IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 11, Issue 10 Ver. I (October. 2018), PP 55-58
www.iosrjournals.org

Oxidative cleavage of alpha amino acids ℓ–glycine and ℓ–valine by1,3-dichloro-5,5-dimethylhydantoin in medium of aqueous acetic acid medium

Arvind Prasad Dwivedi[1] Shweta Neeraj[2]
[1] *Department of Chemistry, Govt. Sanjay Gandhi Smrati Auto., P.G., College Sidhi M.P*
[2]*Department of Chemistry, Govt. Girls P.G. College (NAAC) Rewa-486001 (M.P.) India*
Corresponding Author; Arvind Prasad Dwivedi

Abstract: *1,3-dichloro-5,5-dimethylhydantoin (DCDMH) hydrolysed of this compounds leads to the formation of active positive halogen species like HOCl and H_2O^+Cl. The H_2O^+Cl in non-polar or less polar media, extensively used as a chlorinating and oxidizing agents in organic substrate. The rate of reaction is enhanced by the increasing $[H^+]$ and percentage of acetic acid. The main product of the oxidation is corresponding aldehydes. The thermodynamic parameters for the oxidation have been computed in the show step mechanism. The observed rate law was in good conformity with the mechanism.*

Key Words: *Conformity, decarboxylation, consistent, deamination.*

Date of Submission: 01-11-2018 Date of acceptance: 15-11-2018

I. Introduction

The chemistry of reactions of halo-compounds form a separate branch, which is a great synthetic importance.[1-4] N-halo compounds have been extensively employed as oxidising agents for the catalysed and uncatalyzed reactions.[5-12] An the recent development one such halo compounds 1,3-dichloro-5,5-dimethylhydantoin which is a mild oxidation. A lot of works on the oxidation of amino acids have been reported by different **oxidants**.[21-23] There is ℓ–glycine (NH_2CH_2COOH), and ℓ–valine ($(CH_3)_2CHCHNH_2COOH$) gives corresponding aldehydes.

II. Experimental

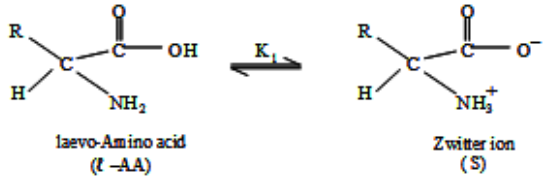
All the reagents and solvents used were of analytical grade (B.D.H., C.D.H. and Acros). The solutions used in study were made by using doubled distilled water. DCDMH was prepared in aqueous acetic acid was put in storage in a flask to prevent photochemical deterioration. All the reagents were freshly prepared just before the reactions were carried out phenolphthalein as an indicator. The solution of acrylonitrile monomer was also prepared by standard method for the identification of free radicals formed if during the course of reaction.

III. Results And Discussion

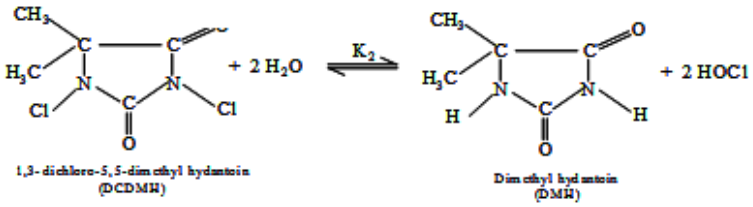
The completion of the reaction showed 1:1 (AA : DCDMH) stiochiometry. The oxidation products were indentified as formaldehyde and butyraldehyde respectively. The reactions occur at measurable rate within a temperature range 303 and 308 K respectively. The kinetic study was performed at several initial concentration of the amino acids at constant [DCDMH] $[H^+]$ and fixed percentage of acetic acid and temperature. The double reciprocal plot k^{-1} against $[substrate^{-1}]$ (Table 1, Fig. 1) is liner passing through origin with unit slope indicated first-order dependency with [substrate]. In order to determine the effect of dielectric constant of the medium on rate, the oxidation of ℓ–amino acids by DCDMH were studied in aqueous acetic acid mixtures of various compositions (Table 2). The plot of log k_1 vs. 1/ D were obtained linear with positive slope (Fig. 2) which accounts ion-dipole nature of the reaction.

MECHANISM

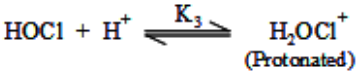
1,3-dichloro-5,5-dimethylhydantoin (DCDMH) on hydrolysis yields finally dimethyl- hydantoin (DMH) in aqueous solution. The following equilibrium exists.



