International Journal of Advanced Research in Chemical Science (IJARCS)
Volume 5, Issue 9, 2018, PP 1-5
ISSN No. (Online) 2349-0403
DOI: http://dx.doi.org/10.20431/2349-0403.0509001
www.arcjournals.org

Oxidative Cleavage and Thermodynamic Study of ℓ-Leucine and ℓ-Valine by 1,3-Dichloro-5,5-Dimethylhydantoin in Aqueous Acetic Acid Medium

Shweta Neeraj[1], Arvind Prasad Dwivedi[2], S.S. Parihar[1]

[1]*Department of Chemistry, Govt. Girls P.G. College (NAAC) Rewa-486001 (M.P.) India*

[2]*Department of Chemistry, Govt. Sanjay Gandhi Smrati Auto., P.G., College Sidhi M.P*

Corresponding Author:** ***Shweta Neeraj, *Department of Chemistry, Govt. Girls P.G. College (NAAC) Rewa-486001 (M.P.) India*

Abstract: *The kinetics of reaction between ℓ-leucine and ℓ–valine and 1,3-dichloro-5,5-dimethylhydantoin have been studied in aqueous media yielding aliphatic aldehydes as the final products by oxidative cleavage. The observed order of reactivity ℓ-leucine > ℓ–valine was explained on the basis of steric and inductive effect. Reaction mechanism and rate law supported by thermodynamic parameters was discussed.*

Keywords: *Oxidative cleavage, steric effect, inductive effect, aliphatic aldehydes, rate law.*

1. Introduction

Chemical kinetics is often treated as a side issue of the most disciplines of chemical science. Basilar principle of chemical kinetics[1-13] in chemistry of particular importance the last law says temperature and so ambient conditions have influence on chemical reactivity. The fundamental passage for the development of modern kinetics was brought in light by S.A. Arrhenius[14] when stage of reaction was associated with definite thermodynamic parameters. The two important ℓ-leucine and ℓ–valine was taken to be as a substrates identified by Human Nutrition Research Centre of Clermont-Ferrand. DCDMH oxidant[15-17] or its hydrolytic product H_2OCl^+, hypochlorous acidium ion, a strong electrophile acts an active oxidizing species.

2. Experimental

Reagents and solvents used in the entire investigation were of analytical grade (B.D.H. C.D.H. and Acros). The solutions (ℓ-leucine and ℓ–valine) were prepared in requisite volume of glycial acetic acid. The oxidant's (DCDMH) standard solution was prepared. The others solutions of oxalic acid, sodium hydroxide, hydrochloric acid were prepared in standard form. The solution of sodium thiosulphate was prepared in a doubly distilled water and was standardized against copper sulphate solution using KI and starch as an indicator iodometrically. The rate constant (k) was determined by integration and least square method. The end-products aliphatic aldehydes were identified by carrying spot tests.

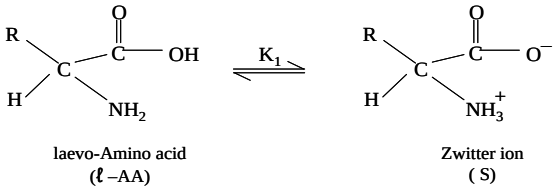
3. Results and Discussion

The probe of reactions occur at measurable rate within a temperature range 303 K. The kinetic data have been collected under the experimental condition [substrate] >> [DCDMH] ($1.25 – 5.0 \times 10^{-3}$ mol dm^{-3}). The unit slope of plot of log [a-x] vs. time was found to be linear indicating first-order dependency of rate. The first-order kinetic rate was obtained within concentration rate of ℓ-leucine and ℓ–valine ($0.50 – 5.00 \times 10^{-2}$ mol dm^{-3}). The reaction rate constants was measured at various $[H^+]$ (0.25 – 1.25 mol dm^{-3}) (Table:1) . The plot of log k vs. log $[H^+]$ (Fig. 1) is obtained linear with approximately unit slope showing the rate of reaction was found catalyzed and proportional to the first power of [HCl]. The rate was enhanced by increasing the percentage composition of solvent polarity. Insignificant effect of 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 understudy (Table:2). The Arrhenius plots of log k vs. 1/T (Figs. 2 and 3),

