

Kinetics and Mechanism of KMnO_4 Oxidation of Ketones in NaOH Medium.

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ABSTRACT

The kinetics and mechanism of KMnO_4 oxidation of ketones in NaOH medium was carried out by studying the effect of [oxidant], [ketone], $[\text{OH}^-]$, ionic strength and temperature on the reaction. The stoichiometry of the reaction was determined and the products of the reaction were identified using spectroscopic techniques and thin-layer chromatography. The kinetic study was monitored via pseudo-first order condition using uv-1800 Shimadzu spectrophotometer at 525nm. Standardization of KMnO_4 was carried out in acidified Ferrous ammonium sulphate.

The kinetics showed first order dependence with respect to [oxidant], [ketone] and fractional order with respect to $[\text{OH}^-]$. However, it is unaffected by ionic strength of the solution. Michaelis-menten kinetics showed the presence of an intermediate complex and the addition of acrylonitrile solution to the reaction mixture did not show polymerization, indicating absence of free radicals. Same values of ΔG^\ddagger indicates common mechanism. Activation parameters were evaluated from Arrhenius and Eyring's equation. A scheme and rate law is proposed.

(Keywords: butanone, 2-pentanone, potassium nitrate, potassium permanganate, propanone and sodium hydroxide)

INTRODUCTION

Potassium permanganate is a versatile oxidant in chemistry. It has been used to oxidize several chemical reactions in both acidic and alkaline media¹. The kinetics and mechanism of the oxidation of ketones in acidic and alkaline media have been reported by several researchers using oxidants like Dodecatungstocobaltate(III)₄², quinolinium dichromate³, N- Bromosuccinimide⁴,

Chloramine-T⁵, tris(1,10-phenanthroline)Fe(III)⁶, and thallium(III)⁷.

Moreover, several research works have been reported on the oxidation of ketones in acidic medium, while a few investigations have been carried out in alkaline medium^{8,9,10}. The rate dependence of the permanganate ion oxidation of ketones have been attributed to hydrogen ion concentration via protonation of the permanganate ion and to enolization of the ketone or the formation of an intermediate complex in the pre-equilibrium step which breaks down to the end products in the rate determining step.

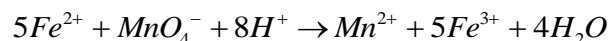
Consequently, the kinetics of the oxidation of Propanone, Butanone, 2-Pentanone ketones by a two equivalent oxidant like potassium permanganate was undertaken in sodium hydroxide medium with the view to appraising the previous scanty works in this area of study.

MATERIALS AND METHODS

Propanone, Butanone, and 2-Pentanone were all Analar grade. Sodium hydroxide, potassium nitrate, potassium permanganate and Ferrous ammonium sulphate (BDH(AR) grade).

Standardization of Potassium Permanganate

Stock solution of potassium permanganate was standardized in acidified ferrous ammonium sulphate¹¹.



Spectral Measurement

λ_{\max} for KMnO_4 was obtained at 525nm using a uv-1800 Shimadzu spectrophotometer.

Kinetic Measurement

The measurement of the kinetic data were established by monitoring the decrease in absorbance of KMnO_4 at absorption maximum as a function of time with uv-1800 Shimadzu spectrophotometer connected to a computer. The reaction components were calculated and mixed in 1cm^3 (3ml) quartz cell in the following sequence: distilled water, sodium hydroxide, potassium nitrate, substrate and the oxidant. A constant temperature at 298K was maintained using the combination of a cryocool cc-60T compressor, a Gallenkamp thermostating unit and a Techne circulator c-100 which pumps water from the water bath at the required temperature around the cell compartment.

The kinetic runs were performed under pseudo first- order kinetics. The observed first order rate constants were obtained from the slope of $\ln A$ versus time.

Product Analysis

The IR showed a very broad absorption at 3400-2400 cm^{-1} (OH stretching) , a broad band at 1730-

1700 cm^{-1} (C=O stretching) and an absorption of medium intensity between 1320 and 1210 cm^{-1} (C-O stretching) for carboxylic acids. The R_f obtained was 0.20 which further confirmed the presence to carboxylic acid as one of the products.

