

Oxidative and Thermodynamic Study of Aliphatic Amino Acids By 1,3-Dichloro-5,5-Dimethylhydantoin In Aqueous Acetic Acid Medium

ARVIND PRASAD DWIVEDI¹, SHWETA NEERAJ²

¹Department of Chemistry, Govt. Sanjay Gandhi Smrati Auto., P.G., College Sidhi M.P, India

²Department of Chemistry, Govt. Girls P.G. College (NAAC) Rewa, (M.P.), India

Abstract -- The kinetics of reaction between aliphatic ℓ -amino acids and 1,3-dichloro-5,5-dimethylhydantoin have been studied in aqueous acetic acid medium yielding aliphatic aldehydes as the end-products by the ring cleavage oxidation. The catalytic effect of acid in the reaction rate reveal an interaction between oxidants species H_2O+Cl and substrates. The observed order of reactivity ℓ -amino acids (ℓ -Glycine > ℓ -Alanine) was explained based on conformational considerations. A plausible mechanism and rate law supported by thermodynamic parameters was discussed.

Indexed Terms: aliphatic aldehydes, demonstrates, reveals, plausible.

I. INTRODUCTION

The kinetics of the reactions involving the redox system¹ in chemistry of reactions of halo-compounds such form a separate branch, which is of great synthetic importance.²⁻⁴ N-halo compounds have been extensively employed as oxidizing agents for the catalysed and uncatalysed reactions.⁵⁻¹² DCDMH is of immense importance and has found limited applications. It is stable, commercially cheap and eco-friendly easily available market which has been rarely used as source of chlorine¹³ or chlorination^{14,15} and oxidation reactions^{16,17}. Only few reports are available of its use in organic synthesis¹⁸ and oxidation of chalcones,¹⁹ carbohydrates²⁰ etc. Although a lot of works on the oxidation of amino acids have been reported by different oxidants,²¹⁻²³ but no systematic study was made on oxidation of ℓ -alanine (CH_3CHNH_2COOH), ℓ -glycine (NH_2CH_2COOH) by 1,3-dichloro-5, 5-dimethylhydantoin, in aqueous acid medium.

II. EXPERIMENTAL

All the reagents and solvents used were of analytical grade (B.D.H. C.D.H. and Acros). The solution of DCDMH is standardized iodometrically.²⁴ The solution of sodium thiosulphate was prepared by taking a B.D.H. grade sample in a doubly distilled water and was standardized against copper sulphate solution using KI and starch as an indicator odometrically. The standard solution of HCl was determined by titrating it against standard NaOH solution using phenolphthalein as an indicator. Other solutions of NaCl, KCl, DMH were prepared by dissolving their requisite amount of AnalaR sample in distilled water. The reaction kinetics was studied by using thermostat maintained at constant temperature. The rate constant was determined by integration method.