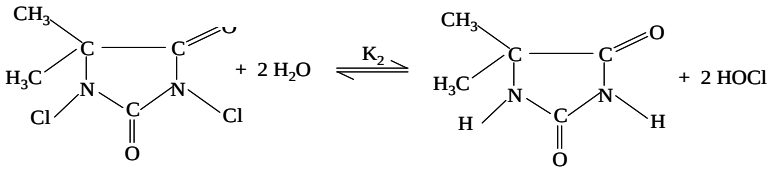
suggested the more reactive amine has lowest energy of activation and the thermodynamic parameter such as $\Delta H^{\#}$ and $\Delta S^{\#}$ play important role in controlling the rates of reactions.

Mechanism

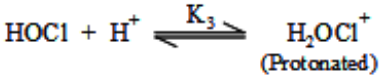
The oxidant DCDMH yields the following equilibrium exists.



laevo-Amino acid (ℓ –AA) Zwitter ion (S) (1)

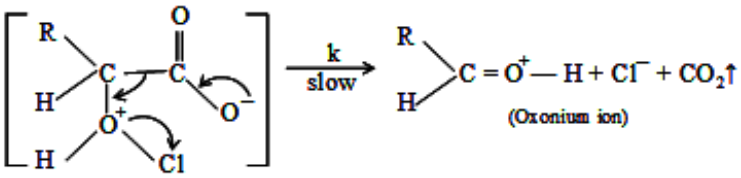


1,3- dichloro-5, 5-dimethyl hydantoin (DCDMH) Dimethyl hydantoin (DMH) (2)

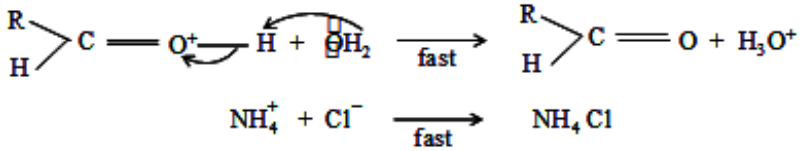


(3)

(4)



(5)



(6)

(7)

Where, R = $-CH_2CH(CH_3)_2$ and $-CH(CH_3)_2$ for corresponding aldehydes.

The rate law was formulated using steady state approximation as:

$$\frac{-d}{dt}[DCDMH] = \frac{k\,K_1\,K_2\,K_3\,[S]\,[H^+]}{[DMH] + K_2} \quad (8)$$

The observed order of reactivity was found as :

ℓ-leucine > ℓ-valine

The similar mechanism has also been reported by authors[18-20] in her previous communication for the study of ℓ-AA-DCDMH system. The end-products was identified as characterized by physical methods isovaleraldehyde and butyraldehyde respectively.

4. CONCLUSION

1,3-dichloro-5,5-dimethylhydantoin (DCDMH) has been found as a non-hazardous and moderate oxidant for the oxidation of ℓ–amino acids. Electrophilic H_2O^+Cl species attack of the carboxylate anion of amino acid leads to the formation of short lived intermediate complex at transition state in equilibrium with the substrates, which then decomposes in a slow step. The thermodynamic data supported the proposed mechanism.

