



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

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ABSTRACT

Paramagnetic oxidation of 4-amino Acetophenone has been investigated at 25°C using UV-Visible double beam spectrophotometer under acidic condition. The effect of variation of substrate, oxidant and H₂SO₄ 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 [H₂SO₄]. The effect of salts such as KCl, KBr, KI, AlCl₃, Al(NO₃)₃, Ca(NO₃)₂ and MgCl₂, etc. on oxidation of 4-amino acetophenone was studied.

Keywords: Spectrophotometer, KMnO₄, Oxidation, 4-amino acetophenone (4-AA).

INTRODUCTION

In the recent years, kinetic studies of oxidation of various organic compounds by oxidants such as hexacyanoferrate [1] perchlorates [2] tripropyl ammonium florochromate[3] potassium dichromate [4-5] Quinolinium fluorochromate [6], potassium permanganate [7-10], lead tetra acetate [11], N-chloro-p-tolunesulfonamides [12], N-bromobenzamide [13], N-bromosucinimide [14], Pyridinium bromochromate [15], benzyltriethyl ammonium chlorochromate [16], peroxydisulphate [17] etc. have been reported. Literature survey reveals that very little work is reported on oxidation of benzaldehyde using KMnO₄. The utility of KMnO₄ as an oxidant in the kinetic study may be attributed to the vital role of it in various paramagnetic synthesis also in various media such as acidic, basic, neutral or even in organic solvents. The present investigation reports the oxidation of 4-aminoacetophenone 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-amino acetophenone over the oxidant at 25° C. Requisite amount of solution of substrate, H₂SO₄ and water were equilibrated. A measured amount of KMnO₄ 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-amino acetophenone (0.1M), KMnO₄ (0.2M), H₂SO₄ (1M) and water (total volume to 100ml) kept aside for 24 hours. The unconsumed KMnO₄ was determined spectrophotometrically and the product 4-amino benzoic acid was isolated which was confirmed by TLC, M.P. and qualitatively.

RESULTS AND DISCUSSION

Oxidation of organic compounds is widely studied system; little attention has been given to oxidation of substituted acetophenones (4-AA). The oxidation of 4-AA was carried using permanganate in acidic media. In ordinary condition to oxidize acetophenones were difficult but in acidic medium oxidation of acetophenones is easy to monitor by spectrophotometer. Absorbance values were recorded at various time intervals by varying concentration of 4-AA from 1×10^{-4} M to 9×10^{-4} M and keeping the concentration of KMnO_4 1×10^{-3} M constant and H_2SO_4 as 1 M. The absorbance decreases gradually and then becomes constant. The initial rate of reaction was determined and tabulated in table 1. These values decrease with increase in concentration with some irregularity. The first order rate constant shows that the rate increases and then decreases indicating that the oxidation product obtained is unstable and decomposes, such reactions are called as oscillatory reactions. The first order rate constant shows that rate increases initially with increase in concentration of 4-AA, which attributes to first order dependence of rate on the concentration of 4-AA. The absorbance values decreases with time for variation in oxidant KMnO_4 .

The pseudo first order rate constant for KMnO_4 variation represents that as concentration increases rate constant also increases. This clearly shows first order dependence on concentration of KMnO_4 when the kinetic runs were carried out at 3×10^{-4} M 4-AA and 1×10^{-3} M KMnO_4 and varying concentration of H_2SO_4 . The initial rate increases with few irregularities and rate constant decreases and then becomes constant. In the oxidation of ketones by halogen the rate controlling step is enolisation step of ketones. The rate of reaction increases with increase in concentration of hydrogen ion, which indicates acid catalysed enolisation step in the reaction mechanism. If enolisation is considered to be the rate determining step, the catalysis is considered to be the rate determining step, the catalysis enolisation of 4-amino acetophenone by hydrogen ion showed first order dependence with respect to hydrogen ion. The acid catalysed enolisation was further supported by the effect of ionic strength on the rate of reaction as there is no effect of ionic strength the reaction might be between an ion and molecule.