Stoichiometry

The stoichiometry of the reaction was determined by spectrophotometric titration. Absorbances of solutions containing various concentrations of ketones within the range $2.00 \times 10^{-2} - 7.00 \times 10^{-2}$ M and a constant initial concentration of KMnO_4 of 1.50×10^{-3} M, $l = 0.3$ M and $[\text{NaOH}] = 1.00 \times 10^{-2}$ M was measured at λ_{\max} of KMnO_4 , after the reaction had gone to completion. The stoichiometry was evaluated from the plots of absorbance vs [ketone] curve. Stoichiometry was investigated to be 1:1 (ketone: KMnO_4).

RESULTS AND DISCUSSION

Oxidation of Propanone, Butanone, and 2-Pentanone were investigated in alkaline KMnO_4 via pseudo-first order kinetics. The straight line plot of $\ln A$ versus time indicated a first order dependence. There was no appreciable variation in pseudo-first rate constant (k_{obs}) with [oxidant], which also confirms the first order dependence on oxidant concentration (Table 1).

Table 1: Variation of Pseudo-First Order Rate Constant as a Function of [Oxidant].

$10^3[\text{oxidant}]/\text{M}$	$10^2 k_{\text{obs}}/\text{s}^{-1}$		
	Propanone	Butanone	2-Pentanone
0.80	1.85	2.62	3.28
1.00	1.92	2.55	3.40
1.50	1.85	2.60	3.00
2.00	2.00	2.55	3.31
2.50	1.90	2.62	3.40

[S] 3.00×10^{-2} M [OH⁻] 1.00×10^{-2} M [KNO₃] 0.30 M T= 298K

Dependence of the Reaction Rate on the Substrate Concentration

The effect of substrate concentration on the rate of oxidation was monitored by varying initial substrate concentrations and keeping other parameters constant. Pseudo- first order rate constant (k_{obs}) increased with increase in substrate concentrations (Figure 1).

Second order rate constant were obtained from the plot of k_{obs} vs $[S]$. The values obtained were: propanone, $1.97 \text{ M}^{-1}\text{S}^{-1}$; Butanone, $1.82 \text{ M}^{-1}\text{S}^{-1}$; and 2-Pentanone, $1.31 \text{ M}^{-1}\text{S}^{-1}$. The linearity of $\ln k_{obs}$ vs $\ln[S]$ indicate that the complex formation took place between substrate and the oxidant. Michaelis-menten plot of $1/k_{obs}$ vs $1/[S]$ gave an intercept, indicating the presence of an intermediate complex (Figure 2). The slope of the Plot of $\ln k_{obs}$ vs $\ln[S]$ showed that the order with respect to each of the substrate was 1.