Table1. *Effect of concentration of Acid on rate of reaction*

10^3 × [DCDMH] (mol dm^{-3}) = 2.50 (1, 2) ;
10^2 × [ℓ-AA] (mol dm^{-3}) = 2.50 (1, 2) ;
CH_3COOH- H_2O % (v/v) = 50 (1, 2) ;
Temp. K = 303 (1, 2)

S. No.	$[H^+]$ (mol dm^{-3})	⟵ $10^4 k_1$ (s^{-1}) ⟶	
		ℓ-leucine ($(CH_3)_2CHCH_2CHNH_2COOH$) (1)	ℓ-valine ($(CH_3)_2CHCHNH_2COOH$) (2)
1.	0.25	1.19	0.91
2.	0.33	1.61	1.34
3.	0.40	2.25	1.67
4.	0.50	2.52	2.13
5.	0.80	4.05	3.82
6.	1.00	5.11	4.19
7.	1.25	6.31	4.96

1. *ℓ-leucine* 2. *ℓ-valine*

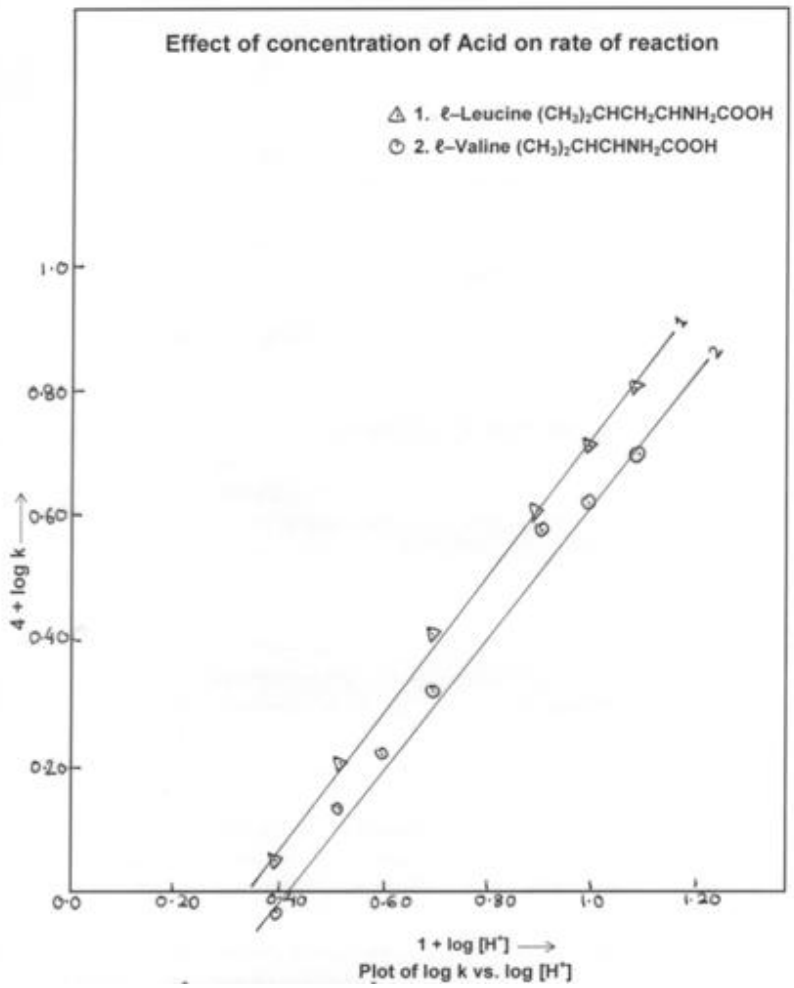


Fig1. *10^3[DCDMH] (mol dm^{-3})=2.50 (1,2); 10^2[Substrate] (mol dm^{-3})=2.50 (1,2); HOAc-H_2O % (v/v) = 50 (1,2); Temp.K = 303 (1,2)*

