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Kinetics of permagnetic oxidation of 4-hydroxy acetophenone in acidic media

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ABSTRACT

Paramagnetic oxidation of 4-hydroxy Acetophenone has been investigated at 25°C using UV–Visible double beam spectrophotometer under acidic condition. The effect of variation of substrate, oxidant and H_2SO_4 was studied under pseudo first order reaction conditions. The order of reaction was found to be first order on oxidant, substrate and first order on $[H_2SO_4]$. The effect of salts such as KCl, KBr, KI, $AlCl_3$, $Al(NO_3)_3$, $Ca(NO_3)_2$ and $MgCl_2$, etc. on oxidation of 4-hydroxy acetophenone was studied.

Keywords: Spectrophotometer, $KMnO_4$, Oxidation, 4-hydroxyacetophenone.

INTRODUCTION

In the recent years, kinetic studies of oxidation of various organic compounds by oxidants such as Quinolinium fluorochomate[1], permangnete[2-3], lead tetra acetate[4], N-chloro-p-tolunesulfonamides [5], Nbromobenzamide [6], N-bromosucinimide [7], Pyridinium bromochromate [8], benzyltriethyl ammonium cholorochromate [9], peroxydisulphate [10] hexacyanoferrate [11-12] etc. have been reported.

The utility of $KMnO_4$ as an oxidant in the kinetic study may be attributed to the vital role of it in various paramagnetic synthesis also in various media[2] such as acidic, basic, neutral or even in organic solvents. The present investigation reports the oxidation of 4-hydroxyacetophenone by potassium permanganate under pseudo first order reaction conditions in acidic medium.

MATERIALS AND METHODS

All chemicals used for kinetic study were A.R. grade. Purity of chemicals checked by reported method. Kinetic investigations were performed under pseudo first order conditions with excess of the 4-hydroxy acetophenone over the oxidant at 25° C. Requisite amount of solution of substrate, H_2SO_4 and water were equilibrated. A measured amount of $KMnO_4$ was rapidly added to the reaction mixture with stirring. The progress of the reaction was monitored by double beam UV-Visible spectrophotometer (Elico-198) at its maximum absorption at 526nm. The course of the reaction was studied for 2 hours and pseudo first order rate constant k' calculated by least square method.

Stoichiometry

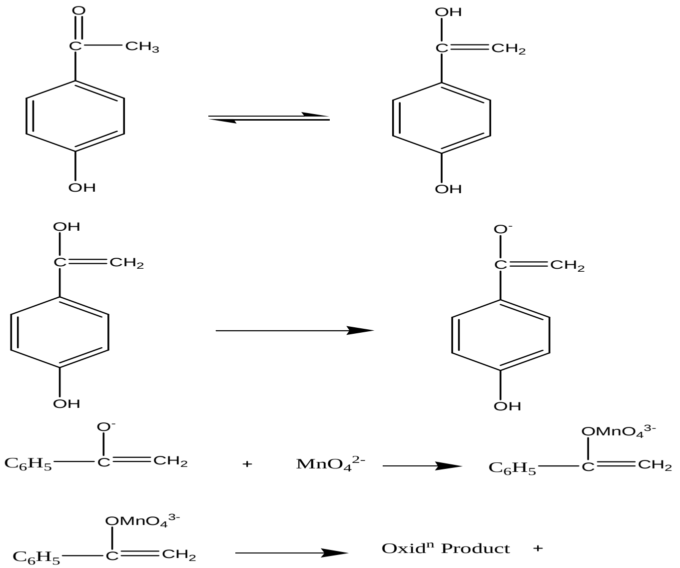
4-hydorxy acetophenone (0.1M), $KMnO_4$ (0.2M), H_2SO_4 (1M) and water (total volume to 100ml) kept aside for 24 hours. The unconsumed $KMnO_4$ was determined spectrophotometrically and the product 4-hydroxy benzoic acid was isolated which was confirmed by TLC, M.P. and qualitatively. This was identified as salicylic acid by its IR spectrum (KBr), which showed a band at (m) 1703cm^{-1} due to –C=O stretching of the acid, a broad band at 2922 cm^{-1} due to O–H stretching of the acid and 3394 cm^{-1} due to phenolic -OH. 1:1 reaction stoichiometry was shown with yield above 90%.

