

Study of Reactions between *p*-substituted acetophenones and 1,3-dichloro-5,5-dimethyl hydantoin

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Abstract: The kinetics of deprotonation from C-H bond of enolic *p*-chloroacetophenone and *p*-methoxyacetophenone by DCDMH has been studied in aqueous acetic acid medium. The substrate order is complex whereas rate is independent of the concentration of oxidant. The action of entropy ($-\Delta S^\ddagger$) indicates the presence of a symmetrical transition state in the slow process of rate-determining step. The analysis revealed the products of the reaction to be *p*-chloro- and *p*-methoxy phenyl glyoxals.

Key words: *p*-chloroacetophenone, *p*-methoxy acetophenone, oxidation, enolization, kinetics..

1. INTRODUCTION

1,3-dichloro-5,5-dimethyl hydantoin (DCDMH) is economically affordable, mild un-harmful, eco-friendly halo-oxidant. Basically this compound was known for its halogenating property,^[1-3] and find immense importance in bio-technology,^[4] and in organic synthesis.^[5-9] There are only a few reports on the mechanistic aspects of catalysed oxidation reactions of DCDMH in the literature.^[10-12] However, kinetic studies in aqueous acetic acid medium are scanty owing to an interaction of HOCl and H₂O⁺Cl species of oxidant in such systems. Therefore, this research is aimed at investigating the kinetics and mechanism of oxidation of *p*-chloroacetophenone and *p*-methoxy acetophenone by a halo-oxidant like DCDMH in aqueous acetic acid medium.

2. Materials and Methodology

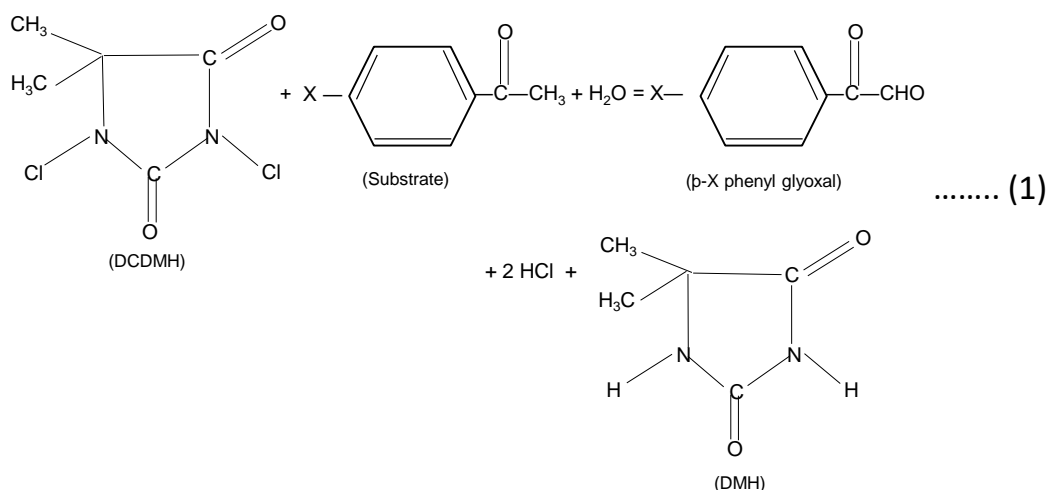
The solution of DCDMH (Across-A.G.) was prepared in acetic acid (B.D.H.) and standardized iodometrically before commencement of each reaction. The *p*-chloroacetophenone and *p*-methoxy acetophenone (Fluka) were distilled, under reduced pressure^[13] before use and solutions were prepared in appropriate volume of acetic acid and water. All other reagents employed in the kinetic study were of guaranteed reagent grade and were used as received.

