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Oxidation of Formaldehyde by Mn(VII) in Alkaline Medium, A Kinetic Study

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ABSTRACT

The kinetic reaction on the oxidation of formaldehyde by potassium permanganate in alkaline medium was investigated at 525 nm with a double beam spectrophotometer via pseudo first order condition. The oxidation led to the formation of salt of carboxylic acid. The reaction was first order in each of $KMnO_4$ and HCHO, and fractional order in hydroxyl ions. Michaelis-Menten plot showed the presence of an intermediate complex in the course of the reaction. Activated parameters obtained from Arrhenius and Erying's equations were 34.37 kJ mol^{-1}, -0.197 kJ mol^{-1}K^{-1} and 93.076 kJ mol^{-1} for $\Delta H^{\#}$, $\Delta S^{\#}$, $\Delta G^{\#}$ respectively. Potassium permanganate in aqueous alkaline media combined with alkali to give an alkali-permanganate specie, $[MnO_4.OH]^{2-}$ in a pre-equilibrium step, which is in agreement with the order of less than unity with respect to alkali. The formation of $[MnO_4.OH]^{2-}$ in solution was further supported by the Michelis-Menten plot showing an intercept. A plausible mechanism via inner sphere mechanism was reported involving attack on formaldehyde by the active $[MnO_4.OH]^{2-}$ specie.

KEYWORDS: Formaldehyde, kinetics, mechanism, potassium permanganate, rate law.

INTRODUCTION

Formaldehyde was first reported in 1859 by the Russian chemist, Aleksandr Butlerov (1828-1886). However, it was conclusively identified by August Wilhelm Von Hofmann [1, 2]. Formaldehyde, otherwise known as methanol, is the simplest aldehyde known. Aldehydes undergo a wide variety of chemical reactions in acidic and alkaline media and their reactivity is centered on the highly polar C=O bond of the carbonyl group present in them [3]. Reports on the kinetics of aldehyde oxidation included the use of oxidants like benzimidazol dichromate [4], sodium n-bromo aryl sulphonamide [5], acid permanganate [6], chromic acid [7], peracetic acid [8], bis(2,2$^{/}$ -bipyridyl) copper(II) permanganate [9], bromine [10], imidazolium dichromate [11], molecular oxygen [12], benzimidazolium fluorochromate [13], N-chloronicotin amide [14], sodium chlorite-hydrogen peroxide [15] and tetraethyl ammonium chlorochromate [16], quinolinium dichromate [17, 18] N- chlorosuccinimide [19], benzyltrimethyl ammonium fluorochromate [20]. Oxidation of aldehydes have been reported extensively in acidic medium. Hitherto, few or scanty work were seen on the oxidation of aldehydes in alkaline medium. Therefore, this research is aimed at investigating the kinetics of the oxidation of formaldehyde by potassium permanganate in alkaline medium with the view to establishing kinetic data of the reaction and to report a plausible mechanism for the reaction via the $[MnO_4.OH]^{2-}$.

MATERIALS AND METHODS

The chemicals were of highest purity (potassium permanganate, formaldehyde, potassium nitrate and sodium hydroxide). Distilled water was utilized to prepare all the stock solutions. The ionic strength was maintained constant at 0.05 M with KNO_3.

Kinetic measurement

Pseudo-first order conditions were maintained by keeping excess (x10 or greater) of [HCHO] over $[KMnO_4]$. All stock solutions were prepared in standard flasks blackened from outside in order to prevent any photochemical reaction as $KMnO_4$ is sensitive to light.

Requisite amount of the reactants in the order: Formaldehyde, distilled water, NaOH, KNO_3 and lastly $KMnO_4$ were introduced into a 1 cm quartz cuvette from the standard flasks kept in a water bath at desired temperature. The temperature was maintained constant using the combination of a Cryocool cc-60T compressor, a Gallenkamp thermostating unit and a Techne circulator c-100, which pumped water from the water bath at the required temperature around the cell compartment. Consequently, absorbance change (A) with time (t) was monitored using unicam-1800 Schimadzu spectrophotometer at 525 nm. Furthermore, pseudo-first order (k_{obs}) rate constants were obtained from the slopes of the plots of In A versus time.