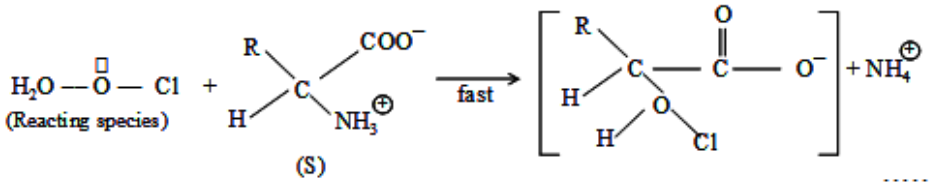
..... (1)



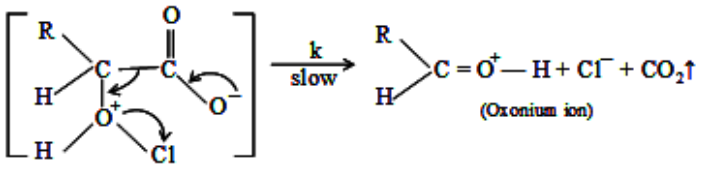
..... (2)



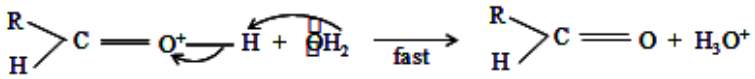
..... (3)



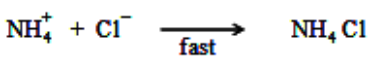
..... (4)



..... (5)



..... (6)



..... (7)

where, R = H and –CH–$(CH_3)_2$ for corresponding aldehydes.
The rate law is represented by equation (8).

$$k_{obs} = \frac{\text{Rate}}{[DCDMH]_T} = \frac{k\,K_1K_2K_3\,[S]\,[H^+]}{[DMH] + K_2} \qquad \text{..... (8)}$$

The order of reactivity is

ℓ-glycine (NH_2CH_2COOH) > ℓ-valine ($(CH_3)_2CHCHNH_2COOH$)

IV. Conclusion

Dichlorodimethylhydantoin (DCDMH) has been found as a moderate oxidant for the oxidation of ℓ–glycine and ℓ–valine. The thermodynamic and activation parameters determined are well in accordance with for the reacting involving Zwitter ions which supported the rate determining step in the proposed mechanism.

Table 1 : Effect of varying Amino acid on the rate of reaction
$10^3 \times$ [DCDMH] (mol dm^{-3}) = 2.50 (1, 2) ;
$[H^+]$ (mol dm^{-3}) = 0.50 (1), 0.80 (2) ;
CH_3COOH- H_2O % (v/v) = 20 (1), 50 (2) ;
Temp. K = 308 (1), 303 (2)

S. No.	10^2×[ℓ-AA] (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1}) ⟵ ⟶	
		ℓ-glycine ($NH NH_2 COOH$)	ℓ-valine ($((CH_3)_2CHCHNH_2 COOH$)
1.	0.50	1.95	-
2.	1.00	4.14	1.31
3.	1.25	4.75	1.74
4.	2.00	7.16	2.75
5.	2.50	8.91	3.82

Table 2 : Effect of Dielectric constant of the medium on the rate of oxidation
10^2 × [Substrate] (mol dm^{-3}) = 2.00 (1), 2.50 (2) ;
10^3 × [DCDMH] (mol dm^{-3}) = 2.50 (1, 2) ;
$[H^+]$ (mol dm^{-3}) = 0.66 (1), 0.80 (2) ;
Temp. K = 303 (1,2)

S. No.	CH_3COOH-H_2O % (v/v)	10^3/ D	k_1×10^4 (s^{-1}) ⟵ ⟶	
			ℓ-glycine ($NH NH_2 COOH$)	ℓ-valine ($((CH_3)_2CHCHNH_2 COOH$)
1.	10	15.50	4.28	-
2.	20	17.17	4.75	-
3.	30	19.15	5.16	-
4.	40	21.98	5.49	3.54
5.	50	25.64	-	3.82
6.	60	30.36	-	4.10
7.	70	38.04	-	4.33

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.V., 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]. Balasubramaniyan, P.V., and Mathiyalagan, 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.

