

Oxidation of Some 1-Aryl Ethanol Using Permanganate in Aqueous Acetic Acid Medium: A Kinetic Study

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Kinetic studies on the permanganate oxidation of some 1-aryl carbinols in aqueous acetic medium have been carried out. The reaction showed first order dependence with respect to both the oxidant and the substrate concentration. The rate increased with increase in the $[H^+]$ but with a complex order. Effects of ionic strength and dielectric constant of the medium have been investigated. The effects of the various substituents at the *para* position of the benzene ring gave quite interesting results and were not in conformity with the Hammett equation. Both the electron-releasing and the electron-withdrawing groups have been found to enhance the rate. A plausible mechanism guided by frontier molecular orbital theory was suggested.

Key Words: Oxidation, 1-Aryl ethanol, Kinetics.

INTRODUCTION

Oxidations of organic compounds are quite important from the synthetic and technological viewpoints. Many industrially important organic compounds like aldehydes, ketones, carboxylic acids, etc. are produced by the oxidation of related substrate by the use of suitable oxidising agents. The oxidants more commonly used for oxidation include many inorganic oxidants such as permanganate, dichromate, hypochlorite, bromate, etc. Kinetic studies on the oxidation of secondary carbinols are scanty¹ though there are some similar works related to primary alcohols²⁻⁴ and hence the present work. We report here the kinetics and mechanism of the oxidation of some 1-aryl ethanol using potassium permanganate in aqueous acetic acid medium.

EXPERIMENTAL

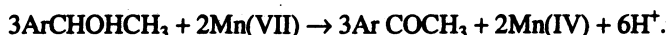
1-Phenyl ethanol used was commercially available (E. Merck German). The *p*-Me, *p*-Cl, *p*-OMe and *p*-NO₂ 1-phenyl ethanol were prepared by the sodium borohydride reduction of corresponding acetophenones and were purified according to literature. AR grade glacial acetic acid used was refluxed for 6 h with chromic acid and acetic anhydride and fractionally distilled before use. Stock solutions of the substrate were prepared in purified glacial acetic acid as and when required. All other chemicals used were of AnalaR grade. Double distilled water was always used.

The kinetic measurements were made under pseudo first order condition by maintaining [substrate] \gg [oxidant]. Appropriate quantities of the oxidant, acetic acid and water were taken in a pyrex glass bottle in a thermostatic bath. The reaction was initiated by adding requisite amount of thermally equilibrated solutions of the substrate to the above mixture. Aliquots were removed at definite time intervals and the unreacted permanganate ions were estimated iodometrically. The rate constants were calculated by the method of least squares. Duplicate kinetic runs showed that the rate constants were reproducible to within $\pm 3\%$. All the kinetic runs were carried out in 40% (v/v) aqueous acetic acids medium, unless mentioned otherwise.

RESULTS AND DISCUSSION

The product of the oxidation was ascertained to be acetophenone from the formation of the corresponding 2,4-dinitrophenyl hydrazone (DNP).

The stoichiometry of the reaction was established by equilibrating a known concentration of the substrate with an excess known concentration of the oxidant in 40% v/v aqueous acetic acid medium. From the value of unreacted permanganate concentration it has been found that 3 moles of alcohol reacted with 2 moles of permanganate.



The plots of $\log [\text{KMnO}_4]$ vs. time were linear showing first order dependence with respect to the oxidant concentration. The observed rate constants were found to be the same for different concentrations of the oxidant. The k_{obs} increased with increase of concentration of the substrate. These are shown in Table-1. The plot of $\log k_{\text{obs}}$ vs $\log [\text{PhCHOHCH}_3]$ was linear with positive slope equal to unity indicating first order dependence with respect to substrate concentration. The constancy of k_2 value obtained by dividing k_{obs} with substrate concentration further supports the first order dependence with respect to [carbinol]. The plot of $1/k_{\text{obs}}$ vs. $1/[\text{carbinol}]$ was linear passing through the origin which rules out the possibility of formation of a long lived intermediate during the oxidation.

TABLE-1
EFFECT OF SUBSTRATE CONCENTRATION AND OXIDANT CONCENTRATION ON
THE RATE OF OXIDATION OF 1-PHENYL ETHANOL

Medium-40% aq HOAc (v/v)			T = 303 K
$[\text{KMnO}_4] \times 10^3$ (mol dm ⁻³)	$[\text{PhCHOHCH}_3] \times 10^2$ (mol dm ⁻³)	$10^5 k_{\text{obs}}$ (s ⁻¹)	$10^3 k_2$ (dm ³ mol ⁻¹ s ⁻¹)
0.50	1.00	15.62	15.62
0.75	1.00	15.69	15.69
1.00	1.00	15.23	15.23
1.25	1.00	15.54	15.54
1.00	1.50	22.72	15.14
1.00	2.00	31.47	15.73
1.00	2.50	39.15	15.68
1.00	3.00	46.06	15.35

The addition of salt did not produce any primary salt effect and the rate constant remained practically constant with the different concentration of added NaCl. The effect of $[H^+]$ was studied using sulphuric acid (0.020 to 0.150 mol dm⁻³). The result showed that the k_{obs} increased from $17.27 \times 10^{-5} s^{-1}$ to $32.97 \times 10^{-5} s^{-1}$ for a change of $[H^+]$ from 0.02270 to 0.1590 mol dm⁻³. The plot of $\log k_{obs}$ vs. $\log [H^+]$ was not linear but concave upwards with intercepts on the y-axis. The observation led to the conclusion that the reaction is acid catalysed and follows a path involving singly protonated and doubly protonated forms of the reactive species at moderate and higher concentrations of acids as has been observed elsewhere¹.