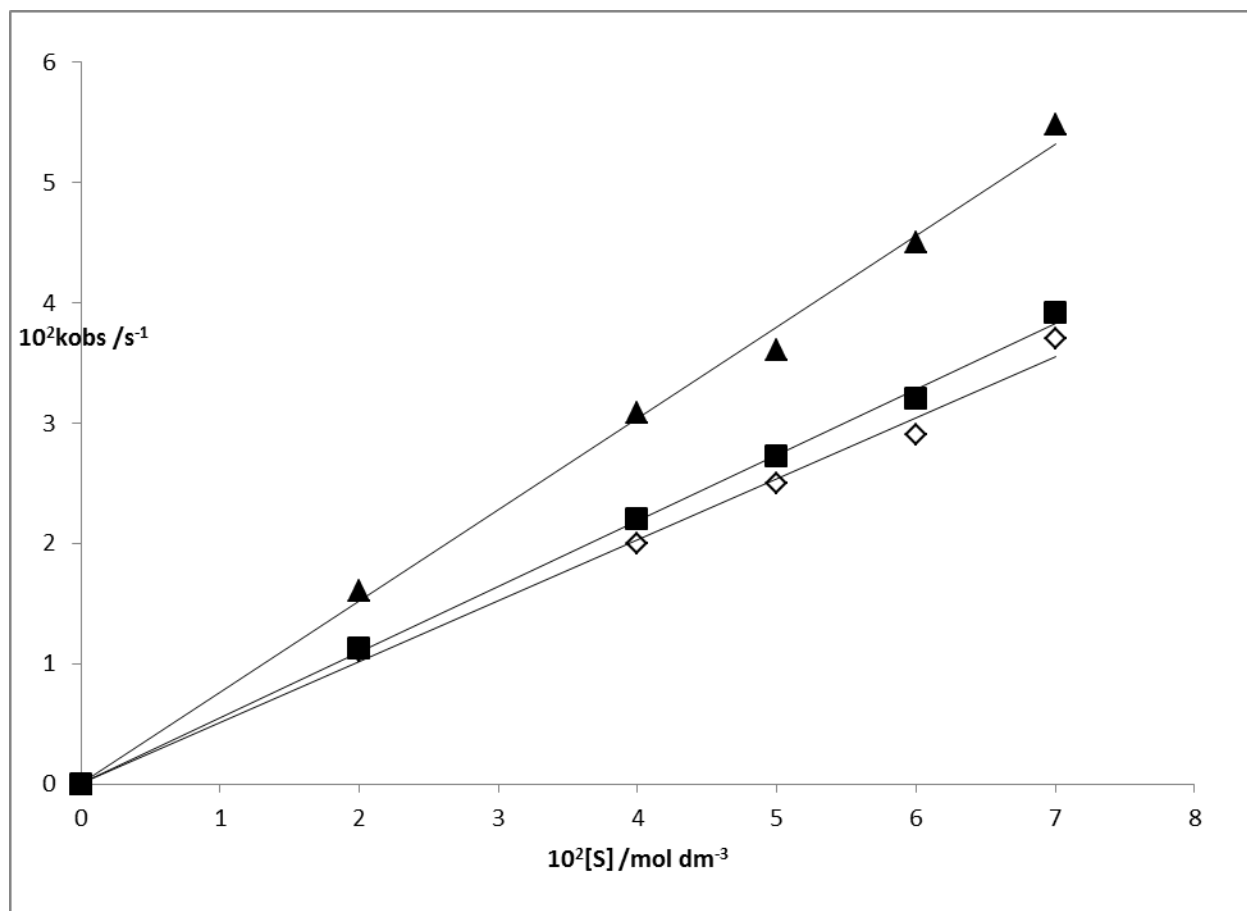


Figure 1: Plot of k_{obs} versus $[S]$.

(\square Propanone \blacksquare Butanone \blacktriangle 2-Pentanone)

