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Effect of Oxidant 1, 3-Dichloro-5-5-Dimethylhydantoin and 5, 5-Dimethylhydantoin for ℓ–Glycine, ℓ-Alanine and ℓ–Leucine: The Kinetic Measurements

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Abstract: *The kinetic study with different concentration of oxidant 1,3-dichloro-5,5-dimethylhydantoin and 5,5-dimethylhydantoin with ℓ–glycine,ℓ-alanine and ℓ–leucinie. 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 of ℓ-amino acids (ℓ-glycine > ℓ–alanine > ℓ-leucine) was demonstrate on the basis of hydrolysis of reacting species.*

Keywords: *Kinetic study, concentration, catalytic effect, demonstrates reacting species.*

1. Introduction

N-chlorinated hydantoin have also received attention from the pharmacological community The myriad of adverse side- effects associated with hydantoin-based on drugs such as the anti-convulsant Dilantin and the aldose reductase inhibitor sorbinil have been attributed to N-chlorometabilities generated in vivo via chlorination by mycloperoxidase and hydrogen peroxide.[1-3] One approach involves passing chlorine gas through an aqueous alkaline solution of hydantoin.[4] The second method involves treatment of the hydantoin with an aqueous sodium hypochlorite solution (Chlorox®) followed by extraction.[5] TCCA has also been employed previously to chlorinate various amides and carbamates, although hydantoins were not represented in the studies.[6-7] The parent chiral hydantoins were prepared in high enantiomeric purity(confirmed by optical rotation) from the corresponding chiral α–amino acids by known methodology.[8-10]

2. Materials And Methods

All the chemicals and solvents used wee of analytical grade (B.D.H., C.D.H. and Acros). The solution of DCDMH is standardized iodometrically. The solution of sodium thiosulphate was prepared by taking a B.D.H. grade simple in a doubly distilled water and was standardized against copper sulphate solution using KI and starch as an indicator iodometrically. The 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.

3. Results And Discussion

The kinetic data have been collected for five-fold concentrations of the oxidant [DCDMH] (1.25 – 5.0 × 10^{-3} mol dm^{-3}) and at fixed concentration of ℓ–glycine at 308 K temperature (Table:1 and Fig. 1). The unit slope of plot of log [DCDMH] vs. time was found to be linear indicating first-order dependency on the reaction rate. The effect of [5,5-dimethylhydantoin] (DMH) on the rate of oxidation of was investigated by taking its varying five-fold concentration of (0.50 – 5.00 × 10^{-2} mol dm^{-3}) maintaining. The concentration of ℓ–alanine and ℓ–leucine constant at fixed temperature (Table: 2 and Fig. 2). The inverse plot of k^{-1} vs. [DMH] was obtained linear in each substrate.

Table1: *Effect of concentration of DCDMH on rate of reaction*

10^3 × [Substrate] (mol dm^{-3}) = 1.25;

$[H^+]$ (mol dm^{-3}) = 0.50;

CH_3COOH- H_2O % (v/v) = 20;

Temp. K = 308

S. No.	[DCDMH] $\times 10^3$ (mol dm^{-3})	⟵ $k_1 \times 10^4$ (s^{-1}) ⟶
		ℓ-glycine (NH_2CH_2COOH)
1.	1.25	4.69
2.	2.00	4.71
3.	2.50	4.75
4.	3.33	4.79
5.	4.00	4.73
6.	5.00	4.70

Table2: *Effect of variation of [5, 5-dimethylhydantoin] (DMH) on reaction rate*

10^3 × [DCDMH] (mol dm^{-3}) = 2.00 (1), 2.50 (2);

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

CH_3COOH- H_2O % (v/v) = 30 (1), 50 (2);

Temp. K = 303 (1, 2)

S. No.	[5,5-dimethylhydaotoin]$\times 10^3$ (mol dm^{-3})	⟵ $k_1 \times 10^4$ (s^{-1}) ⟶	
		ℓ-alanine (CH_3CHNH_2COOH) (1)	ℓ-leucine ($(CH_3)_2CHCH_2\,CHNH_2COOH$) (2)
1.	0.00	4.65	4.05
2.	0.50	4.37	3.81
3.	1.00	3.91	3.57
4.	1.25	3.68	3.33
5.	2.00	3.18	2.96
6.	2.50	2.81	2.62