RESULTS AND DISCUSSION

The oxidation of 4-HA were carried out using permanganate in acidic media. The ketones are difficult to oxidize at ordinary conditions, but in acidic media, the oxidation was sufficiently moderate to be monitor through spectrophotometer. The absorbance values were recorded at various time intervals by varying concentration of 4-HA from 1 x 10^{-3}M to 8 x 10^{-3}M and keeping the concentration of $KMnO_4$ 1 x 10^{-3} constant and H_2SO_4 as 1M. The absorbance decreases gradually and then becomes constant.] The pseudo first order rate constant for $KMnO_4$ variation [table1] represent that, as concentration increases rate constant also increases, and shows first order dependence on concentrations of $KMnO_4$. When the kinetic runs were carryout out at 4 x 10^{-4} M 4-HA and 1 x 10^{-3} M $KMnO_4$ and varying concentration H_2SO_4, the initial rate increases with few irregularity and rate constant decreases then became constant. Rate controlling step is enolisation step of ketones. The rate of reaction increases with increase in concentration of hydrogen ion, which may be attributed to the acid catalysed enolisation step in the reaction mechanism. If enolisation is considered to be the rate determining step, the catalysis of enolisation of acetophenone by hydrogen ion showed indicates first order dependence with respect to hydrogen ion. The acid catalysed enolisation were further supported by the effect of ionic strength on the rate of reaction as there were no effect of ion strength, the reaction might be between an ion and molecule.

The oxidation of organic compounds by potassium permanganate is usually multistage process. The degradation of organic compounds proceeds by rupture of discrete two electron bonds whereas manganese undergoes an overall five electron transition in acidic medium. Various intermediate ions of Mn are formed. The anions MnO_4^- and MnO_4^{2-} of high valency states are structurally so different; it is rational to suppose that their chemical reactivities should also differ in type. Involvement of various species are reported by various researchers [13-14]

The mechanism of oxidation of acetophenone can be predicted as



In this mechanism a hypo magnate ion MnO_4^{3-} is quickly formed and then decomposed to give product. The stability of MnO_4^{3-} ion depends on the concentration of reactant and temperature. The formation of such intermediate is facilitated by the polarization of the Mn-O bond.

Literature survey reveals that organic compounds such as olefins, acetylenes, alcohols, phenols, aldehydes, amines, alkyl halides, thiols, sulphides, disulphides and sulfoxides all have one thing in common i.e. excess of valence electron over and above those needed for bonding, hence they get more easily oxidized compared to ketones[15-16].

The exact nature of the oxidizing species in solutions of the various strong inorganic oxidants has been the subject of much investigation and speculation. Since the attack on the reductant is assumed to be an electronegative site, such attack is favoured by the complete or partial electropositive site on the oxidizing agent.

$$2H^+ + MnO_4^- \rightleftharpoons H_2\overset{+}{O}MnO_3 \ (H_2O + Mn\overset{+}{O}_3)$$

The $\overset{+}{MnO_3}$ formed is called permanganyl ion which are much more powerful oxidizing agent, compared to $KMnO_4$. However, all permanganate oxidations are usually complicated which may be attributed to the different oxidation state of Mn.

The ketones in acidic media, may get protonated which react with Mn^{2+} to give a complex. This complex breaks down to yield enol in a rate determining step. The enol is subsequently cleaved to form product.

The rate law and rate equations can be expressed as :

$$S + H^+ \overset{K}{\rightleftharpoons} SH^+$$

$$SH^+ + Mn^{7+} \overset{K_1}{\rightleftharpoons} \text{Complex(C)}$$

$$\text{Complex} \overset{K_2}{\rightleftharpoons} \text{enol}$$

$$\text{enol} + \text{Oxidant} \xrightarrow{\text{fast}} \text{Product}$$

$$Rate = K_2[Complex]$$

$$Rate = K_2\,\mathrm{K_1}[\mathrm{SH}^+][\mathrm{Mn}^{2+}]$$

$$Rate = K_2\,\mathrm{K_1K}[\mathrm{S}][\mathrm{H}^+][\mathrm{Mn}^{2+}]$$

$$Rate = \frac{K_2\,\mathrm{K_1K}[\mathrm{S}]_\mathrm{T}[\mathrm{H}^+][\mathrm{Mn}^{2+}]}{\{1+K_2[\mathrm{H}^+]\}\{1+\mathrm{K_1}[\mathrm{Mn}^{+2}]\}}$$

$$Rate = \frac{K_2\,\mathrm{K_1K}[\mathrm{S}]_\mathrm{T}[\mathrm{H}^+][\mathrm{Mn}^{2+}]_\mathrm{T}}{\{1+K_2[\mathrm{H}^+]\}\{1+\mathrm{K_1}[\mathrm{Mn}^{+2}]\}\{1+\mathrm{K_2K_1}[S][H^+]\}}$$

The condensed compound obtained has a smaller molar absorptivity as compared to that of permanganate ion at 525nm and can explain the initial steep decrease of the absorbance.

$$CH_3COC_6H_4OH + MnO_4^- + H^+ \rightleftharpoons CH_3COC_6H_4OMnO_3 + H_2O$$

On the other hand oxidation of Mn^{2+} to Mn^{3+} by permanganate under the same acid concentration are slower than the oxidation of organic substrate itself. The condensed compound may decompose to form Mn^{6+} by mono electron transfer process or Mn^{5+} by dielectron transfer process.