Autocatalysis is general phenomenon for the oxidation of amines by permanganate ions. [18-19] The solutions remained totally clear throughout the reaction and a brown precipitate of MnO_2 was observed the day after. The reaction rate vs. time plots showed a definite bell shape profile. The rate calculated point by point from the experimental data as minus the derivative of the permanganate concentration with respect to time, indicates the reaction is autocatalytic. Hence there must be two mechanisms involved; one for acceleration and another for decay period of the reactions. [20] assuming the noncatalytic mechanism is first order, since the excess of substrate concentration were taken for kinetic run. The differential rate law can be given as

$$r_{\text{non}} = K_1 [\text{R}] \quad (1)$$

In autocatalytic reaction product itself involves in reaction and hence

$$r_{\text{cat}} = K_2 [\text{R}] [\text{P}] \quad (2)$$

Since in reaction both noncatalytic and autocatalytic process takes place, hence

$$r = K_1 [\text{R}] + K_2 [\text{R}] [\text{P}] \quad (3)$$

Where K_1 and K_2 are pseudo rate constants corresponding to the noncatalytic and catalytic mechanism respectively.

If the initial concentration of permanganate were C_0 and concentration permanganate at time t is C then $[\text{R}] = C$ and $[\text{P}] = C_0 - C$ can be substituted in equation

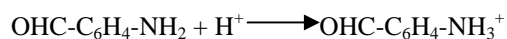
$$\begin{aligned} dC/dt &= K_1 C + K_2 (C_0 - C) C \\ &= K_1 C + [K_2 C_0 - K_2 C] C \end{aligned}$$

Which on integration gives

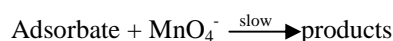
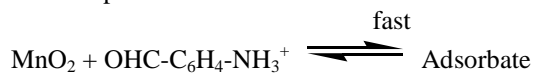
$$(K_1 + K_2 C_0) = 1/t [\ln [(K_1 + K_2 C_0 - K_2 C)/C] - \ln (K_1/C_0)]$$

The log K_1 Vs log [Sub] plot is linear; the slope of correlation is 0.4434. Thus the non catalytic mechanism is first order dependence on substrate concentration.

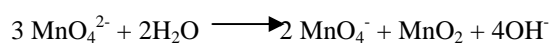
Alternative mechanism involves the participation of amino group. It is possible that amine gets protonated in presence of acid.



It has been reported that there is formation of soluble form of colloidal manganese dioxide temporarily stabilized in aqueous solution by adsorption of phosphate buffers.[21] Hence this manganese dioxide acts as a catalyst and reaction proceeds further.



The MnO_2 is known to adsorb cations strongly on its surface.[22] This adsorbed substrate may suffer an oxidation attack by a permanganate ion from double layer surrounding the colloidal particles. As a result, the reaction products are formed. The manganese dioxide is formed from dismutation of manganate ion.



Ammonia was one of the products obtained from the permanganate degradation of primary amines, while aldehyde is obtained as reaction products from the oxidation of primary, secondary and tertiary amines by aqueous potassium permanganate [23-24]

Hence the rate equation associated is given as

$$r_2 = K' [\text{MnO}_4^-] [\text{Adsorbate}]$$

If the ratio between the adsorbate and manganese dioxide concentrations is given by the Langmuir equation [25] as function of the concentration of substrate ion in solution.