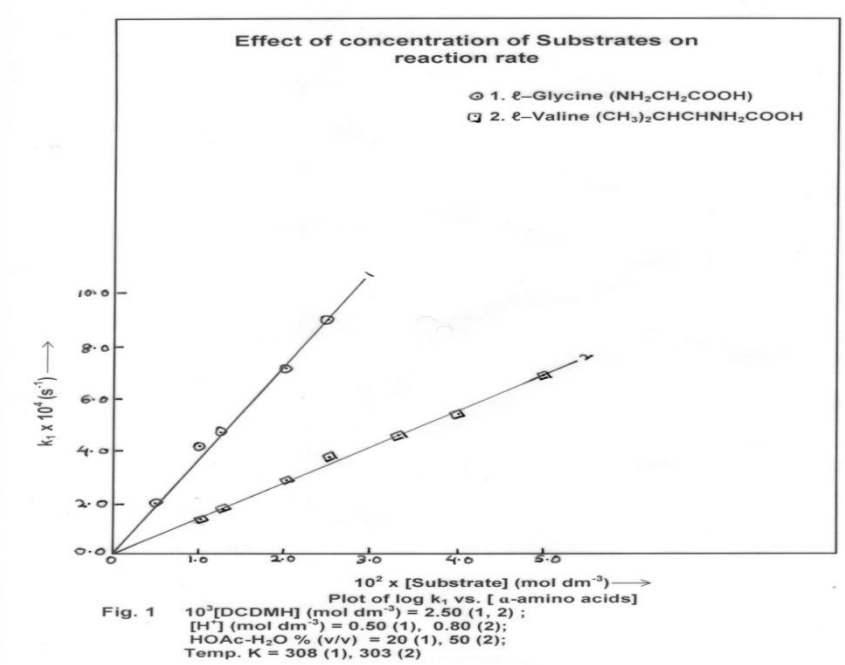


Fig. 1 10^3[DCDMH] (mol dm^{-3}) = 2.50 (1, 2) ;
$[H^+]$ (mol dm^{-3}) = 0.50 (1), 0.80 (2);
HOAc-H_2O % (v/v) = 20 (1), 50 (2);
Temp. K = 308 (1), 303 (2)

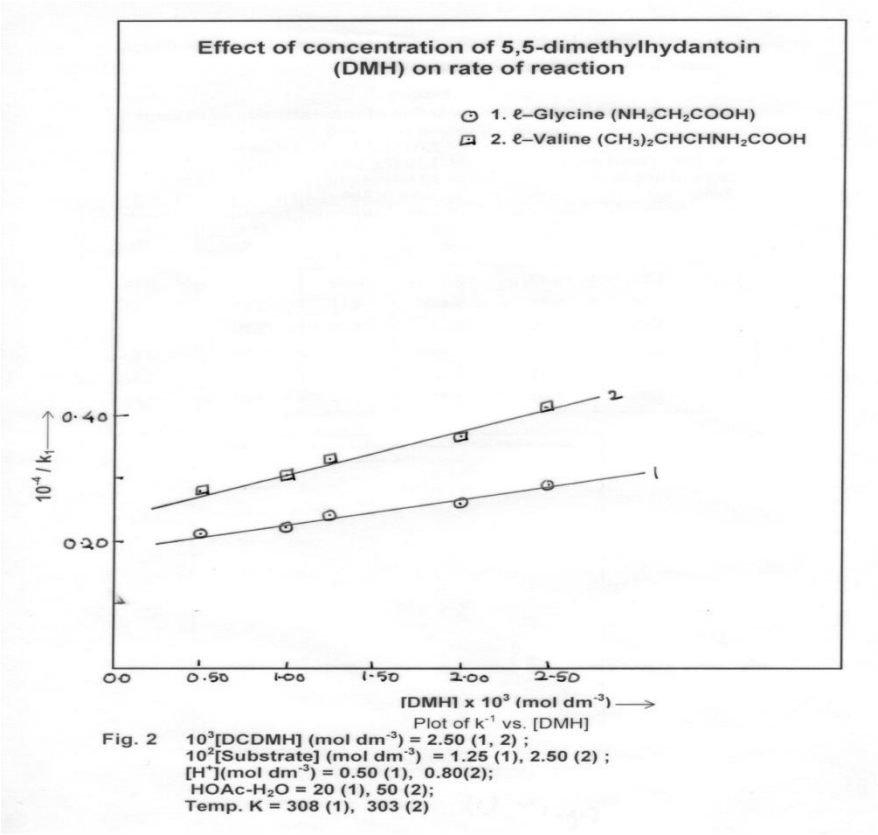


Fig. 2 10^3[DCDMH] (mol dm^{-3}) = 2.50 (1, 2) ;
10^2[Substrate] (mol dm^{-3}) = 1.25 (1), 2.50 (2) ;
$[H^+]$(mol dm^{-3}) = 0.50 (1), 0.80(2);
HOAc-H_2O = 20 (1), 50 (2);
Temp. K = 308 (1), 303 (2)

IOSR Journal of Applied Chemistry (IOSR-JAC) is UGC approved Journal with Sl. No. 4031, Journal no. 44190.

Arvind Prasad Dwivedi. " Oxidative cleavage of alpha amino acids ℓ–glycine and ℓ–valine by1,3-dichloro-5,5-dimethylhydantoin in medium of aqueous acetic acid medium." IOSR Journal of Applied Chemistry (IOSR-JAC) 11.10 (2018): 55-58