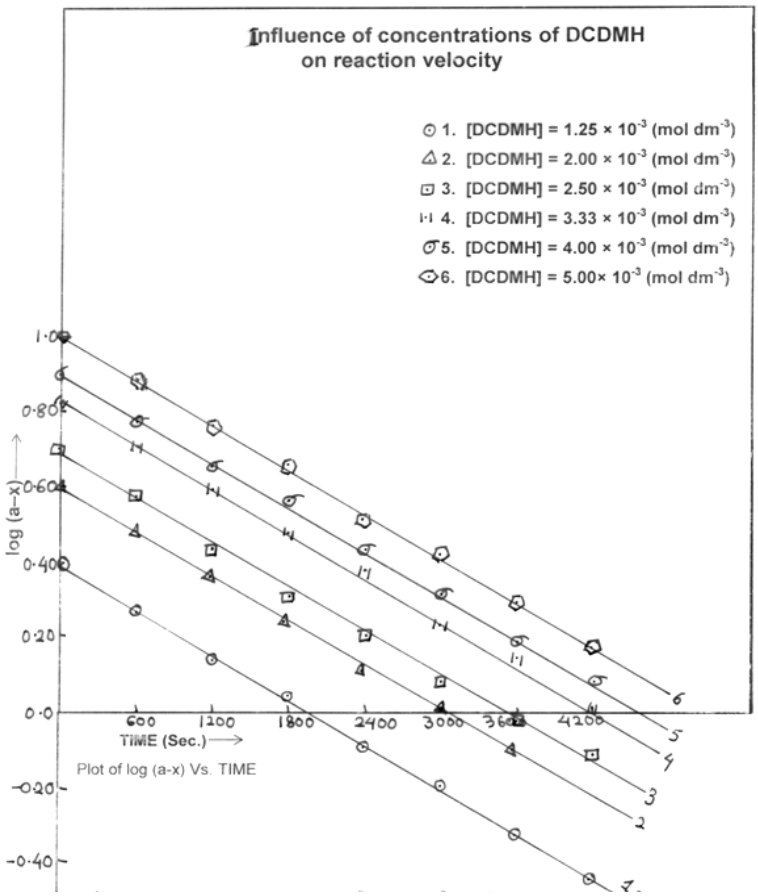


Fig1. *[ℓ-glycine] = 1.25 × 10^{-2}(mol dm^{-3}); $[H^+]$ = 0.50(mol dm^{-3}); HOAc-H_2O = 20% (v/v); Temp=308 K*

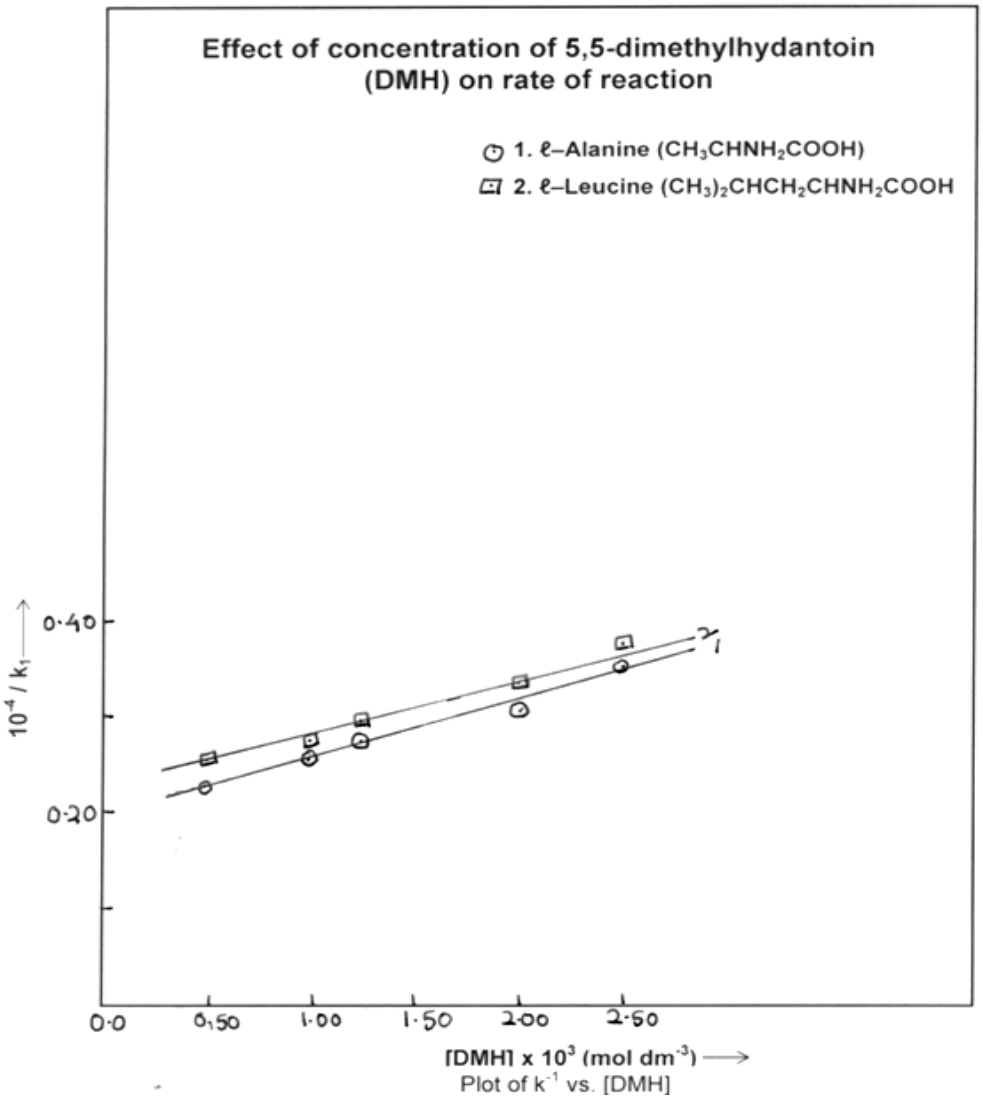
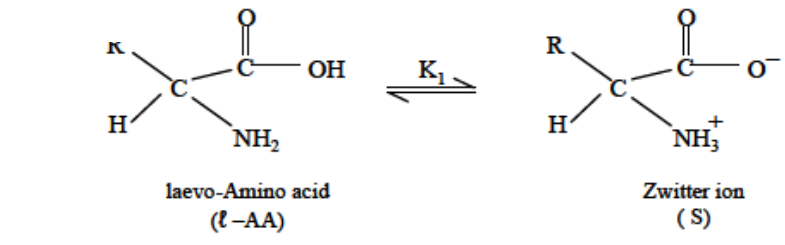