The polarity of the medium was varied by using different percentage of acetic acid (10 to 80% v/v). The study gave quite interesting results. The rate of oxidation decreased first as the % of acetic acid in the reaction mixture was increased up to 50% v/v (decrease of polarity). The value of k_2 decreased from 25.3×10^{-3} to $11.94 \times 10^{-3} dm^3 mol^{-1} s^{-1}$. Beyond the increase in the % of acetic acid, the rate was found to be increased. The k_2 increased from 11.94×10^{-3} to $21.80 \times 10^{-3} dm^3 mol s^{-1}$ for a change of % of acetic acid from 50 to 80% v/v. A plot of $\log k_2$ vs $1/D$ of the medium was linear with a negative slope up to 50% (v/v) of acetic acid, suggesting an anion-dipole interaction in accordance with the Amis equation⁵. The increase in the rate constant when the % composition of acetic acid larger than 50% (v/v) could be probably due to the involvement of a more powerful oxidising species, HMnO₄ from the solvent catalytic effect. At this stage apparently the interaction might become that between two dipoles (HMnO₄ and alcohol). Thus below 50% v/v of acetic acid concentration the effect might be purely dielectric while above 50% v/v of acetic acid it might be solvent acid catalytic effect.

Temperature coefficient of the rate oxidation was studied by varying the temperature from 303 to 318 K. The activation parameters for the various 1-aryl ethanols were calculated from the plots of $\log k_2$ vs $1/T$ and $\log k_2/T$ vs $1/T$ (Table-2).

TABLE-2
ACTIVATION PARAMETERS OF THE OXIDATION OF VARIOUS 1-PHENYL
ETHANOLS BY KMnO₄ IN 40% Aq. HOAc

$$[\text{Carbinol}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$$

$$[\text{KMnO}_4] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$$

Carbinols	$k_2 \times 10^3$ at temperature (K) (dm ³ mol ⁻¹ s ⁻¹)				Activation parameters			
	303 K	308 K	313 K	318 K	E_a kJ mol ⁻¹	ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger J K ⁻¹ mol ⁻¹	ΔG^\ddagger kJ mol ⁻¹
PhCHOHCH ₃	15.23	22.72	30.00	39.16	49.30	46.73	-125.59	84.78
<i>p</i> -MePhCHOHCH ₃	24.65	34.82	47.65	63.50	50.42	47.82	-118.09	83.59
<i>p</i> -ClPhCHOHCH ₃	16.98	23.61	32.95	44.04	51.08	48.49	-118.97	84.54
<i>p</i> -OMePhCHOHCH ₃	84.52	134.34	210.39	324.86	71.92	69.46	-36.42	80.50
<i>p</i> -NO ₂ PhCHOHCH ₃	28.88	43.03	66.41	88.61	63.29	60.72	-74.21	83.20

The study on the effects of various substituents like $-\text{CH}_3$, $-\text{OCH}_3$, $-\text{Cl}$ and $-\text{NO}_2$ at the *para* position of phenyl ring of 1-phenyl ethanol gave results not in conformity with the requirements of Hammett linear free energy relation. The electron-releasing and the electron-withdrawing groups enhanced the rate with respect to the parent carbinol. The reaction rate increased in the order $-\text{H} < p\text{-Cl} < p\text{-Me} < p\text{-NO}_2 < p\text{-OMe}$. The plot of $\log k_2$ vs. σ (Fig. 1) is suggestive of a transition state undergoing structural variations depending on the specific electronic demand available from the substituents in the making and the breaking of bonds. Results in which the electron withdrawing groups as well as electron releasing groups accelerating the rate with respect to the parent compound have been reported by Henbest *et al.*⁶ while studying the oxidation of substituted stilbenes by permanganate in aqueous dioxane. This may probably arise as a result of the relative dominance of the type of bond breakage controlling the rate of the reaction.