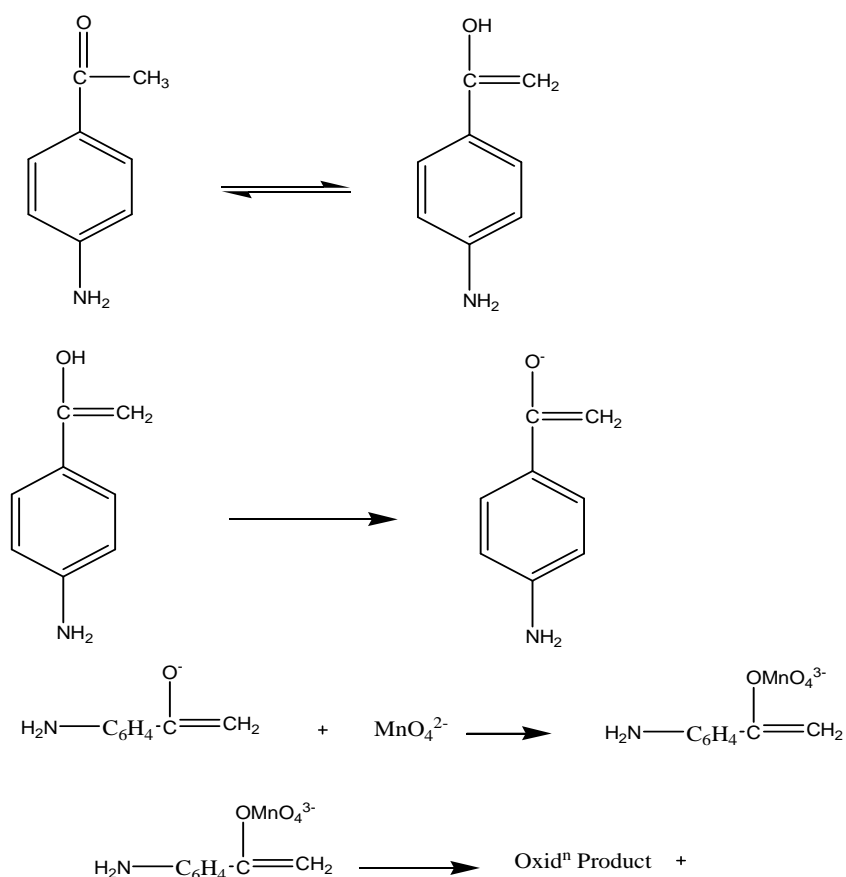
$$[\text{Adsorbate}]/[\text{MnO}_2] = a[\text{OHC-C}_6\text{H}_4\text{-NH}_3^+]/1 + b[\text{OHC-C}_6\text{H}_4\text{-NH}_3^+]$$

$$r_2 = a K' [\text{MnO}_4^-][\text{MnO}_2] [\text{OHC-C}_6\text{H}_4\text{-NH}_3^+] / 1 + b[\text{OHC-C}_6\text{H}_4\text{-NH}_3^+]$$

Under the pseudo rate first order condition, above equation because

$$r_2 = a K' [\text{OHC-C}_6\text{H}_4\text{-NH}_3^+] / 1 + b[\text{OHC-C}_6\text{H}_4\text{-NH}_3^+]$$

The mechanism of oxidation of 4-amino acetophenone can be predicated as:



In this mechanism a hypomanganate 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 blue colour and then fading it to colorless is indicative of formation at Mn(V) ion. The formation of such intermediate was facilitated by the polarization of the Mn-O bond.

The organic compounds like, Olefins, acetylenes, alcohols, phenols, aldehydes, amines, alkyl halides, thiols, sulfides, disulphide's and sulfoxides because of having excess of valence electrons over and above these are needed for bonding get more easily oxidized compared to ketones. It is difficult to know the exact nature of oxidizing species in solution of the various strong inorganic oxidants. As the attack on the reductant was assumed to be on electronegative site, such attack is favoured by the complete or partial electropositive site on the oxidizing agent.

The MnO_3^+ formed called permanganyl ion which are much more powerful oxidizing agent compared to KMnO_4 . However all permanganate oxidations are usually complicated because of many oxidation state of Mn.