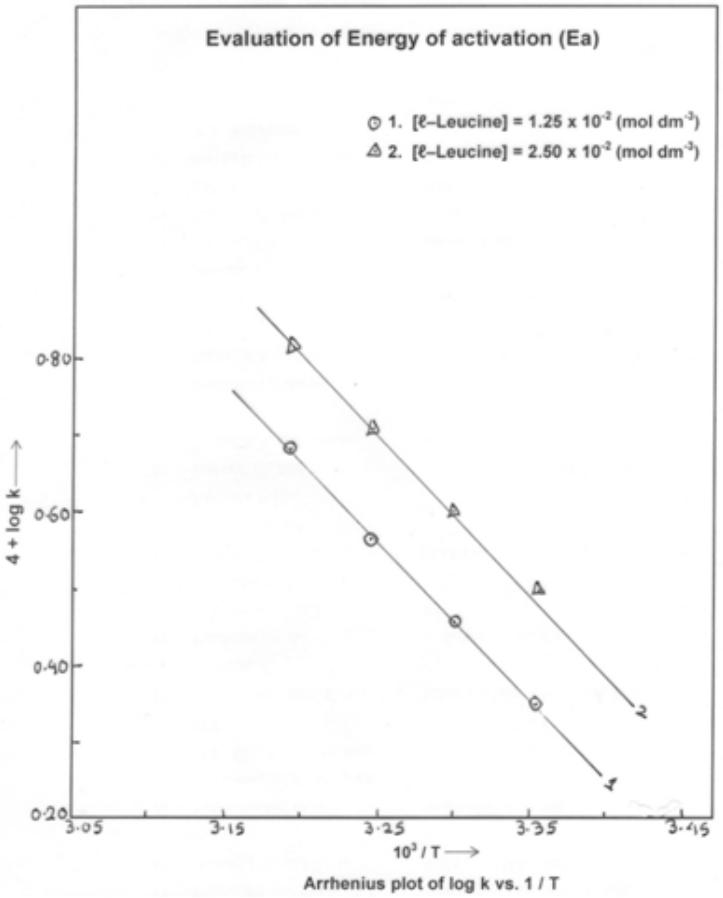


Fig2. *[DCDMH] = 2.50 x 10^{-3} (mol dm^{-3}); $[H^+]$ = 0.80 (mol dm^{-3}); HOAc-H_2O = 50% (v/v)*

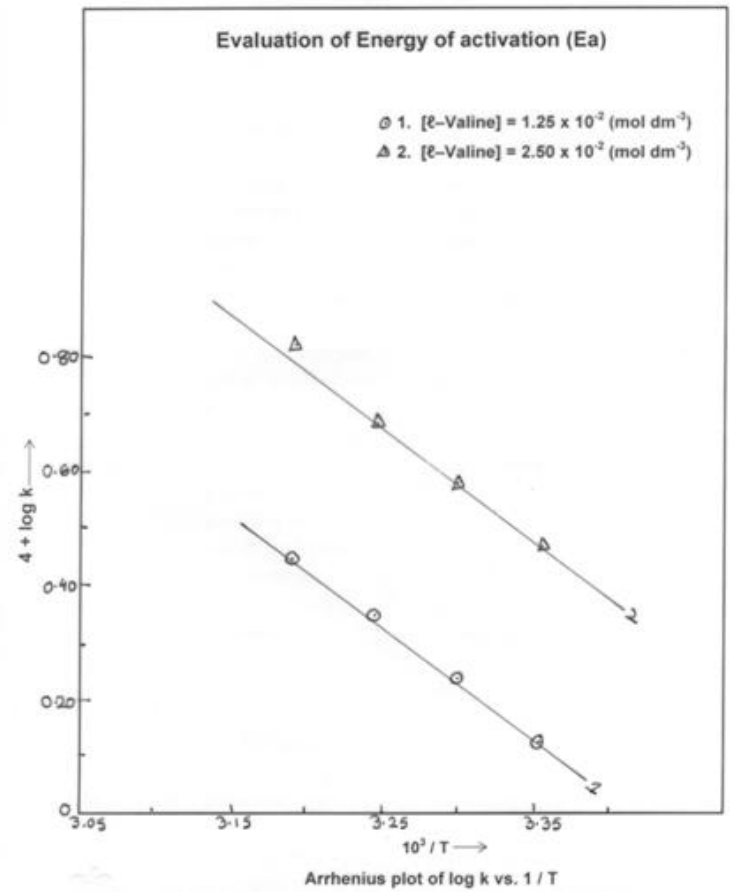


Fig3. *[DCDMH] = 2.50 x 10^{-3} (mol dm^{-3}); $[H^+]$ = 0.80 (mol dm^{-3}); HOAc-H_2O = 50% (v/v)*

