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Oxidation of ℓ–Alanine and ℓ–Leucine by 1,3-Dichloro-5,5-Dimethylhydantoin in Aqueous Acetic Acid Medium : A Kinetic Study

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Abstract: *The oxidation of ℓ–alanine and ℓ-leucine with 1,3-dichloro-5,5-dimethylhydantoin (DCDMH) was investigated in aqueous acetic acid medium at 303 K. The reactions follow pseudo first-order kinetics each in [DCDMH] and [ℓ-amino acids]. The reaction was observed acid catalysed. The study completely discarded the formation of complex and the involvement of free radicals. The study reveals that the reaction velocity retarted with increase in solvent composition. Thermodynamic parameters were computed. A suitable mechanism consistent with kinetic results has been proposed.*

Keywords: *Complex, versatile, exploration, scanty, probe, deterioration.*

1. INTRODUCTION

The versatile nature of oxidant 1,3-dichloro-5,5-dimethylhydantoin[1,2] is due to their ability to act as sources of halonium ion species which act as both bases and nucleophiles. DCDMH has been developed as an iodometric titrant[3] for the determination of certain pharmaceuticals kinetics exploration of ℓ–amino acids have been studied by utilising several oxidants, such as chloramine-B,[4] chloramine-T,[5-7] bromamine-T,[8,9] bromamine-B,[10,11] N-bromoacetamide,[12] N-chloronicotinimide,[13] etc. but survey of literature showed that oxidation of ℓ–alanine and ℓ–leucine by DCDMH is scanty in acetic acid medium. Hence, the authors have taken this problem for kinetic probe.

2. EXPERIMENTAL

All the chemicals and reagents in this investigation were of analytical grade. The solution of DCDMH (Acros 99%) was obtained by dissolving its weighed quantity in 100% acetic acid (B.D.H.) and stored in a black-coated flask to prevent any photo- chemical deterioration. Standard solution of ℓ–alanine and ℓ–leucine, sodium thiosulphate solution ($Na_2S_2O_3.5H_2O$) (C.D.H.), KCl, NaCl, H_2SO_4, $CuSO_4 \cdot 5H_2O$, DMH were prepared with distilled water and finally its concentration was iodometrically[3] using starch solution as an indicator. The kinetic study was initiated by mixing the requisite amount of DCDMH, acetic acid and $[H^+]$ placed at experimental temperature in a thermostat of sensitivity + 0.1^0C.

3. RESULTS AND DISCUSSION

After completion of the reaction showed 1:1 (AA: DCDMH) stiochiometry. The oxidation products were indentified as aldehydes and 5,5-dimethylhydantoin characterised by their spot test. The effect of varying [DCDMH] five-fold was examined by maintaining all other concentration of the reactants at constant temperature and fixed percentage of acetic acid. The values of rate constant were found to be constant, indicating first-order dependence of rate on [DCDMH] as evaluated from slope of plots (log (a-x) vs. time). The first-order rate constants were found to increase linearly with increase in [AA] (Table 1). The plot of 1/ k versus 1/[AA] (Fig.1) are linearly passing through the origin with unit slope showing first-order kinetics with respect to [AA]. The reaction rate measured with various $[H^+]$ were found to accelerate with increasing $[H^+]$ ion. It was also confirmed from the plot of log k against log $[H^+]$. The rate of oxidation increases moderately with increase in the percentage of acetic acid,

that is in increasing dielectric constant of the medium (Table 2 and Fig. 2). The H_2O^+Cl has been postulated as a prime reacting species participating the oxidation reactions.