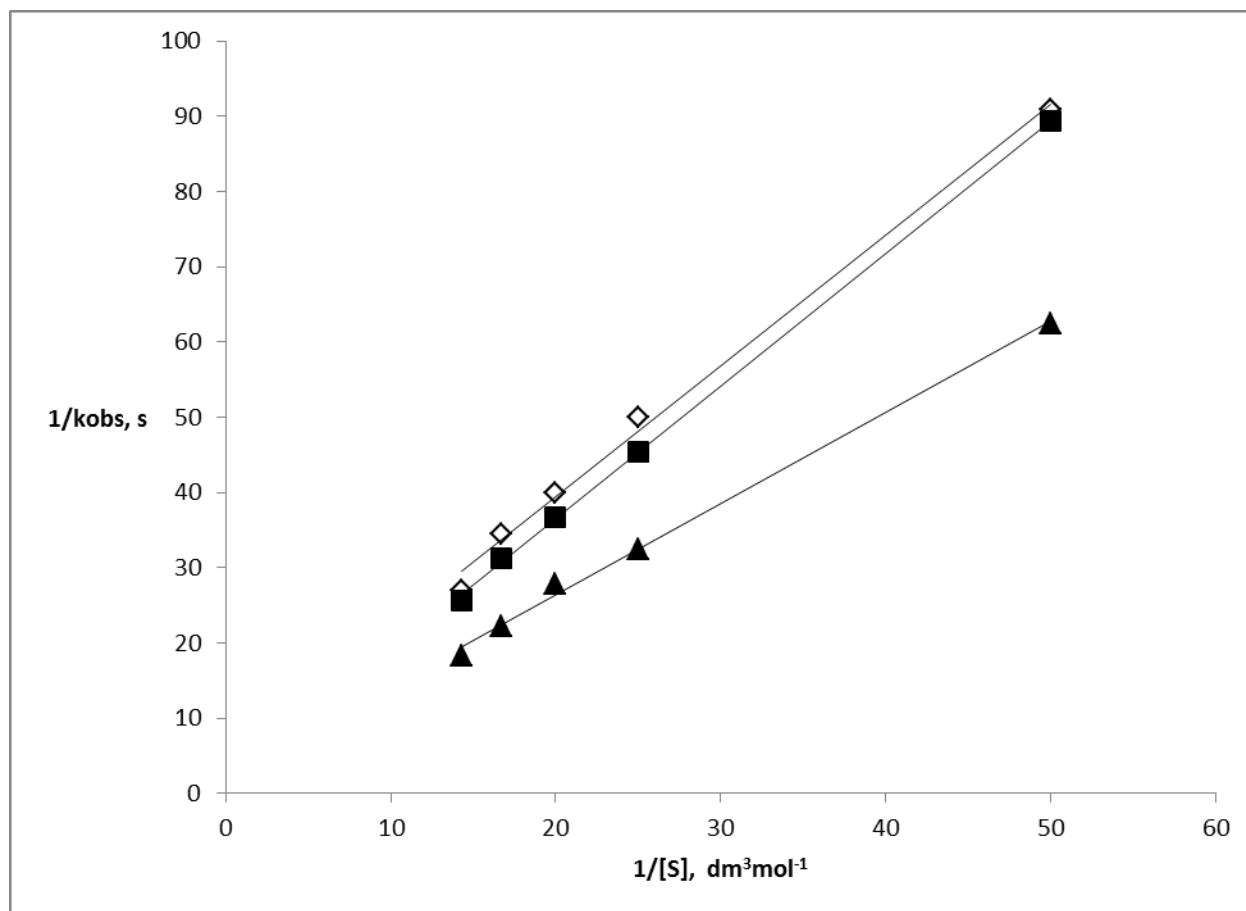


Figure 2: Plot of $1/k_{\text{obs}}$ versus $1/[S]$.

(□ Propanone ■ Butanone ▲ 2-Pentanone)

Dependence of the Reaction Rate on the [OH⁻] Concentration

Generally, the pseudo-first order rate constant increased with increase in [OH⁻] (Table 2). Slope of $\ln k_{\text{obs}}$ versus $\ln[\text{OH}^-]$ showed fractional order dependence with respect to [OH⁻].

Dependence of the Reaction Rate on the Ionic Strength

Variation in the [KNO₃] did not affect the rate of oxidation. This is an indication of the presence of a neutrally charged specie in the rate limiting step as shown from the plot of $\ln k_{\text{obs}}$ vs $I^{1/2}$ (Figure 3).

Dependence of the Reaction Rate on Temperature

Pseudo-first order rate constants k_{obs} were obtained at various temperatures within the range 298K-318K and the initial concentrations of all reactants were kept constant. Table 3 shows the values of the Activation Energies (E_a) and all the activation parameters were obtained by using the below relationship.

Given that:

$$\log k = \log A - \frac{E_a}{2.303RT}$$

$$\ln\left(\frac{k}{T}\right) = \frac{-\Delta H^\ddagger}{RT} + \ln\left(\frac{k'}{h}\right) + \left(\frac{\Delta S^\ddagger}{R}\right)$$

$$\ln\left(\frac{k'}{h}\right) = 23.76$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

Mechanism and Rate Law

Kinetic and spectral results were used to formulate the mechanism:

- (i) Ketone Oxidation in Alkaline medium have been established to be via electron abstraction from the enolate.
- (ii) The non-dependence of the oxidation reaction on ionic strength indicates

the presence of a neutral molecule in the rate determining step.