The alternative mechanism suggests in acidic media the ketone may get protonated and then react with Mn^{+2} to give a complex. The resultant formed complex breaks down to give enol in a rate determining step. The products are formed by subsequent cleavage of enol.

The rate and law and rate equation are given as follows:

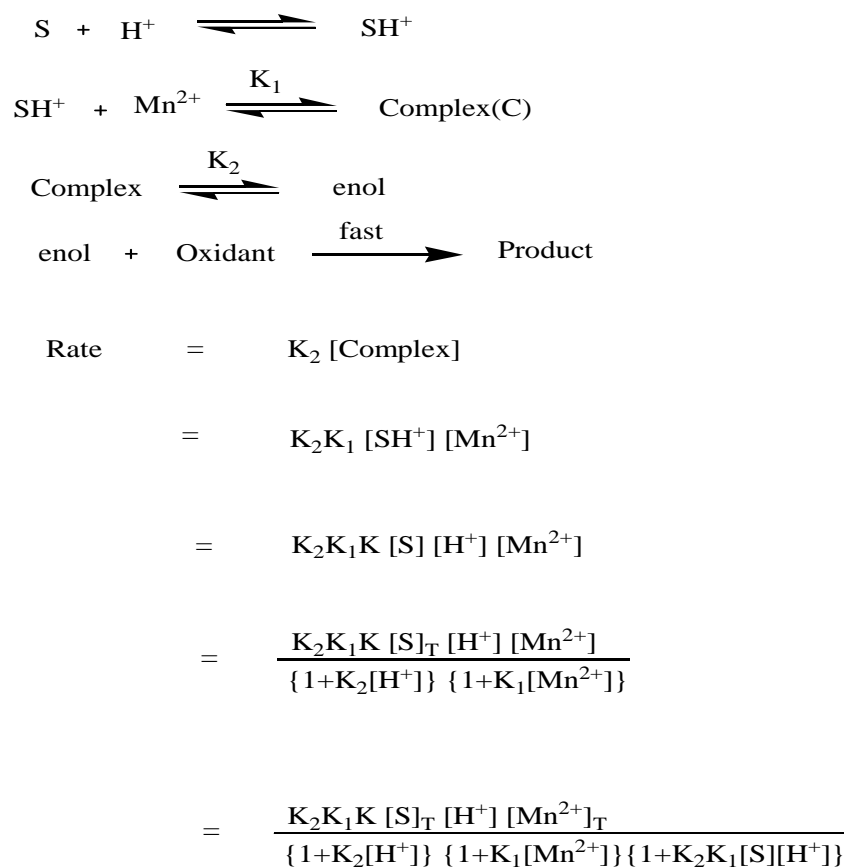


Table 1. Effect of varying concentration of reactants at 25°C

[4-HA] 10 ⁻⁴ M	10 ⁻³ M [Oxidant]	[H ₂ SO ₄] M	K' (sec ⁻¹)
1.0	1.0	1.0	0.0451
2.0	1.0	1.0	0.0329
3.0	1.0	1.0	0.0381
4.0	1.0	1.0	0.0539
5.0	1.0	1.0	0.0723
6.0	1.0	1.0	0.0634
7.0	1.0	1.0	0.0435
8.0	1.0	1.0	0.0299
9.0	1.0	1.0	0.0216
3.0	1.0	1.0	0.0048
3.0	2.0	1.0	0.0052
3.0	3.0	1.0	0.0047
3.0	4.0	1.0	0.0007
3.0	5.0	1.0	0.0058
3.0	6.0	1.0	0.0049
3.0	7.0	1.0	0.0052
3.0	8.0	1.0	0.0047
3.0	9.0	1.0	0.0046
3.0	1.0	0.1	0.0184
3.0	1.0	0.2	0.0549
3.0	1.0	0.3	0.0423
3.0	1.0	0.4	0.0398
3.0	1.0	0.5	0.0402
3.0	1.0	0.6	0.0364
3.0	1.0	0.7	0.0335
3.0	1.0	0.8	0.0341
3.0	1.0	0.9	0.0341