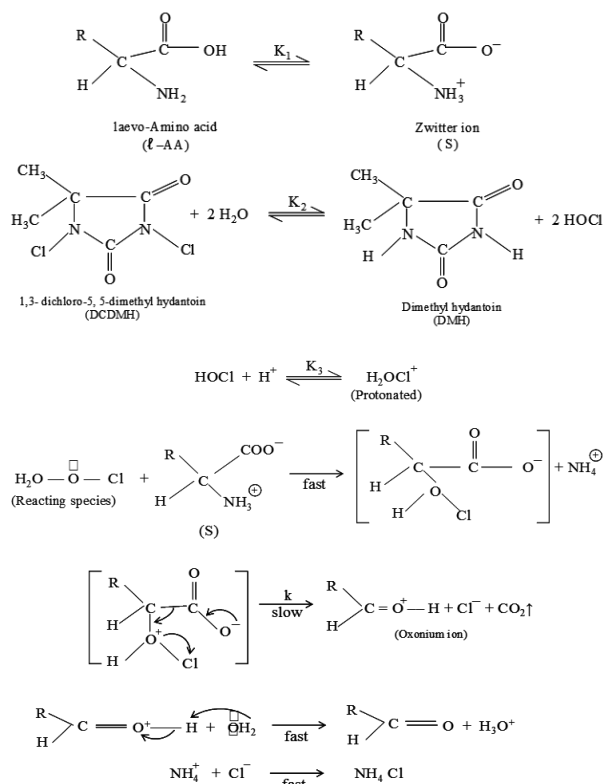
III. RESULTS AND DISCUSSION

The probe of reactions occurs at measurable rate within a temperature range 303 and 308 K respectively. The kinetic data have been collected for under the experimental condition [substrate] > [oxidant] [DCDMH] ($1.25 - 5.0 \times 10^{-3} \text{ mol dm}^{-3}$) and at fixed concentration of other reactants at constant temperatures. The unit slope of plot of $\log [DCDMH]$ vs. time was found to be linear indicating first-order dependency of rate. The first-order kinetic rate was obtained with in concentrations of ℓ -amino acids ($0.50 - 5.00 \times 10^{-2} \text{ mol dm}^{-3}$) The reaction rate constants was measured various $[H^+]$ ($0.20 - 1.25 \text{ mol dm}^{-3}$) (Table:1) which was found catalyzed in reactions. The plot of $\log k$ vs. $\log [H^+]$ (Fig. 1) is obtained linear with approximately unit slope showing the rate of reaction is proportional to the first power of $[HCl]$. The rate was enhanced by increasing the percentage composition of solvent polarity. Insignificant affection

rate was observed by successive addition of primary salts. The Dimethyl hydantoin found to retard the reaction rate. The activation and thermodynamic parameters were evaluated for the reactions under study (Table:2). The Arrhenius plots of log k vs. 1/T (Figs. 2 & 3). Suggested the more reactive Amine has lowest energy of activation substrate. Similar mechanism prevail in both the substrate over all the reactions are enthalpy controlled. The Arrhenius plot of log k_{obs} vs. 1/T were plotted which were found to be liner. It is obvious from the thermodynamic parameter that ΔH[#] and ΔS[#] which play important role in controlling the rates of reactions.

IV. MECHANISM

1,3-dichloro-5,5-dimethylhydantoin (DCDMH) on hydrolysis yields finally dimethyl- hydantoin (DMH) in aqueous solution. The following equilibrium exists.

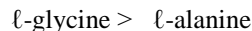


where, R = CH₃, -H for corresponding aldehydes.

The final rate law derived based on mechanism using steady state approximation is represented by equation (8).

$$\frac{-d}{dt} [\text{DCDMH}] = \frac{k K_1 K_2 K_3 [\text{S}] [\text{H}^+]}{[\text{DMH}] + K_2}$$

The observed order of reactivity was found in sequence



The similar mechanism has also been earlier reported by authors^{25,26} for the study of l-AA- DCDMH system. The reaction yielded acetaldehyde and formaldehyde as the end-products which is characterized by the spot test and other modern physical methods.

V. CONCLUSION

1,3-dichloro-5,5-dimethylhydantoin (DCDMH) has been found as moderate oxidant for the oxidation of l-alanine and l-glycine. The thermodynamic and activation parameters determined are well in accordance with the reactions involving Zwitter ions which supported the rate determining step in the mechanism.

Table 1 : Effect of concentration of Acid on rate of reaction

10³ × [DCDMH] (mol dm⁻³) = 2.50 (1, 2) ;

10² × [Substrate] (mol dm⁻³) = 2.00 (1), 1.25 (2) ;

CH₃COOH- H₂O % (v/v) = 30 (1), 20 (2) ;

Temp. K = 303 (1), 308 (2)

S. No.	[H ⁺] (mol dm ⁻³)	10 ⁴ k _{obs} (s ⁻¹)	
		l-alanine (CH ₃ CHNH ₂ COOH)	l-glycine (NH ₂ CH ₂ COOH)
		(1)	(2)
1.	0.20	1.33	1.82
2.	0.25	1.55	2.42
3.	0.33	2.29	2.89
4.	0.40	2.71	3.63
5.	0.50	3.47	4.75

