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Kinetics of Permanganate Oxidation of Acetophenones in Aqueous Acetic acid : A Mechanistic Study

P.S. SHEEBA† and T.D. RADHAKRISHNAN NAIR*
Department of Chemistry
Calicut University, Calicut-673 635, India

The kinetics of oxidation of acetophenone by potassium permanganate have been studied in 50% aqueous acetic acid medium. The reaction is first order with respect to both, substrate and oxidant. The oxidation is catatyzed by H_2SO_4. Acetic acid in the reaction mixture retards the rate. Ionic strength effect is negligible. The stoichiometry of 1 mol of acetophenone : 1 mol of permanganate was observed. The order of reactivity of the acetophenones decreases as p-NO_2 > m-NO_2 > p-Br > p-Cl > -H > p-CH_3 > p-OCH_3. Hammet's plot gave linear relation with ρ-value of +7210, indicating that electron withdrawing groups accelerate the process. Activation parameters have been evaluated. Exner's plot gave linear relation and the isokinetic relationship has been found operating. A suitahle mechanism has been proposed.

Key Words: Kinetics, Oxidation, Acetophenones, Potassium permanganate, Mechanism.

INTRODUCTION

The kinetic and mechanistic aspects of oxidation of acetophenones by a number of oxidants have received considerable attention. Mechanism of oxidation of acetophenones with two-electron oxidants[1–5] differs from that of one-electron oxidants[6–8] mainly in the involvement of enol or keto form of the substrates. Even though the oxidation of acetophenone by potassium permanganate in acidic conditions has been mentioned along with the oxidation studies of some aliphatic and cyclic ketones[4], a detailed kinetic study of oxidation of acetophenone by permanganate is lacking. The present investigation is an attempt in this direction.

EXPERIMENTAL

Acetophenones (BDH, India) were distilled under reduced pressure before use. Acetic acid (AnalaR quality) used was distilled twice from potassium dichromate. Doubly distilled water was used for the entire work.

The kinetic experiments were carried out above room temperature in thermostatic water baths in the temperature range of 308–323 K. The concentration of acetophenone in aqueous acetic acid was maintained in large excess over the concentration of permanganate. The progress of the reaction was followed by measuring the absorbance of the unreacted permanganate (λ_{max} 526 nm) using Shimadzu (UV-1602) spectrophotometer.

†Department of Chemistry, Malabar Christian College, Calicut, India.

RESULTS AND DISCUSSION

Stoichiometry of the reaction has been investigated by equilibrating known amounts of acetophenones and permanganate at room temperature for about 2 days. The completion of the reaction was ensured by estimating the oxidant remaining in excess by iodimetric titration method. It was found that one mole of permanganate consumed one mole of acetophenone. The product of the oxidation was identified as benzoic acid.

Kinetic investigation of the oxidation of acetophenone by potassium permanganate was made at several concentrations by keeping [AcPh] constant and varying the $[MnO_4^-]$. Studies were also made by varying [AcPh] at constant $[MnO_4^-]$. The rate constants obtained are given in Table-1.

TABLE-1
EFFECT OF THE CONCENTRATION OF SUBSTRATE AND OXIDANT ON REACTION RATE

Acetic acid = 50% (v/v), Temp. = 308 K

$[MnO_4^-] \times 10^3$ mol dm^{-3}	[AcPh] $\times 10^2$ mol dm^{-3}	$k_{obs} \times 10^5$ sec^{-1}
0.5	1.0	4.22
1.0	1.0	4.29
1.5	1.0	4.26
2.0	1.0	4.33
1.0	1.0	4.29
1.0	1.5	6.25
1.0	2.0	8.98
1.0	2.5	10.82

Under the conditions [AcPh] $\gg$ $[MnO_4^-]$, the plots of log $[MnO_4^-]$ *vs.* time were linear indicating first order reaction with respect to $[MnO_4^-]$. This was further confirmed by the constancy in the pseudo-first order rate (k_{obs}) constants, for varying $[MnO_4^-]$. The plots of log k_{obs} *vs.* log [AcPh] were linear with unit slope indicating the first order dependence on [AcPh] (Fig. 1A). This was confirmed from the second order rate constant ($k_2 = k_{obs}/[AcPh]$) obtained. The double reciprocal plot of $1/k_{obs}$, *vs.* 1/[AcPh] (Lineweaver-Burke plot) passes through the origin indicating that no stable complex is formed or the complex even if formed has only a transitory existence (Fig. 1B).