Effect of salt

The effect of salt on rate constant shows appreciable decrease, this may be due to the negative catalytic effect of salt. It is observed that rate constant in presence of K₂SO₄, MgCl₂, Ca(NO₃)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
 $[4-AA] = 3 \times 10^{-4} M$, $[H_2SO_4] = 1M$, $[KMnO_4] = 1 \times 10^{-3} M$, Temp. = 25 °C

M [salt]	K ₂ SO ₄	KBr	AlCl ₃	KI	MgCl ₂	Ca(NO ₃) ₂	KCl	Al(NO ₃) ₃
0.01	0.03640	0.0385	0.0358	0.0325	0.0192	0.0337	0.0285	0.0356
0.02	0.03710	0.0860	0.0330	0.0471	0.0349	0.0334	0.0354	0.0334
0.03	0.03700	0.0922	0.0331	0.0216	0.0350	0.0372	0.0346	0.0356
0.04	0.03520	0.0248	0.0334	0.0097	0.0359	0.0348	0.0357	0.035
0.05	0.03520	0.0108	0.0323	0.0159	0.0344	0.0343	0.0349	0.0364
0.06	0.03520	0.0217	0.0326	0.0240	0.0339	0.0366	0.034	0.0378
0.07	0.03470	0.0085	0.0322	0.0090	0.0351	0.0354	0.0345	0.0362
0.08	0.03440	0.0236	0.0343	0.0387	0.0339	0.0357	0.0346	0.0364
0.09	0.03530	0.0098	0.0326	0.0364	0.0353	0.0344	0.0334	0.0364

Effect of Temperature on 4-aminoacetophenone

The effect of temperature was studied keeping constant concentration of all reactants such as $[KMnO_4] = 1 \times 10^{-3} M$, $[4-AA] = 3 \times 10^{-4} M$ and $[H_2SO_4] = 1M$. The temperature variation was done in the range of 20 to 50° C (table 3). The energy of activation was calculated by plotting graph between log k versus 1/T, a straight line was obtained. The free energy change (ΔG^\ddagger) enthalpy changes (ΔH^\ddagger) and entropy change (ΔS^\ddagger) was determined. The modest enthalpy of activation and higher rate constant of slow step indicate that the oxidation presumably occurs by an inner sphere mechanism. ΔS values indicate that the transition state is highly organized due to loss of number of degrees of freedom. Thus the thermodynamic parameters are favourable for the reaction.

Table 3. Effect of Temperature on 4-aminoacetophenone
 $[4-AA] = 3 \times 10^{-4} M$, $[H_2SO_4] = 1M$, $[KMnO_4] = 1 \times 10^{-3} M$
 $E_a^\ddagger = -12397.7744 J/mole^{-1}$

Rate k	t °C	T K	1/T	logk	ΔH^\ddagger (J mole ⁻¹)	ΔS^\ddagger (J mole ⁻¹)	ΔG^\ddagger (J mole ⁻¹)
0.0260	10	283	0.00353	-1.58503	14750.6364	141.9878	28431.9135
0.0317	20	293	0.00341	-1.49894	14833.7764	140.7482	26405.4380
0.0284	30	303	0.00330	-1.54668	14916.9164	140.6598	27703.0094
0.0420	40	313	0.00319	-1.37675	15000.0564	138.7966	28443.2675
0.0510	50	323	0.00310	-1.29243	15083.1964	137.6765	29386.3224
Average					14916.9164	139.9738	27473.9902

CONCLUSION

The oxidation of 4-AA with $KMnO_4$ in acidic medium involves formation of a complex between protonated substrate with oxidant which decomposes to yield corresponding carboxylic acid. The overall mechanistic sequence described here is consistent with product, mechanistic and kinetic studies.

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