6.	0.66	4.65	-
7.	0.80	5.98	7.23
8.	1.00	7.24	8.87

1. ℓ -alanine 2. ℓ -glycine

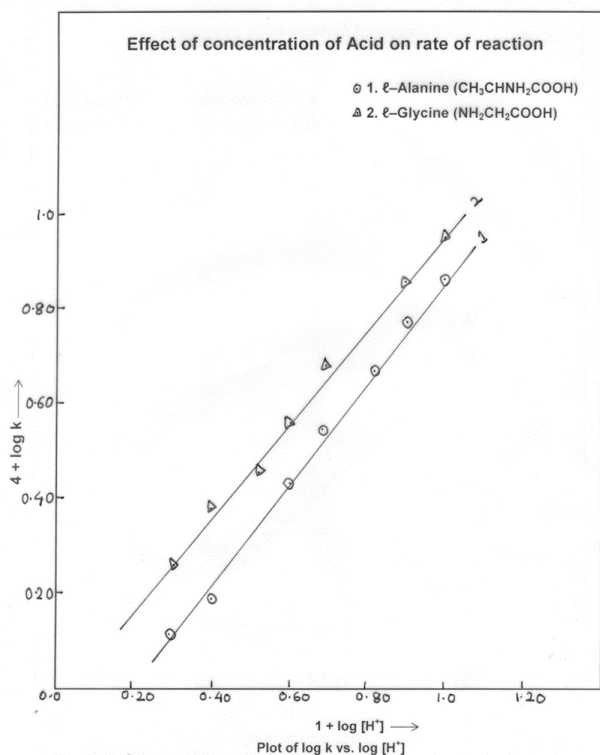


Fig. 1 $10^3[\text{DCDMH}]$ (mol dm^{-3}) = 2.50 (1, 2);
 $10^2[\text{Substrate}]$ (mol dm^{-3}) = 2.00 (1), 1.25 (2);
 HOAc-H₂O % (v/v) = 30(1), 1.25 (2);
 Temp. K = 303 (1), 308 (2)

Figure 1.

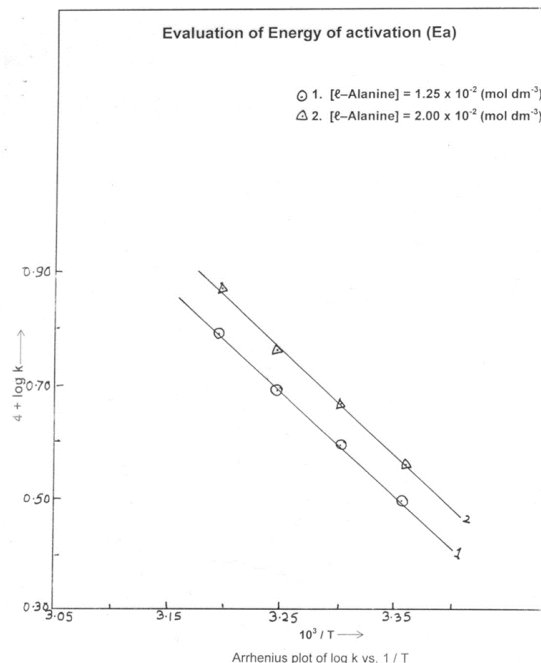


Fig. III-15 [DCDMH] = 2.50×10^{-3} (mol dm^{-3}); [H^+] = 0.66 (mol dm^{-3});
 HOAc-H₂O = 30 % (v/v)

Figure 2.

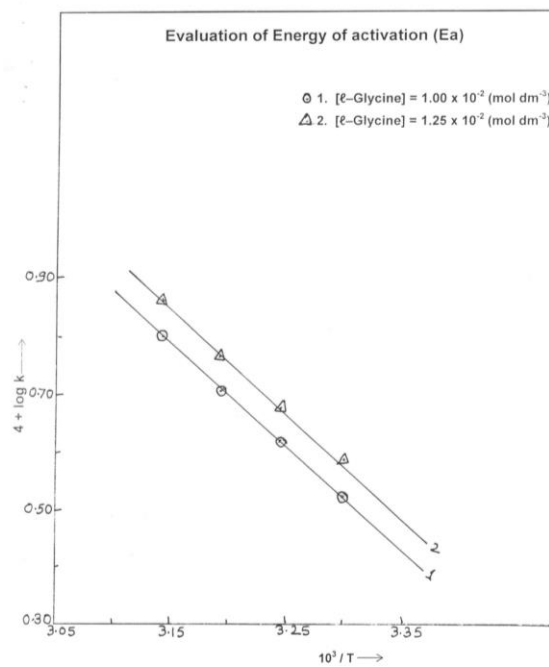


Fig. III-16 [DCDMH] = 2.50×10^{-3} (mol dm^{-3}); [H^+] = 0.50 (mol dm^{-3});
 HOAc-H₂O = 20 % (v/v)

Figure 3.