3. Kinetic procedure

Kinetic experiments were installed in a water-bath thermostated at $\pm 0.1^\circ\text{C}$ unless stated otherwise. The reaction ingredients except DCDMH were kept in glass-stoppered Erlen-Meyer flasks. DCDMH was taken separately and the flasks were then immersed in water-bath. When these solutions attained the bath temperature, a volume of the requisite [DCDMH] was added to reaction mixture to initiate the reaction an aliquot (2 ml) of the reaction mixture was withdrawn periodically to monitor the disappearance [DCDMH] by estimating it with the help of iodometric process. Initial rates were computed by employing integration and graphical methods. Duplicate rate determinations were reproducible to within $\pm 3\%$.

4. Results and Discussion

The stoichiometry of DCDMH- *para*-substituted acetophenone reaction was determined from the change in values of DCDMH, it was established that one mole of DCDMH was required to oxidize one mole of substrate as conformed to overall equation :



where, X = Cl⁻, and p-CH₃O- for p-chloroacetophenone and p-methoxy acetophenone respectively. The corresponding products p-chloro- and p-methoxy phenyl glyoxals were analysed by TLC method and also with the help of forming their 2:4 DNP derivatives. The oxidation of p-substituted acetophenones by DCDMH in an atmosphere of nitrogen did not respond to induce polymerization of acrylamide^[14] and had no effect on the rate.

The concentration of DCDMH was varied from 1.0×10^{-3} to 4.0×10^{-3} (mol dm⁻³) at constant concentrations of other reaction ingredient and temperature. The plots of log (a-x) vs. time yields parallel lines and slope was obtained unity. This shows first-order dependence with regards to [DCDMH].

Michaelis-Menten type kinetics has been observed with respect to p-X acetophenones (Table 1). A plot of $\frac{1}{k_{obs}}$ versus $\frac{1}{[p-X \text{ acetophenone}]}$ is noticed linear with definite intercepts on the rate ordinate (Fig.1) indicating fractional-order kinetics for substrate.

Table 1: Dependence of rate on para-substituted acetophenone

$10^3 \times [\text{DCDMH}]$ (mol dm⁻³) = 3.33(1, 2) ; $[\text{H}^+]$ (mol dm⁻³) = 0.001(1, 2) ;
CH₃COOH-H₂O %, (v/v) = 25 (1), 50 (2), Temperature K = 318 (2), 323 (1)

$10^2 \times [\text{p-substituted acetophenone}]$ (mol dm ⁻³)	$10^4 k$ (sec ⁻¹)	
	p-Cl C ₆ H ₄ COCH ₃ (1)	p-CH ₃ O C ₆ H ₄ COCH ₃ (2)
1.00	1.34	1.75
1.50	1.83	2.46
2.00	2.66	2.91
2.50	-	2.73
3.33	3.80	-
4.00	-	4.55
5.00	4.42	4.77
6.25	4.58	-

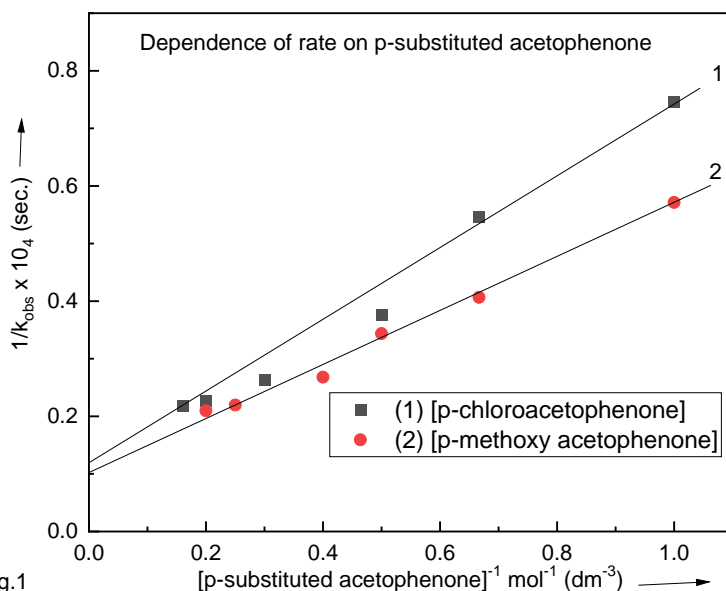


Fig.1

Michaelis-Menten plot of $1/k_{obs}$ vs. $1/[\text{p-substituted acetophenone}]$

$10^3 \times [\text{DCDMH}]$ (mol dm⁻³) = 3.33 (1, 2), $[\text{H}^+]$ (mol dm⁻³) = 0.001 (1, 2) ;
CH₃COOH-H₂O %, (v/v) = 25 (1), 50 (2), Temperature K = 318(2), 323 (1)

