Kinetic Study of 1,3-dichloro-5,5-dimethyl hydantoin oxidation of þ-nitroacetophenone

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Abstract: ***The kinetic data for the oxidation of para-nitro acetophenone in 50% aqueous acetic acid with 1,3-dichloro-5,5-dimethyl hydantoin (DCDMH) at constant ionic strength (μ) is reported. A complex mechanism which involves H_2OCl^+ reacting species of oxidant in a rupture of C-H bond from the enolic para-nitro acetophenone in the rate determining step is suggested. The stoichiometry and rate law in conformity with observed kinetic features has been determined.***

Key words: þ-nitroacetophenone, DCDMH, kinetics, oxidation, stoichiometry.

1. INTRODUCTION

Halo-oxidant 1,3-dichloro-5,5-dimethyl hydantoin (DCDMH) is a source of positive halogens and has earlier been employed in the oxidation of organic substrates[1,2] and gaining synthetic importance in synthetic organic chemistry.[3-5] Most of this investigation related to substrate, where there is a possibility of enolization p-nitro acetophenone possess conjugate double bonds and completely delocalized by π-electron system on benzene ring. The > C=O or > C–OH group of the substrate is attacked by the oxidant. The kinetic and oxidation of p-nitroacetophenone by various oxidants like $kMnO_4$,[6] SeO_2,[7] CAT,[8] H_2CrO_4,[9] NDC,[10] Tl(III),[11] and MnO_4,[12] have been extensively reported by many eminent workers.

The available surveyed literature provides no information on the kinetics of oxidation of para-nitro acetophenone by DCDMH.

2. Experimental

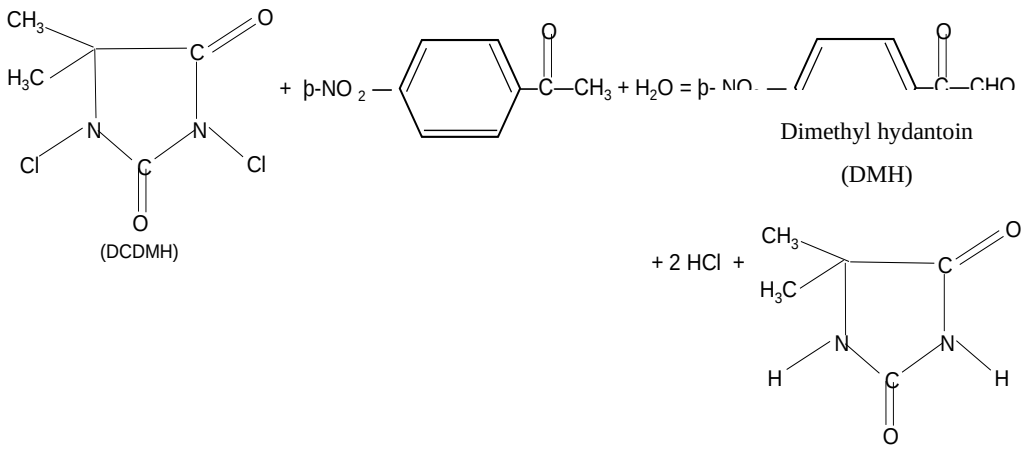
The þara-nitroacetophenone used was of Sigma (A.G.) grade and redistilled before use further purification. Its standard solutions was made in required volume of acetic acid (B.D.H.) and double distilled water. The solution of DCDMH was used in each set of experiment after its standardisation by iodometric process. All the reagents were freshly prepared just before the reactions were carried out.

3. Rate Measurements

The reaction vessels separately containing requisite volumes of standard DCDMH and p-nitroacetophenone along with other gradients were placed in an electrically operated thermostat fitted with stirrer maintained at 318 K (±0.1 K) for thermal equilibrium. After about half an hour when reactants had attained temperature of the bath, reaction was initiated by adding specified amount of DCDMH solution to reaction mixture. The progress of reaction was followed by estimating amounts of remaining DCDMH (2 ml.) at different intervals of time iodometrically using starch as an indicator. Care was taken to prevent the occurrence of any of the photochemical reactions of DCDMH. The rate constant (k_{obs}) was determined from the slope of the linear plots of log [titre] versus time. Replicate runs showed that k_{obs} for the oxidation rection was reproducible within 3%.

Stoichiometry and product analysis

The stoichiometry of the reaction was estimated by doing several sets of experiments under condition [DCDMH] >> [þ-nitroacetophenone] for 36 hours at 45^{0}C. The unconsumed [DCDMH] after completion of the reaction showed 1:1 (þ-nitro acetophenone : DCDMH ratio) stoichiometry formulated as



The oxidation products p-nitro phenyl glyoxal and DMH, were detected by TLC and spot tests.
The appearance of free radicals in reaction mixture is lacking when tested with acrylonitrile (monomer).