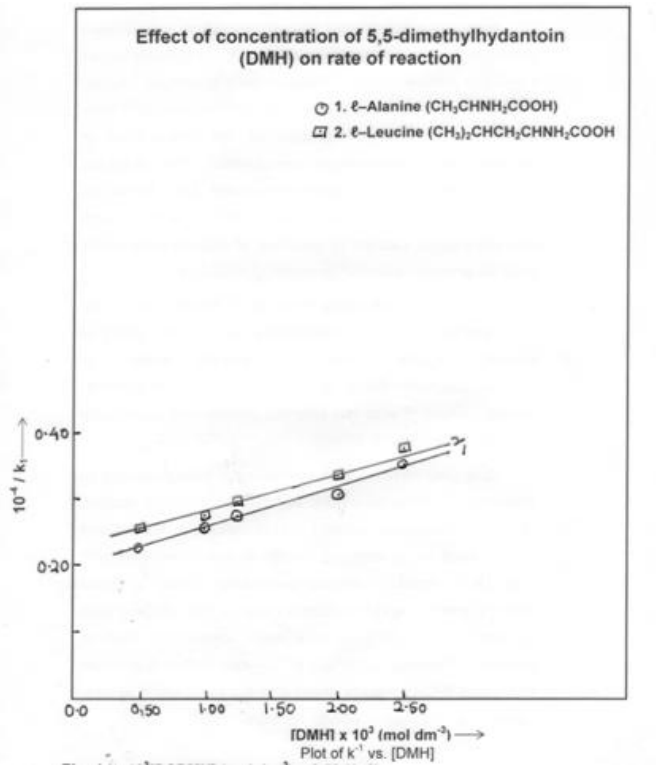


Fig1. *10^3[DCDMH] (mol dm-^{3}) = 2.50 (1,2); 10^2 [Substrate] (mol dm^{-3}) = 2.0 (1), 2.50 (2); [H^+] (mol dm^{-3}) = 0.66(1), 0.80(2); HOAc-H_2O = 30(1), 50(2); Temp.K = 303 (1,2)*

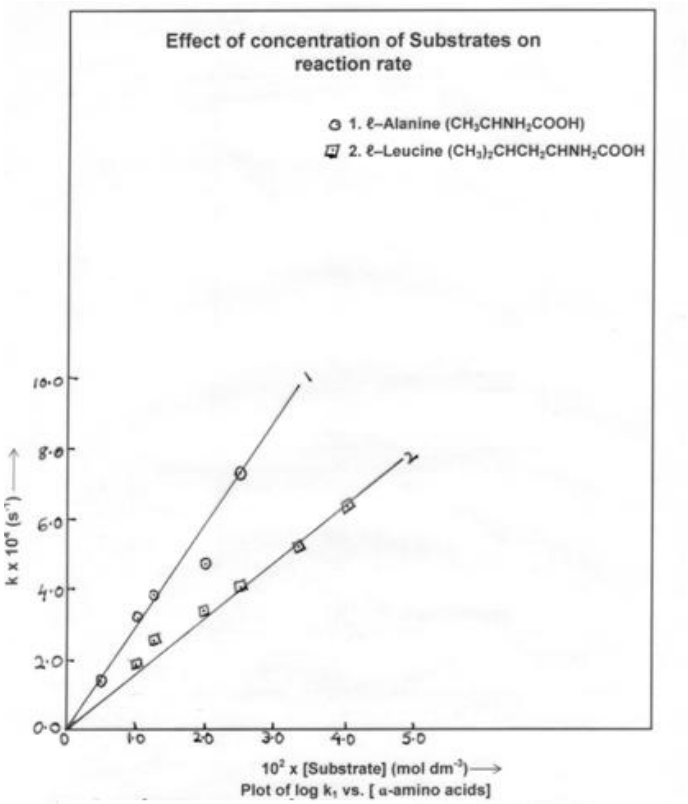
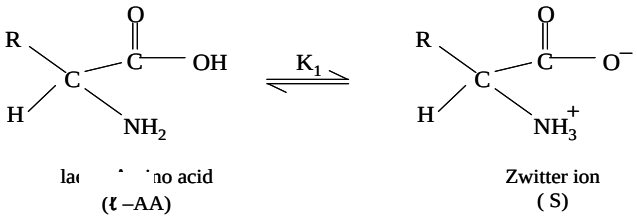


Fig2. *10^3 [DCDMH] (mol dm^{-3}) = 2.50 (1,2); [H^+] (mol dm^{-3}) = 0.66 (1), 0.80(2); HOAc-H_2O % (v/v) = 30 (1), 50 (2); Temp.K = 303 (1,2)*

4. MECHANISM

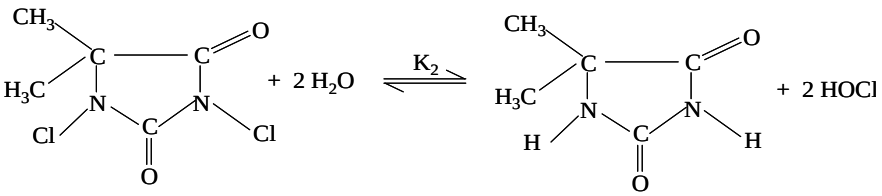
The following steps occur in the mechanism is given below:



la[illegible]no acid
(ℓ –AA)