The reaction rate was observed 1 to 0 order with respect to $[\text{H}^+]$ (Table 2). The log-log plots of k_{obs} vs. $[\text{H}^+]$ (Fig.2) for each p-X acetophenone with non-zero intercept suggesting to follows two paths- one is independent of $[\text{H}^+]$ and other one is dependent. The rate law thus consists of two terms

$$k_{obs} = a + b [\text{H}^+] \dots \dots (2)$$

Table 2: Dependence of rate on [Acid] at 323 K

$10^2 \times [\text{p-substituted acetophenone}]$ (mol dm⁻³) = 1.50 (1), 2.0 (2) ;
 $10^3 \times [\text{DCDMH}]$ (mol dm⁻³) = 3.33 (1, 2) ; CH₃COOH-H₂O %, (v/v) = 25 (1), 50 (2)

Temperature K = 318 (2), 323 (1)

$10^3 \times [\text{H}^+]$ (mol dm ⁻³)	$10^4 k$ (sec ⁻¹)	
	p-Chloroacetophenone (1)	p-methoxy acetophenone (2)
0.50	1.15	1.71
0.80	-	2.51
1.00	1.83	2.91
1.25	2.21	-
1.50	-	3.70
1.66	2.87	-
2.00	3.34	4.57
2.50	3.86	5.37
3.33	4.13	-