- (iii) Same values of ΔG^\ddagger indicates same mechanism for the reaction and negative values of ΔS^\ddagger revealed entropy decrease upon achieving the transition state, which often indicate an associative mechanism and it shows that the reaction occurred between ions of similar charges.
- (iv) The IR showed a very broad absorption at 3400-2400 cm^{-1} (OH stretching), a broad band at 1730-1700 cm^{-1} (C=O stretching) and an absorption of medium intensity between 1320 and 1210 cm^{-1} (C-O stretching) for carboxylic acids. The R_f obtained was 0.20 which further confirmed the presence to carboxylic acid as one of the products.
- (v) Michaelis-Menten plot showed the presence of an intermediate complex.

Table 2: Effect of [OH⁻] on Pseudo-First Order Rate Constant.

10 ² [OH ⁻]/M	10 ² k _{obs} /s ⁻¹		
	Propanone	Butanone	2-Pentanone
0.20	1.22	1.30	1.98
0.40	1.40	1.52	2.21
0.60	1.62	1.84	2.50
0.80	1.85	2.21	2.71
1.00	2.01	2.42	3.06

[KMnO₄] 1.50 X 10⁻³M [S] 4.00 X 10⁻²M [KNO₃] 0.30M T= 298K

Table 3: Activation Parameters.

Ketone	E _a (kJmol ⁻¹)	ΔH [‡] (kJmol ⁻¹)	ΔS [‡] (kJK ⁻¹ mol ⁻¹)	ΔG [‡] (kJmol ⁻¹)
Propanone	15.64	13.08	-0.23	81.62
Butanone	17.01	13.77	-0.23	82.31
2-Pentanone	21.42	5.54	-0.25	80.04

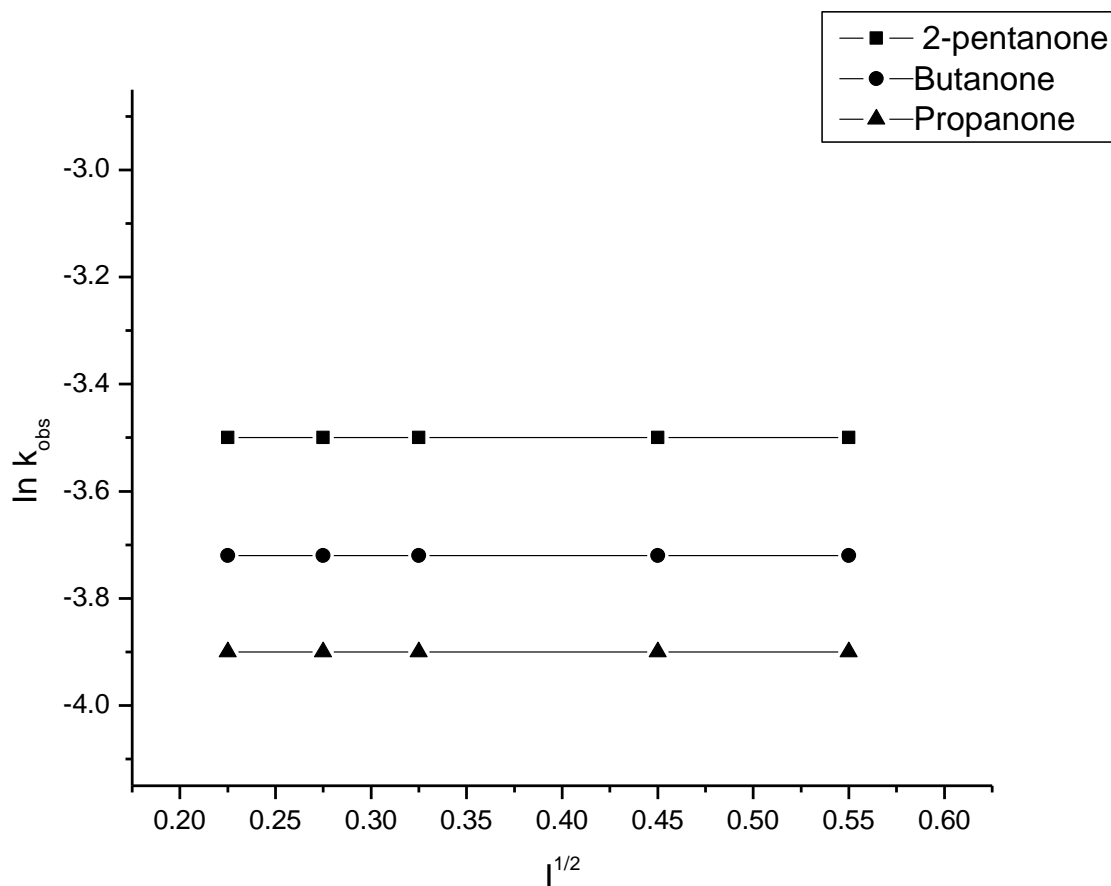
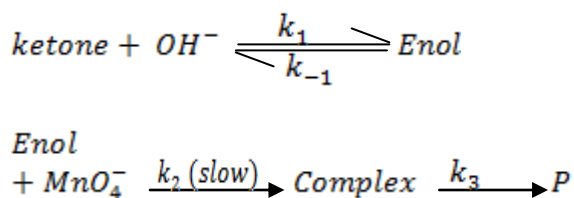