RESULTS AND DISCUSSION

Stoichiometry

Reaction mixtures containing fixed $[KMnO_4]$ at $5x10^{-5}$ M and 1.00×10^{-3} M $\leq$ [HCHO] $\leq$ 4.33×10^{-3} M, [NaOH] 1.33×10^{-3} M and ionic strength 0.05 M at 298K were prepared. The absorbance of the solutions were taken at 525 nm after the reaction had gone to completion after 24 hours. The stoichiometry was evaluated from the plot of absorbance versus [HCHO] curve. The result showed that 1 mole of HCHO consumed 1 mole of $KMnO_4$.

Oxidation of Formaldehyde by $KMnO_4$ in alkaline medium results in the formation of salt of carboxylic acid.

The overall reaction may be written as:

$$\mathrm{Mn^{7+} + HCHO + 3OH^- \rightarrow Mn^{5+} + HCOO^- + 2H_2O}$$

Polymerization Test

There was no indication of gel formation when 10% acrylamide was added to the reaction mixture. This suggests absence of free radicals in the course of the reaction.

Effect of [$KMnO_4$]

There was a linear increase in the observed rate constant (k_{obs}) with increase in [$KMnO_4$] (Table 1). The slope of the plot of In k_{obs} versus In [$KMnO_4$] was unity, which indicates a first order dependence with respect to [$KMnO_4$].

Table 1: The variation of observed rate constant with [$KMnO_4$]

10^5[$KMnO_4$]/M	10^4kobs/s^{-1}
1.00	0.98
2.00	1.35
3.00	2.48
5.00	3.51
6.00	4.32
7.00	4.93

[HCHO] 3 x 10^{-3} M, [OH^-] 1.33x10^{-3} M, μ= 0.05M, T= 298K

Effect of [HCHO]

The observed rate constant also increased with increase in [HCHO] as shown in Table 2. The oxidation reaction is also first order in [HCHO]. Double reciprocal plot indicates the presence of an intermediate in the course of the reaction as shown in Fig.1.

Table 2: The variation of observed rate constant with [HCHO]

10^3[HCHO]/M	10^4kobs/s^{-1}
1.00	0.93
1.67	1.44
2.33	2.26
3.00	2.62
4.00	3.30
4.33	3.62

[$KMnO_4$] 5 x 10^{-5} M, [OH^-] 1.33 x 10^{-3} M, μ= 0.05 M, T= 298K

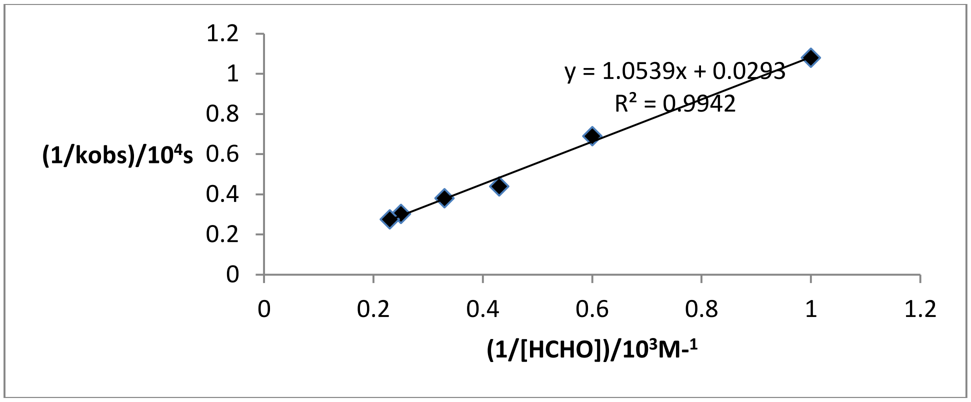

Fig. 1: Double reciprocal plot

Effect of [NaOH]

Literature report showed that a lot of research have been reported on the oxidation of aldehydes by KMnO4 in acidic medium and scanty investigation have been reported in alkaline medium. The observed rate constant increased with increase in [OH-] as shown in Table 3. The oxidation reaction is fractional order in [OH$^-$].