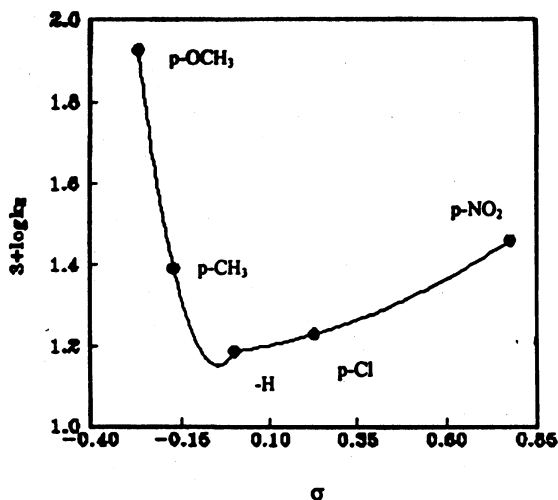
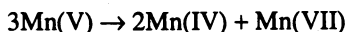


Fig. 1. Hammett plot for the oxidation of 1-phenyl ethanols using KMnO_4 in 40% HOAc

The plot of ΔH^\ddagger vs ΔS^\ddagger was linear (correlation coefficient 0.998) with the isokinetic temperature 260 K. The plot of $\log k_2$ at 318 K vs. $\log k_2$ at 303 K (Exner's plot) was also linear with isokinetic temperature 252 K. The existence of the isokinetic temperature and the almost constant value of ΔG^\ddagger are suggestive of operation of a similar mechanism for the oxidation of 1-aryl ethanols by KMnO_4 in aqueous acetic acid medium.

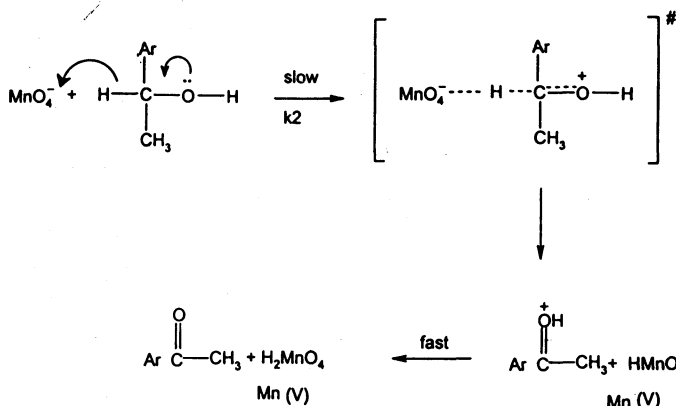
A probable mechanism for the oxidation of the 1-phenyl ethanols in aqueous acetic acid medium can therefore be formulated according to the following Schemes 1 and 2.

The manganese(V) formed disproportionate to Mn(IV), the experimentally observed product.⁷

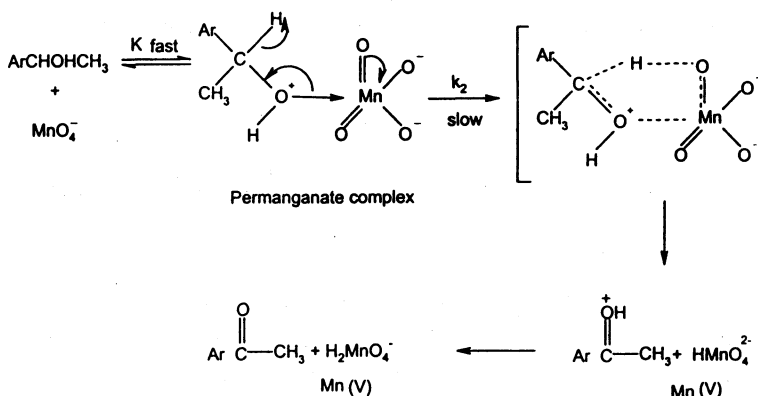


Scheme-1 suggested by Littler and Barter² appears to be quite straightforward.

SCHEME-1



SCHEME-2



The scheme accounts for an electron deficient transition state as a result of hydride ion shift from carbinol to oxidant, which is favoured only by the electron-releasing groups that are present at the *para* position of the benzene ring of carbinol. However, the observed increase in rate by electron-withdrawing substituents cannot be explained by the above scheme. Further, the probability of hydride ion transfer *via* an acyclic one-step bimolecular process was questioned by Bordwell⁸. It is now well established that the transfer of hydrogen takes place only through the involvement of a cyclic transition state and that is a truly symmetrical process involving linear hydride iron transfer⁹. Hence a mechanism that is guided by the consideration of frontier molecular orbital theory is suggested¹⁰. According to this approach the reaction is initiated by an interaction of the 2p electrons in the HOMO of the carbinol with the LUMO of the oxidant to form an active complex. This is followed by a rate limiting decomposition of the complex involving the cleavage of $\alpha(\text{C}-\text{H})$ bond and $\text{O} \rightarrow \text{Mn}$ bond. Depending on the electronic demands from the substituents either the $\alpha(\text{C}-\text{H})$ bond cleavage or $\text{Mn} \rightarrow \text{O}$

bond cleavage is favoured for the reaction. It seems that the electron-releasing substituents enhance the rate by favouring the cleavage of $\alpha(\text{C}-\text{H})$ bond and while electron-withdrawing groups enhance the rate by aiding the cleavage of $\text{O} \rightarrow \text{Mn}$ bond (Scheme-2). This conclusion has been arrived at in attempt to theoretically model reaction in which alcohols are oxidised by high-valent transition metal oxo compounds¹¹. The reaction between transition metal oxides and organic compounds takes place through the formation of active complexes or short lived intermediates have been reported by several workers¹².

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