4. Results and Discussion

The rate of reaction $(-\frac{dc}{dt})$ was found direct proportionality with first-power of [DCDMH]. The derived values of k_{obs} by slopes measurement was found almost unity for the linear plot $\log_{10}$ (a-x) versus time.
The plot of $\frac{1}{k_{obs}}$ vs. $\frac{1}{[p-NO_2C_6H_4COCH_3]}$ is linear with definite intercept on the rate ordinate (Table 1) showing that the reaction is fractional-order in [p-$NO_2C_6H_4COCH_3$]. Hene it is concluded that the existence of complex follows the Michaelis-Menten type of kinetics (Fig.1).

Table 1: Dependence of rate on [þara-nitro acetophenone]

[DCDMH] = 3.33×10^{-3} (mol dm^{-3}) ; [H^+] = 0.002 (mol dm^{-3}) ;
$CH_3COOH \cdot H_2O$ = 30 : 70 %, (v/v) ; Temp. = 323 K

$10^2 \times$ [þ-$NO_2C_6H_4COCH_3$] (mol dm^{-3})	10^4 k (sec^{-1})
1.25	1.21
1.66	1.60
2.50	2.18
3.33	2.64
5.00	3.08
6.25	3.14

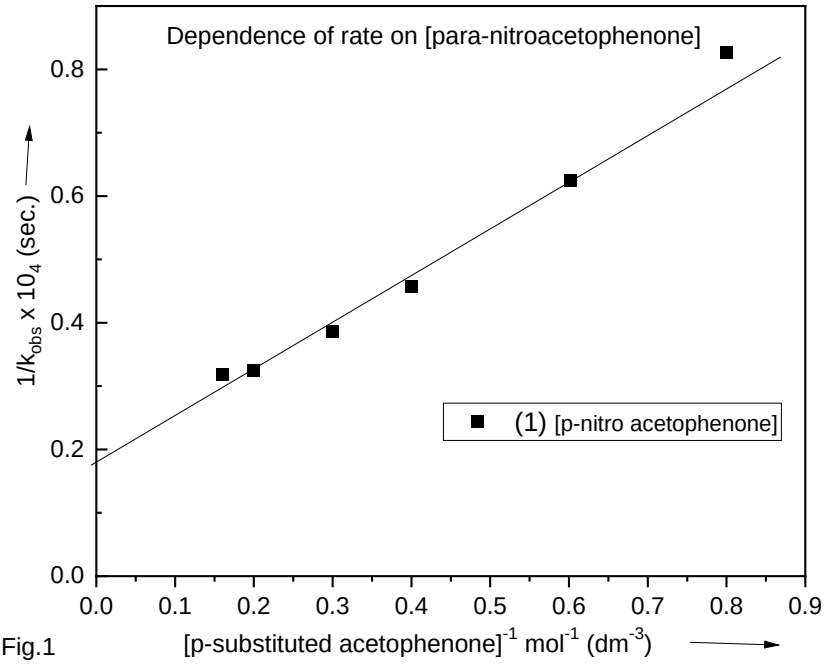


Fig.1 Michaelis-Menten plot of 1/ k_{obs} vs. 1/[p-nitro acetophenone]
[DCDMH] = 3.33 x 10^3 (mol dm^{-3}) ; [H^+] = 0.002 (mol dm^{-3}) ;
CH_3COOH-H_2O = 30 : 70 %, (v/v) ; Temp. = 323 K

The reaction is catalysed by H^+ ions (Table 2). The fractional-order kinetics exhibited [H^+] is further evidenced by plot of log k vs. log [H^+] (Fig.2). The rate constant (k_{obs}) follow two paths as a pattern of [H^+][13,14] of i.e. the hydrogen ion dependence has the following form k_{obs} = a + b [H^+].

Table. 2: Effect of [H^+] on rate

[þ-$NO_2C_6H_4COCH_3$] = 1.66×10^{-2} (mol dm^{-3}) ; [DCDMH] = 3.33×10^{-3} (mol dm^{-3}) ;
$CH_3COOH \cdot H_2O$ = 30 : 70 %, (v/v) ; Temp. = 323 K

$10^3 \times [H^+]$ (mol dm^{-3})	10^4 k (sec^{-1})
1.00	1.10
1.25	1.31
1.50	1.41
2.00	1.60
2.50	1.99
3.33	2.33
4.00	2.65