Table 3: The variation of observed rate constant with [OH$^-$]

10^3[OH$^-$]/M	10^4kobs/s^{-1}
0.70	1.02
1.00	1.19
1.33	1.35
1.67	1.46
2.33	1.72
3.00	1.85

[KMnO$_4$] 5 x 10^{-5} M, [HCHO] 3 x 10^{-3} M, μ= 0.05 M T= 298K

Effect of Temperature

The observed rate constant (k$_{obs}$) increased with increase in temperature. The activation parameters were evaluated from the equations below:

$$In\left(\frac{k}{T}\right) = -\frac{\Delta H^{\#}}{RT} + In\left(\frac{K^{/}}{h}\right) + \frac{\Delta S^{\#}}{R}$$

Where,

$$In\left(\frac{K^{/}}{h}\right) = 23.76$$

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$$

Table 4: Activation Parameters

Aldehyde	$\Delta H^{\#}$	$-\Delta S^{\#}$	$\Delta G^{\#}$
	(kJ mol^{-1})	(kJ mol^{-1}K^{-1})	(kJ mol^{-1})
Formaldehyde	34.37	0.197	93.08

[KMnO$_4$] 5 x 10^{-5}M, [HCHO] 3 x 10^{-3} M, [OH$^-$] 1.33 x 10^{-5}, μ= 0.05 M, T= 298K

Mechanism and Rate law

$$\mathrm{MnO_4^-} + \mathrm{OH^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{HMnO_5^{2-}} \quad \text{(fast step)}$$

$$\mathrm{HMnO_5^{2-}} + \mathrm{HCHO} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{Complex}$$

$$\text{Complex} \xrightarrow{k_3} \text{Products} \quad \text{(slow step)}$$

$$\text{Rate} = \frac{-\mathrm{d[Complex]}}{\mathrm{dt}} = k_3[\text{Complex}] \qquad (1)$$

$$\frac{\mathrm{d[Complex]}}{\mathrm{dt}} = k_2[\mathrm{HMnO_5^{2-}}][\mathrm{HCHO}] - k_{-2}[\text{Complex}] - k_3[\text{Complex}] \qquad (2)$$

Appling steady state approximation

$$0 = k_2[\mathrm{HMnO_5^{2-}}][\mathrm{HCHO}] - k_{-2}[\text{Complex}] - k_3[\text{Complex}] \qquad (3)$$

$$[\text{Complex}] = \frac{k_2[\mathrm{HMnO_5^{2-}}][\mathrm{HCHO}]}{(k_{-2} + k_3)} \qquad (4)$$

$$K_1 = \frac{k_1}{k_{-1}} = \frac{[\mathrm{HMnO_5^{2-}}]}{[\mathrm{MnO_4^-}][\mathrm{OH^-}]} \qquad (5)$$

$$[\mathrm{HMnO_5^{2-}}] = K_1[\mathrm{MnO_4^-}][\mathrm{OH^-}] \qquad (6)$$

Substituting equation (6) into (4)

$$[\mathrm{Complex}] = \frac{\mathrm{K_1k_2[MnO_4^-][OH^-][HCHO]}}{\mathrm{(k_{-2}+k_3)}} \qquad (7)$$

Substituting (7) into (1)

$$\mathrm{Rate} = \frac{-\mathrm{d[Complex]}}{\mathrm{dt}} = \frac{\mathrm{K_1k_2k_3[MnO_4^-][OH^-][HCHO]}}{\mathrm{(k_{-2}+k_3)}}$$

Oxidation of formaldehyde in alkaline medium proceeded via intermediate complex formation as evident by the Michaelis-Menten plot [21]. The insignificant effect of the ionic strength on the reaction rate implies the presence of an ion and a neutral molecule [22] in the rate determining step, a neutral formaldehyde and negative alkaline-permanganate, $[MnO_4.OH]^{2-}$ specie is suggested. Therefore, the reaction mechanism shown in scheme 1 involves attack of the active specie of permanganate $[MnO_4.OH]^{2-}$ on formaldehyde substrate leading to the formation of a complex in a pre-equilibrium step. Consequently the slow cleavage of the complex leads to the formation of the products. The negative entropy of activation shows an ordered transition state and a tendency for an inner-sphere mechanism [23]. Consequently, positive values of $\Delta H^{\#}$ and $\Delta G^{\#}$ indicate that the formation of the complex is endothermic and non-spontaneous respectively.

CONCLUSION

The kinetics of oxidation of formaldehyde by alkaline potassium permanganate has been reported. A plausible mechanism via inner sphere mechanism was reported involving attack on formaldehyde by the active $[MnO_4.OH]^{2-}$ specie.

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