$$CH_3COC_6H_4OMnO_3 \longrightarrow CH_3COC_6H_4O^{\cdot} + Mn^{6+}$$

$$CH_3COC_6H_4OMnO_3 \longrightarrow CH_3COC_6H_4O^{\cdot} + Mn^{5+}$$

The permanganic ester has a smaller molar absorptivity at 525 nm as compared to MnO_4^-. This fact would explain the steep decrease of the absorbance immediately after mixing. Intermediate oxidation states of manganese are obviously involved in the reaction and will eventually generate Mn^{2+} in quite rapid steps in acidic media. It can be concluded from the study that the oxidation of p-hydroxy acetophenone by permanganate in acidic media involves a complicated mechanism and there may be more than probable paths suggested for oxidation.

Table 1. Effect of varying concentration of reactants at 25ºC

[4-HA] 10^{-4} M	10^{-3} M [Oxidant]	[H_2SO_4] M	K'(sec^{-1})
1.0	1.0	1.0	0.0280
2.0	1.0	1.0	0.0373
3.0	1.0	1.0	0.0420
4.0	1.0	1.0	0.0506
5.0	1.0	1.0	0.0616
8.0	1.0	1.0	0.0824
4.0	0.2	1.0	0.0131
4.0	0.5	1.0	0.0289
4.0	0.6	1.0	0.0395
4.0	0.7	1.0	0.0424
4.0	0.8	1.0	0.0462
4.0	0.9	1.0	0.0587
4.0	0.1	0.5	0.0456
4.0	0.1	0.6	0.0462
4.0	0.1	0.7	0.0470
4.0	0.1	0.8	0.0467
4.0	0.1	0.9	0.0471

Effect of salt

The effect of salt on rate constant (table 2) shows appreciable decrease, this may be due to the negative catalytic effect of salt. It is observed that rate constant in presence of K_2SO_4 $MgCl_2$, $Ca(NO_3)_2$ does not depend on the salt concentration. In KBr rate constant increases first and then decreases. Whereas in case of KI and KCl no sequence or trend of rate constant is observed. This may be due to the involvement of I^- and Cl^- oxidation processes.

Table 2. Effect of salts on reaction rate
[4-HA] = 1x 10^{-4} M, [H_2SO_4] =1M, [$KMnO_4$] = 1 x 10^{-3} M, Temp. = 25 ºC

Salt	**Rate Constant in presence of salt (per sec)**							
Mole/dm^3	**K_2SO_4**	**KBr**	**$AlCl_3$**	**KI**	**$MgCl_2$**	**$Ca(NO_3)_2$**	**KCl**	**$Al(NO_3)_3$**
0.01	0.0495	0.0725	0.0481	0.0394	0.0549	0.0520	0.0472	0.0403
0.02	0.0476	0.1021	0.0462	0.0432	0.0520	0.0432	0.0505	0.0461
0.03	0.0472	0.0910	0.0426	0.0381	0.0453	0.0488	0.0524	0.0490
0.04	0.0434	0.0891	0.0420	0.0733	0.0454	0.0540	0.0430	0.0423
0.05	0.0539	0.0640	0.0452	0.0358	0.0482	0.0488	0.0468	0.0408
0.06	0.0512	0.0117	0.0458	0.0239	0.0515	0.0531	0.0529	0.0493
0.07	0.0430	0.0566	0.0417	0.0219	0.0473	0.0498	0.0453	0.0473
0.08	0.0520	0.0563	0.0456	0.0250	0.0478	0.0488	0.0473	0.0429
0.09	0.0464	0.0377	0.0473	0.0532	0.0478	0.0491	0.0476	0.0536

Effect of Temp on 4-hydroxyacetophenone

[4-HA] = $1x10^{-4}$M [H_2SO_4] = 1M [$KMnO_4$]= $1x10^{-3}$M
$Ea^{\#}$ = 30616.2801 J/mole^{-1}

Rate k	**T °K**	**1/T**	**Logk**	**$\Delta H^{\#}$(J mole^{-1})**	**$\Delta S^{\#}$(J mole^{-1})**	**$\Delta G^{\#}$(J mole^{-1})**
0.0202	293	0.00341	-1.6946	-33052.282	-169.3777	16575.3978
0.0513	303	0.00330	-1.2898	-33135.422	-164.6361	16749.3113
0.0646	313	0.00319	-1.1897	-33218.562	-162.5190	17649.8995
0.0672	323	0.00310	-1.1726	-33301.702	-161.1750	18757.5263
Average				-33676.9921	-164.4270	17433.1087

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