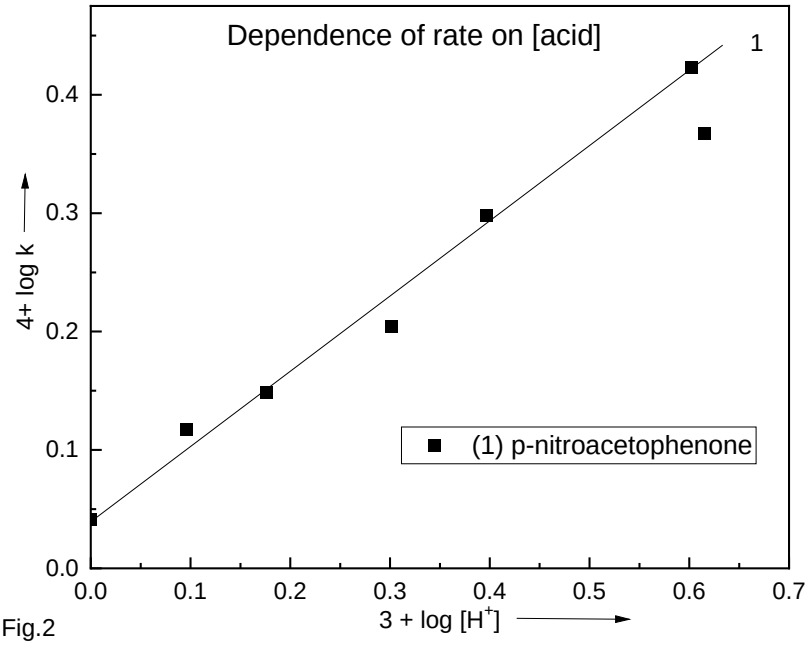


Fig.2

Graphic plot of log k vs. log $[H^+]$

[p-nitro acetophenone] = 1.66 x 10^{-2} (mol dm^{-3}) ;
[DCDMH] = 3.33 x10^3 (mol dm^{-3}) ;
CH_3COOH-H_2O = 30 : 70 % (v/v) ; Temp. = 323 K

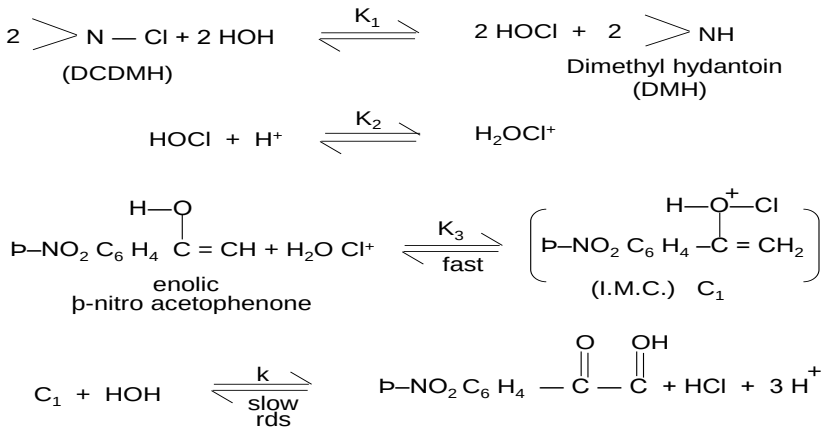
The data clearly revealed that the rate decreases with increase in the percentage of acetic acid.[15] This version shows that the reaction was of ion-ion dipole type. The addition of various amounts of NaCl shows neutrality towards the rate of reaction, while negative effect of variation of [dimethyl hydantoin] on the rate was observed.

Mechanism

þ-nitroacetophenone contains enolic group which is attacked by protonated reactive species H_2OCl^+ to form an unstable intermediate complex at this site which in turn decomposes in a rate determining step by hydrolysis to yield the final products such as þ-nitrophenyl glyoxal and di-methyl hydantoin (DMH).

The considering the kinetic observation, stoichiometry and reacting species H_2O^+Cl, the most probable mechanism of the reaction is constituted.

(Scheme-1)



Final rate law

$$-\frac{d}{dt}[DCDMH] = \frac{k\,K_1K_2K_3[Enol\,[H^+]}{[DMH] + K_1 + K_1K_2[H^+] + K_1K_2K_3[H^+]\,[Enol]}$$

Transforming above equation for Michaelis-Menten plot $\frac{1}{k_{obs}}$ vs. $\frac{1}{[substrate]}$, which gives positive intercept on rate axis provides an evidence for solvated rigid activated complex formation. The rate expression also fully explains all version of observed kinetic results.

The mechanism involves deficient cationic centre transition state is solely responsible for rupture of C-H bond by the inductive effect influence of less electron withdrawing negative mesomeric NO_2 group. The bond fission in rate determining step in the oxidation was also supported by the loss of translational and rotational freedom in the process spectroscopically. The values of Arrhenius parameters have also been measured for the foregoing reaction.

Conclusion

The DCDMH has been proven to be an effective oxidising agent for the oxidation of þ-nitroacetophenone. The kinetic and activation parameters for the reaction of enolic form of substrate by DCDMH were measured and one scheme of the mechanism was formulated. The reaction showed Michaelis-Menten type kinetics. The fission of C–H bond occurs by the influence of -I effect, -M effect and loss of translational and rotational freedom in the process displayed by NO_2 moiety. The stoichiometric substantive quantitative relationship suggested that for each mole of oxidant one mole of þ-$NO_2C_6H_4COCH_3$ was consumed as studied by iodometric method. The study revealed that reaction exhibits first-order rate in [DCDMH] and fractional-order each with respect to [substrate] and [H^+].

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Conflict of Interest

The authors declare no conflict of interest.

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