Zwitter ion
(S)

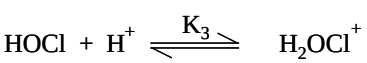
(1)



1,3- dichloro-5, 5-dimethyl hydantoin

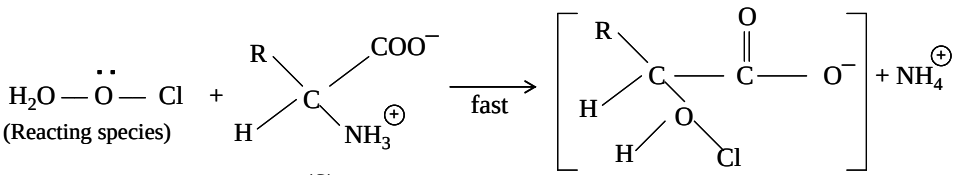
Dimethyl hydantoin

(2)

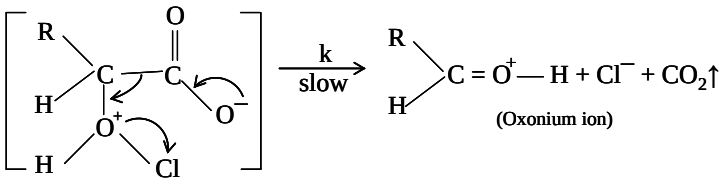


(Protonated)

(3)

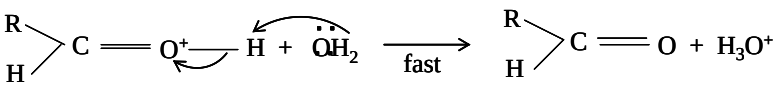


(4)

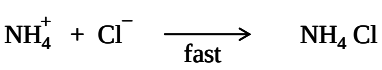


(Oxonium ion)

(5)



(6)



(7)

where, R = –H and $-CH_3$ for corresponding aldehydes.

The rate law based on mechanism is represented by equation (8).

$$\frac{-d}{dt}[DCDMH] = \frac{k\,K_1K_2K_3\,[S]\,[H^+]}{[DMH] + K_2} \qquad (8)$$

The observed order of reactivity was found in sequence ℓ-alanine > ℓ-leucine

The similar mechanism has also been reported in our[14,15] previous work for the oxidation study of ℓ–amino acid by halo oxidant. The rate determining step to give the final products such as acetaldehyde, isovaleraldehyde respectively. The nature of the short lived transition state is the same, for to the substrates studied by the order of observed entropy of activation.

5. CONCLUSION

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

Table1. *Effect of varying amino acids on the rate of reaction*

10^3 × [DCDMH] (mol dm^{-3}) = 2.50 (1, 2) ;

$[H^+]$ (mol dm^{-3}) = 0.66 (1), 0.80 (2) ;

HOAc-H_2O % (v/v) = 30 (1), 50 2) ;

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

S. No.	10^2×[ℓ-AA] (mol dm^{-3})	← $10^4 k_{obs}$ (s^{-1}) →	
		ℓ-alanine (CH_3 NH NH_2 COOH)	ℓ-leucine ($(CH_3)_2CHCH_2CHNH_2COOH$)
1.	0.50	1.43	-
2.	1.00	3.34	1.94
3.	1.25	3.92	2.87
4.	2.00	4.65	3.43
5.	2.50	7.33	4.05

Table2. *Effect of Dielectric constant of the medium on the rate of oxidation*

10^3 × [ℓ-AA] (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), 303 (2)

S. No.	CH_3COOH-H_2O % (v/v)	10 / D	← k_1×10^4 (s^{-1}) →	
			ℓ-alanine (CH_3 NH NH_2 COOH)	ℓ-leucine ($(CH_3)_2$ CH CH_2CHNH_2 COOH)
1.	10	15.50	-	-
2.	20	17.17	4.14	-
3.	30	19.15	4.65	-
4.	40	21.98	4.98	3.73
5.	50	25.64	5.40	4.05
6.	60	30.36	-	4.41
7.	70	38.04	-	4.81

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