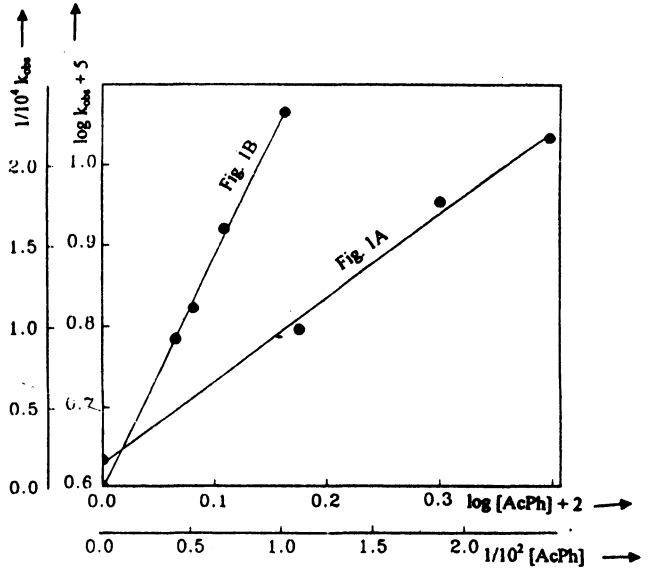


Fig. 1. (A) Plot of log k_{obs} + 5 *vs.* log [AcP] + 2
(B) Lineweaver-Burke plot of $1/10^4$ k_{obs} *vs.* $1/10^2$ [AcP]

The effects of sulphuric acid concentration and sodium chloride concentration have been studied. There is a linear increase in rate with increase of $[H^+]$ and the plot of log k_{obs} *vs.* log $[H^+]$ (Fig. 2A) is linear and shows fractional order dependence with sulphuric acid concentration. The increase in [NaCl] does not affect the rate significantly. Hence the reaction is either between two neutral molecules or between a neutral molecule and an ion or a dipolar entity. However, the addition of $MnSO_4$ decreases the rate (Table-2). This could be possibly due to the fact that Mn atom is involved in some stage of the reaction forming a complex with the substrate. The complexed $MnSO_4$ is not able to oxidize the substrate unlike the MnO_4^- moiety.

TABLE-2
EFFECT OF $[MnSO_4]$ ON REACTION RATE

$[AcPh] = 1.0 \times 10^{-2}$ mol dm^{-3}, $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}, Temp. = 308 K

$[MnSO_4] \times 10^3$ mol dm^{-3}	0	1.0	1.5	2.0
$k_{obs} \times 10^5$ sec^{-1}	4.29	2.84	2.53	2.30

The effect of dielectric constant on the rate of oxidation was also investigated. It was found that the rate constants decreased with increase in composition of acetic acid or decrease of dielectric constant (Table-3). However, there is no linearity for the plot of log k_{obs} *vs.* 1/D (Fig. 2B). This may be due to the inerease in the rate of enolization of acetophenone with the inerease in acetic acid[9].

TABLE-3
EFFECT OF SOLVENT POLARITY ON REACTION RATE

[AcPh] = 1.0×10^{-2} mol dm^{-3}, [MnO_4^-] = 1.0×10^{-3} mol dm^{-3}, Temp. = 308 K

HOAc%	20	40	50	60	80
Dielectric constant	61	47	39.8	32	17.5
$k_{obs} \times 10^5$ sec^{-1}	4.64	4.33	4.29	3.68	3.41