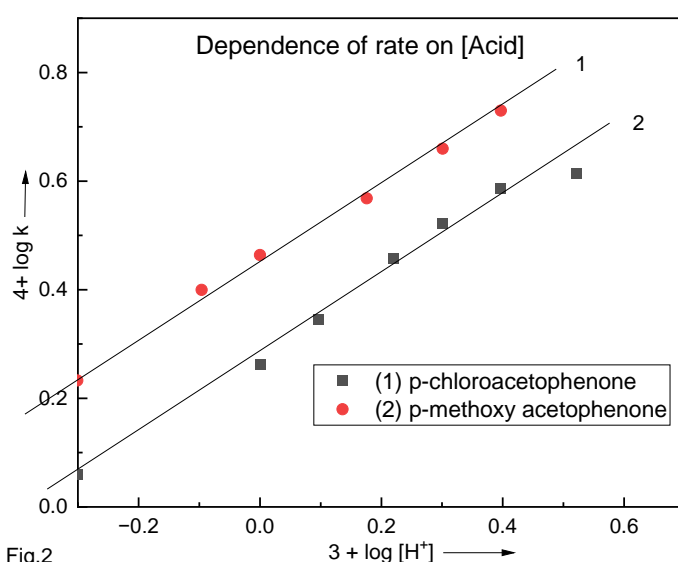


Fig.2

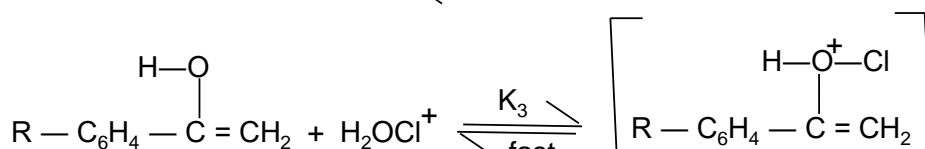
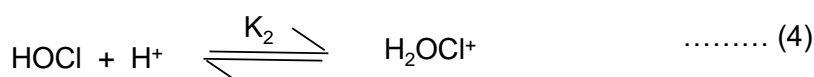
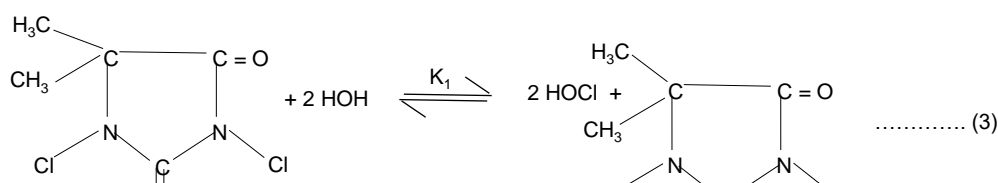
Graphic plot of $\log k$ vs. $\log [\text{H}^+]$
 $10^2 \times [\text{p-substd. acetophenone}]$ (mol dm⁻³) = 1.50 (1), 2.0 (2);
 $10^3 \times [\text{DCDMH}]$ (mol dm⁻³) = 3.33 (1, 2); CH₃COOH-H₂O %, (v/v) = 25 (1), 50 (2);
 Temperature K = 318 (2), 323 (1)

The rate of oxidation inhibited with increase in the percentage composition of CH₃COOH. This shows that all reactions were of ion-ion dipole type. The rate of reaction remains almost unaltered due to primary salt effect. The addition of di-methyl hydantoin diminishes the rate indicating that it does not participate in the reaction mechanism being a part of not reacting species.

The H₂O⁺Cl has been logically assumed as a powerful electrophile species of DCDMH that attacks probably enolic form of substrate in the rate determining step.

Mechanism

In accordance with the experimental observations and stoichiometry, the following reaction mechanism can be proposed for enolic p-X acetophenone :

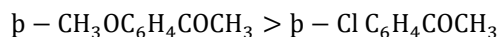


On execution of steady state approach, then such a mechanism leads to final rate law as :

$$k_{obs} = \frac{k K_1 K_2 K_3 [Enol][H^+]}{[DMH] + K_1 + K_1 K_2 [H^+] + K_1 K_2 K_3 [H^+][Enol]} \dots \dots (7)$$

A plot of $(k)^{-1}$ versus $[p\text{-X acetophenone}]^{-1}$ was made from equation (7) that yielded straight line with non-zero intercept supports, the veracity of prevailing rate law and confirms the existence of complex at transition state.

The observed order of reactivity is



The positive and negative inductive, mesmeric, resonance and steric effects in vis-à-vis to percentage of enolic content, and size of ionic radii of additives are copiously responsible for above sequence of reactivity and cleavage of C-H linkage in slow rate-determining step. The activation parameters justifies the order of above mechanism. Energy of activation (E_a) is lowest for fastest reaction (Table 3). Negative value of ΔS^\ddagger indicates an associative mechanism and a nature of rigid transition complex.^[15] The close relative values of Gibbs-free energy (ΔG^\ddagger) at most similar for the two substrates suggests the prevalence of identical mechanism. The reaction was assessed enthalpy and entropy controlled.

Table 3: Activation parameters for DCDMH- para-substituted acetophenone systems

Thermodynamic parameters	p-Cl C ₆ H ₄ COCH ₃	p-CH ₃ O C ₆ H ₄ COCH ₃
E _a (kJ mol ⁻¹)	61.81	52.61
A (s ⁻¹)	2.19 × 10 ⁶	1.16 × 10 ⁵
ΔH [‡] (kJ mol ⁻¹)	61.30	48.97
ΔG [‡] (kJ mol ⁻¹)	91.17	89.58
-ΔS [‡] (JK ⁻¹ mol ⁻¹)	91.74	126.69

Conclusion

In the oxidation of p-substituted acetophenones– DCDMH reaction, scission of C-H bond takes place in rate-determining step. The corresponding p-chloro- and p-methoxy phenyl glyoxal's were found to be the oxidation products. The present study also shows that DCDMH generates H₂O⁺Cl reacting species in presence of H⁺ that attacks enolic substrate to form complex at transition state (1:1) stoichiometrically.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

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