Table2. *Activation and Thermodynamic parameters for ℓ-amino acids - DCDMH system*

S. No.	ℓ-Amino acid	Ea (kJ mol^{-1})	A (s^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})	$-\Delta S^{\#}$ (JK^{-1} mol^{-1})
1.	ℓ-leucine [$(CH_3)_2CHCH_2CHNH_2COOH$]	39.93	1.99×10^3	29.47	84.93	182.09
2.	ℓ-valine [$(CH_3)_2CHCHNH_2COOH$]	40.54	2.72×10^3	29.06	85.47	185.03

REFERENCES

[1] Vant Hoff, J.H. Wilhelmyh : Etudes de dynomique chemique muller, Amsterdam, 1884, **84**

[2] King, M.C. : Experiments with time, Ambix, 1981, **23**, 70-82

[3] Berthelot, P.E.M., and Saint Gilles : Annales de chime et physique, 1873, **68**, 385-422

[4] Guldberg, C.M. and Waage, P. : Journal Prakt. Chem., 1879, **127**, 69-114

[5] Harcourt, A.G.V., and Essan, W. : Phil. Trans. London, 1913, **212A**, 187-204

[6] Ostwald, W. : Uber Katalyse, Liepzig, 1902

[7] Van't Hoff, J.H. : Etudes de dynamique Chimique, Amsterdam, 1884

[8] Arrhenius, S.A. : Z. Phy. Chem., 1887, **1**, 631-648

[9] Evans, M.G., and Polanyi, M.: Trans. Faraday Soc., 1935, **31**, 875-893

[10] Erying, H. : J. Chem. Phys., 1935, **3**, 107-115

[11] Zajc, B. : J. Org. Chem., 1999, **64**, 1902

[12] Laidler, K.J. : Principles of Chemistry, Harcourt, Brace & Word, New York, 1966

[13] Kramers, H.A. : Physica, 1940, **7**, 284-304

[14] Arrhenius, S.A. .: Z. Phys. Chem., 1887, **1**, 631-648

[15] Prasad, S., and Halafihi, T. : Asian J. Chem. 2002, **44(B)**, 1909

[16] Exner, O. : Coll. Czech. Chem. Commun., 1964, **29**

[17] Yalman, R.G. : J. Chem. Edu., 1959, **36**, 215

[18] Neeraj, Shweta, Parihar, S.S. and Dwivedi, A.P. : Int. J. Adv. Research in Chemical Science (IJARCS) 2018, **4**, 9-14

[19] Neeraj, Shweta, Parihar, S.S. and Dwivedi, A.P. : Int. J. Adv. Research in Chemical Science (IJARCS) 2018, **5**, 25-30

[20] Neeraj, Shweta, Parihar, S.S. and Dwivedi, A.P. : Int. J. Adv. Research in Chemical Science (IJARCS) 2018, **5**, 1-5

Citation: *Neeraj, Shweta et al. "Oxidative Cleavage And Thermodynamic Study Of ℓ-Leucine And ℓ-Valine By 1,3-Dichloro-5,5-Dimethylhydantoin In Aqueous Acetic Acid Medium." International Journal of Advanced Research in Chemical Science (IJARCS) 5.9 (2018): 1-5. Web. 20 Nov. 2018.*

Copyright: *© 2018 Authors. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.*