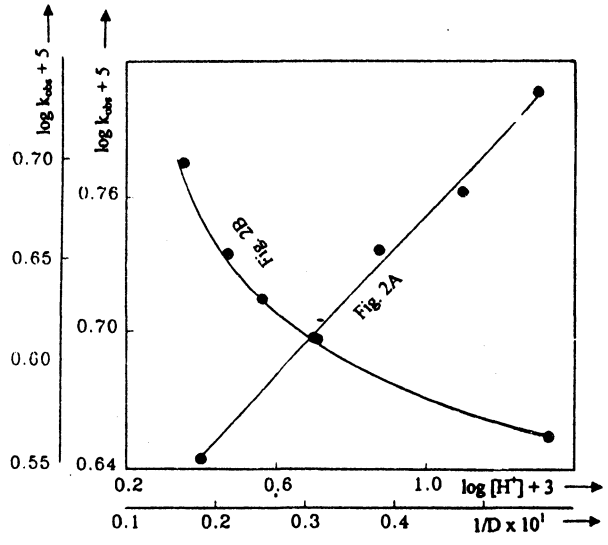


Fig. 2. (A) Plot of log k_{obs} + 5 *vs.* log $[H^+]$ + 3 (B) Plot of log k_{obs} + 5 *vs.* $1/D \times 10^1$

The activation parameters have been studied from the temperature coefficient of rates. The reactions were carried out in the temperature range of 308–323 K and the pseudo-first order rate constants were evaluated for the different acetophenones. The associated thermodynamic parameters were calculated from the Arrhenius plot and the values are given in Table-4. Free energy of activation, $\Delta G^{\#}$ remains practically constant at 90 kJ mol^{-1} for all the acetophenones studied. This is suggestive of similarity in the mechanism for the reaction of all the substrates employed. The isokinetic plot of $\Delta H^{\#}$ *vs.* $\Delta S^{\#}$ further confirms this and the isokinetic temperature ($\beta = 272.0$) evaluated is less than the experimental range of temperature (308–323 K), indicating that the reaction is enthalpy controlled. Exner's plot of log k′ (50°) *vs.* log k′ (35°) is also linear showing the existence of isokinetic relationship ($\beta = 265.15$).

The reactivities of the different substituted acetophenones are found to be in the decreasing order, *p*-NO_2 > *m*-NO_2 > *p*-Br > *p*-Cl > -H > *p*-CH_3 > *p*-OCH_3. The Hammet's plot is linear and a reaction constant of +0.7210 is obtained (Fig. 3). This +ve value indicates that electron-withdrawing groups accelerate the process while electron-donating substituents retard the process and are in agreement with the suggested mechanism.

TABLE-4
EFFECT OF TEMPERATURE ON REACTION RATE

[AcPh] = 1.0×10^{-2} mol dm^{-3}, [MnO_4^-] = 1.0×10^{-3} mol dm^{-3}

Acetophenone	$k_{obs} \times 10^5$ (sec^{-1})	E_a (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$-\Delta S^{\#}$ (JK^{-1} mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
p-NO_2	13.81	65.83	63.24	75.05	86.36
m-NO_2	12.20	57.37	54.73	103.65	86.65
p-Br	5.94	43.24	40.64	155.38	88.50
p-Cl	5.33	48.31	45.67	139.95	88.77
-H	4.29	38.17	35.55	174.60	89.33
p-CH_3	2.80	47.47	44.86	148.89	90.72
p-OCH_3	2.30	30.07	27.45	206.10	90.93