Table 2 : Activation and Thermodynamic parameters for ℓ -amino acids- 1,3-dichloro-5,5-dimethylhydantoin system

S. No.	Substrate	Ea (kJ mol ⁻¹)	A (s ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)	$-\Delta S^\ddagger$ (JK ⁻¹ mol ⁻¹)
1.	ℓ -Alaine (CH ₃ CHN H ₂ COOH)	35.34	2.75 $\times 10^2$	32.80	84.18	168.23
2.	ℓ -Glycine (NH ₂ CH ₂ C OOH)	33.91	1.83 $\times 10^2$	30.82	84.30	175.86

REFERENCES

- [1] Hudlicky, M. : Oxidation of organic chemistry, American Chemical Society, Washington, D.C., 1990.
- [2] Patrocino, F.A. : J. Organomet Chem., 2000, 220(b), 603.
- [3] Dhurn, P.S., Mohe, N.U., and Salunkhe, M.M. : Synth. Commun. 2001, 31, 3653.
- [4] Bondgar, B.P., Uppalla, L.S. and Sadavarte, V.S. : Syn. Lett. 2001, 11, 1715.
- [5] Thenraja, D., Subramanian, P., and Srinivasan, C. ; J. Chem. Soc., Perkin Trans., 2002, 2.
- [6] Mukaiyama, T., Mastsuo, J.I., Lida, D. and Kitagawa, H. : Chem. Lett. 2001, 8, 846.
- [7] Mukherjee, J. and Banerji, K.K. : J. Org. Chem. 1981, 46, 2323.
- [8] Singh, A.K., Singh, V., Rahmani, S., Singh, A.K., and Singh, B. : J. Mol. Catal. A.: 2003, 197, 91.
- [9] Filler, R. : Chem. Rev., 1963, 63, 21.
- [10] Balasubramanian, P.V., and Mathigalagan, N. ; J. Chem. Pharm. Res., 2011, 3, 522.
- [11] Shrinivasan, N.S., and Venkatasubramanian, N. : Tetrahedron Lett. 1970, 11, 2039.
- [12] Vivekanandan, K., and Nambi, K.; J. Indian Chem. Soc., 1999, 76, 198.
- [13] Kolvari, E., Ghorbani-Choghamarani, A., Salehi, P., Shbiini, F., and Zolfigol, M.A. : J. Iran. Chem. Soc., 2007, 4, 126.
- [14] Xu, Z., Zhang, D., and Zou, Z. : Synth. Commun. 2006, 36, 255.
- [15] Skibinska, M., Zahn, F.A., Czarnacka, A., and Lewenstein, W. : Acta. Pol. Pharm. 1969, 6, 25.
- [16] Khazaei, A, Amini-Manesh, A. : J. Chin. Chem. Soc., 2005, 52, 1017.
- [17] Khazaei, A, Amini-Manesh, A. : Synthesis, 2005, 1929.
- [18] Nicolet, B.N., and Shinn, L.A. : J. Am. Chem. Soc., 1929, 51, 1615-1622.
- [19] Tamil selvi, P., and Karunakaran, K. : Asian J. Chem., 2015, 27(5), 17254-1728.
- [20] Mergregor, W.H., and Carpenter, F.H. : J. Bio Chemistgry, 1962, 1, 53-62.
- [21] Wright, N.C. : J. Bio Chem., 1936, 30, 1661-1676.
- [22] Kumar, M.N., Mantelingu, K., Bhardregowda, D.G. and Rangappa, K.S. : J. Mol. Catal. A.: Chem., 2009, 309, 172-177.
- [23] Lingegbowda, N.S., Kumara, M.N., Channegowda, D. Rangappa, K.S. and Made-gowda, N.M. : J. Mol. Catal. A : Chem., 2007, 269, 225-233.
- [24] Rao, Shan, and Dhannure, K. : Ph. D. Thesis, Nagarjuna University, India, 2003.
- [25] Neeraj, Shweta, Parihar, S.S. and Dwivedi, A.P. : Int. J. Adv. Research in Chemical Science (IJARCS) 2018, 4, 9-14.
- [26] Neeraj, Shweta, Parihar, S.S. and Dwivedi, A.P. : Int. J. Adv. Research in Chemical Science (IJARCS) 2018, 5, 25-30.