, 49, 1-5.

[9] Saraswat, S., Sharma, V., and Banergy, K.,K., (2001). Kinetics and mechanism of oxidation of aliphatic aldehydes by pyridinium chlorochromate. *Indian journal of chemistry.*, 40A, 583-587.