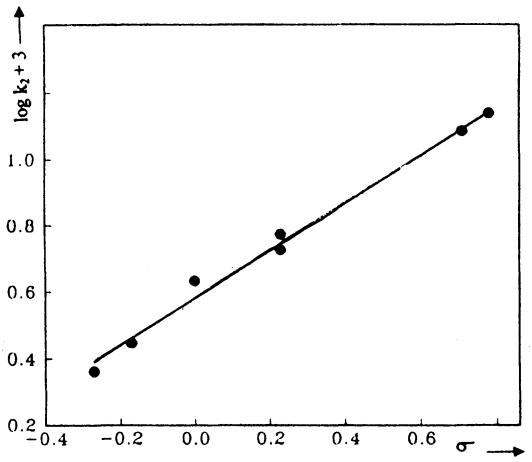
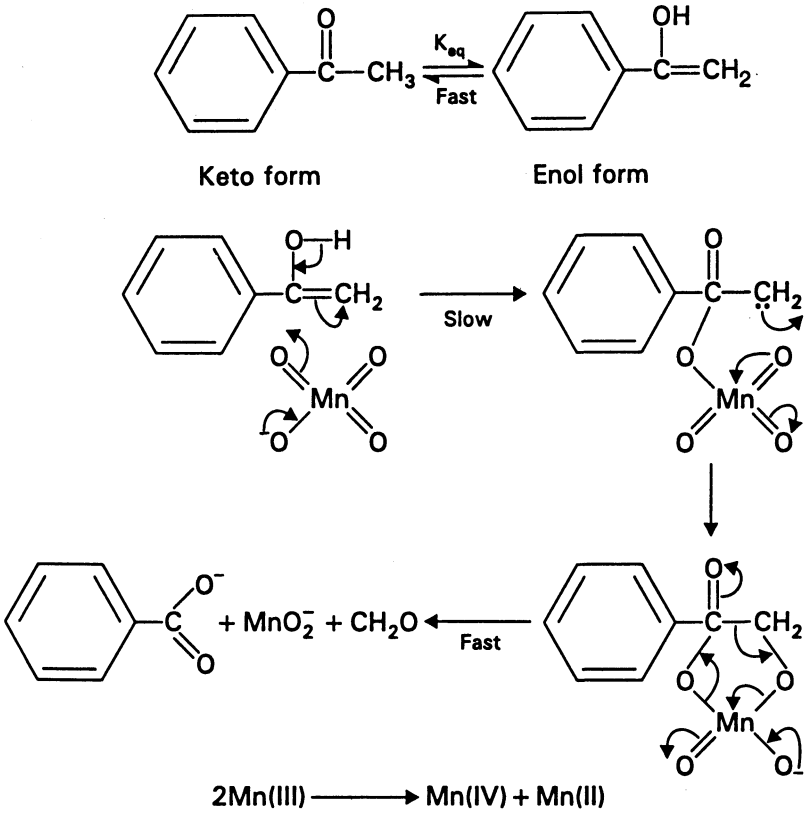


Fig. 3. Hammett plot for the oxidation of acetophenone.

Mechanism

In the light of all the experimental results obtained in the present investigation and the evidences from other investigations the following mechanistic steps have been proposed for the oxidation of acetophenone using $KMnO_4$ in aqueous acetic acid medium.



Scheme-1

The mechanism given above explains the experimental observations and the stoichiometry well (1 : 1 AcPh : $KMnO_4$). It is in keeping with the effect of ionic strength and the influence of dielectric constant of the medium. The activation, parameters, especially the $\Delta S^{\#}$, substituent effects, effect of added mineral acid and the effect of the product of oxidation support the same. The mechanism proposed doesn't involve any free radicals, which is endorsed by the non-polymerization of added acrylonitrile. Thus the reaction proceeds *via* enol form of the acetophenone and the oxidant is permanganate ion. The rate-determining step involves a two-electron transfer from the the enol form of acetophenone, resulting in the formation of an intermediate, which is a fast step gives the products.

The oxidation of all acetophenones was studied at different temperatures and the activation parameters were evaluated. The free energy of activation, $\Delta G^{\#}$, is found to be nearly same for all acetophenones studied (*ca.* 90 kJ mol^{-1}), suggesting that a similar mechanism is operating in the series. The isokinetic and Exner's plot are linear with $\gamma = 0.9974$ and $\gamma = 0.9849$ respectively, further supporting the operation of an identical mechanism for all the acetophenones studied.

Based on the proposed mechanism, the rate law has been deduced as follows.

$$\frac{d[MnO_4^-]}{dt} = k_2\left[C_6H_5{-}\overset{\displaystyle OH}{\overset{|}{C}}{=}CH_2\right][MnO_4^-]$$

where $$\left[C_6H_5{-}\overset{\displaystyle OH}{\overset{|}{C}}{=}CH_2\right] = K_{eq}\left[C_6H_5{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3\right]$$

$$\therefore \quad \frac{d[MnO_4^-]}{dt} = k_2K_{eq}\left[C_6H_5{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3\right][MnO_4^-]$$

The above rate law expression is in agreement with the observed order, *i.e.*, second order kinetics being first order in each reactant, ionic strength, effect of dielectric constant of the medium, etc.

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