Figure 3: Plot of $\ln k_{obs}$ versus $I^{1/2}$

Therefore, the below mechanism was proposed based on the kinetic results and spectral analyses carried out.



$$\frac{d[\text{Complex}]}{dt} = k_2[\text{Enol}][\text{MnO}_4^-] \quad (1)$$

$$0 = k_1[\text{ketone}][\text{OH}^-] - k_{-1}[\text{Enol}] - k_2[\text{Enol}][\text{MnO}_4^-]$$

$$\begin{aligned}
 k_1[\text{ketone}][\text{OH}^-] &= [\text{Enol}] (k_{-1} + k_2[\text{MnO}_4^-])
 \end{aligned}$$

$$[\text{Enol}] = \frac{k_1[\text{ketone}][\text{OH}^-]}{k_{-1} + k_2[\text{MnO}_4^-]} \quad (2)$$

Substituting Equation (2) into (1):

$$\begin{aligned}
 \frac{d[\text{Enol}]}{dt} &= k_1[\text{ketone}][\text{OH}^-] - k_{-1}[\text{Enol}] \\
 &\quad - k_2[\text{Enol}][\text{MnO}_4^-]
 \end{aligned}$$

$$\frac{d[\text{Complex}]}{dt} = \frac{k_1 k_2 [\text{ketone}] [\text{OH}^-] [\text{MnO}_4^-]}{k_{-1} + k_2 [\text{MnO}_4^-]}$$

Limiting Condition:

$$\text{If } k_{-1} \gg k_2 [\text{MnO}_4^-]$$

$$\frac{d[\text{Complex}]}{dt} = \frac{k_1 k_2 [\text{ketone}] [\text{OH}^-] [\text{MnO}_4^-]}{k_{-1}}$$

$$\text{Where } K_1 = \frac{k_1}{k_{-1}}$$

$$\text{Rate} = K_1 k_2 [\text{ketone}] [\text{MnO}_4^-] [\text{OH}^-]$$

CONCLUSION

The rate is first order with respect to [oxidant],[ketone] and [OH]. The rate constant was in the order [Propanone] > [Butanone] > [2-Pentanone]. The reaction was independent on ionic strength indicating the presence of a neutral molecule in the rate determining step. Michaelis-Menton plot revealed the presence of an intermediate complex in the reaction. IR spectroscopy and Thin-Layer Chromatography showed the presence of carboxylic acid as one of the major products. The use of acrylonitrile showed no presence of radical in the reaction. The mechanism proposed is via the formation of an intermediate complex.

ACKNOWLEDGEMENT

I acknowledge the financial assistance given by Osun State University, Osogbo and the technical support by the technical staff of Obafemi Awolowo University, Ile-Ife, Nigeria.

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SUGGESTED CITATION

Latona, D.F. 2016. "Kinetics and Mechanisms of KMnO_4 Oxidation of Ketones in NaOH Medium". *Pacific Journal of Science and Technology*. 17(2):231-238.

 [Pacific Journal of Science and Technology](http://www.akamaiuniversity.us/PJST.htm)