Fig2. *10^3 [DCDMH] (mol dm^{-3}) = 2.50 (1,2); 10^2 [Substrate] (mol dm^{-3}) = 2.0 (1), 2.50(2);[H^+] (mol dm^{-3}) = 0.66 (1), 0.80 (2); HOAc-H_2O = 30 (1), 50 (2);Temp. K =303 (1,2)*

3.1. Mechanism

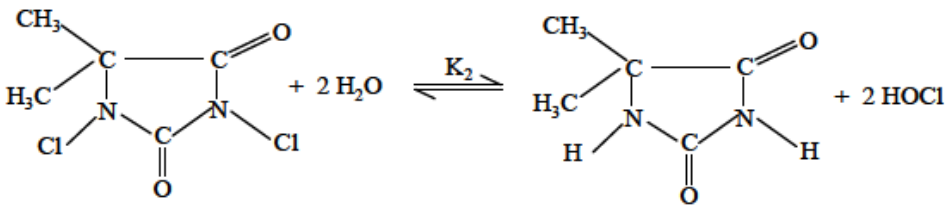
1,3-dihloro-5,5-dimethylhydantoin (DCDMH) on hydrolysis yields finally dimethylhydantoin (DMH) in aqueous solution. The following equilibrium exists.



(1)

laevo-Amino acid (ℓ –AA)

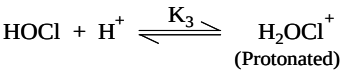
Zwitter ion (S)



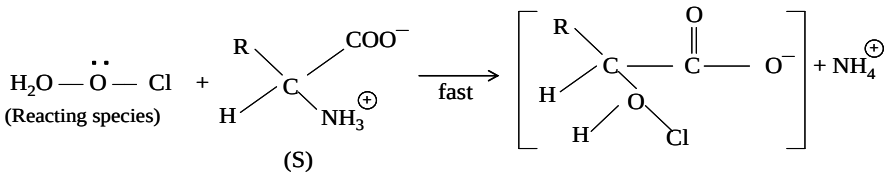
(2)

1,3- dichloro-5, 5-dimethyl hydantoin (DCDMH)

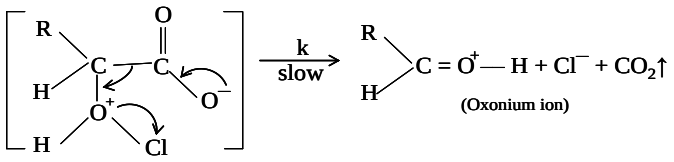
Dimethyl hydantoin (DMH)



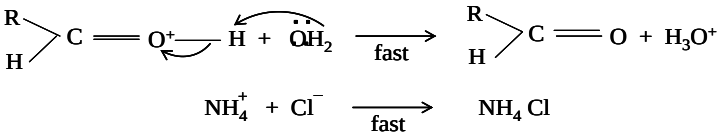
(3)



(4)



(5)



(6)

(7)

where, R = -H, $-CH_3$, $-CH_2CH(CH_3)_2$ for corresponding aldehydes.

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

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

The observed order of reactivity was found in sequence

ℓ-glycine > ℓ-alanine > ℓ-leucine

The similar mechanism has also been earlier reported by authors[11-14] for the study of ℓ-AA-DCDMH system. The reaction yielded acetaldehyde, formaldehyde and isovaleraldehyde end-products which is characterized by the spot test and other modern physical methods.

4. CONCLUSION

In conclusion, we have presented on operationally simple method for preparation of a number of N-chlorinated hydantoins by action of unpurified commercially available TCCA in undistilled solvents. Current efforts in our laboratory include exploiting these new chlorinating reagents for the organic synthesis.

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