Kinetic and Mechanistic Study of Oxidation of 3-Methyl-2-Butanone by Isoquinolinium Bromochromate

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Abstract: *The kinetic and mechanistic study of 3-methyl-2-butanone has been explored with isoquinolinium bromochromate (IQBC) in aqueous acidic acid medium at temperature 308 K. The rate of reactions was found proportional to first power of concentration IQBC and H^+ ion. The study provides an evidence for per complex formation between oxidant's species and enolic ketone. The rate of oxidation increases with, decreasing dielectric constant of the medium. The effect of salt does not alter the rate of reaction. The added catalysts $CuSO_4$ and $MnSO_4$ bring about the change in rate of oxidation. The study discards the involvement of free radicals based mechanism for stoichiometric ratio 1:1 of the reaction. Several thermodynamic parameters were determined at different temperatures. The mechanism and rate law was proposed accordingly.*

Keywords: *Alter, significance, validity, involvement, assumptions.*

1. INTRODUCTION

The investigated 3-methyl-2-butanone, is a aliphatic ketone, shows the phenomenon of tautomerism at equilibrium and exhibited a variety of chemical reactions with different oxidizing reagents such as SeO_2 [1], $NBSA^2$, acid-bromate[3], $[Fe (CN)_4]$ [3-4] etc. The study of such reaction is of great significance and of interest because of its vast implication in understanding the nature of chemical processes involved.

A variety of compounds containing Cr (IV) [5-8] have stabilised to be versatile reagent, capable of commencing oxidations almost every oxidizing functional group. In this series, Isoquinolinium bromochromate has been used in the kinetics and mechanistic study of 2-alkanones,[9] protonation of dialkyl acetone dicarboxyxlates[10] and in bromination of hydroxylated aromatic compounds[11] etc. The current surve of literature reveals that similar study on 3-methyl-2-butanone with IQBC is still lacking. Hence prompted me to take up task for foregoing study.

2. EXPERIMENTAL

All the reagents and solvents used during the investigation are commercially available either B.D.H., E-Merck or S-Merck of extra pure quality except where specifically mentioned. The IQBC was prepared by dissolving weighed quantity of Chromium trioxide followed by addition of hydrobromic acid and Isoquinoline for a specific time period. The purity of crystals was confirmed by spectral method. The solution of the substrate was prepared in purified glacial acetic acid as required. The stock solutions of other reagents were prepared by usual recommended methods. The solutions were kept in a reaction vessels maintained at constant temperature 308 K, in a equilibrated thermostatic bath. The progress of the kinetic reaction was monitored by withdrawing aliquots at definite intervals of time for the unconsumed IQBC iodometrically. The duplicate kinetic runs show reproducible results of rate constant within $\pm$ 3%. The rate constants were evaluated by integration method.

3. RESULTS AND DISCUSSION

The kinetic measurement was performed under pseudo first-order condition by keeping [substrate] >> [oxidant]. The investigation indicated first-order dependency of rate with respect to [IQBC], which is

further evidenced by linear plots of log (a-x) vs. time with unit slope. The order varies from 1 to 0 for substrate at higher concentration which shows the existence of complex mechanism between reacting species of oxidant and enolic from of substrate (Table 1). The double reciprocal plot made between k^{-1} vs. $[substrate]^{-1}$ is linear with positive intercept on Y-axis (Fig. 1). The study reveals that at higher concentration, it tends towards X-axis showing limiting value of rate. It is evident that the rate of oxidation of substrate under probe increases with rising concentration of H^+ ions. The unit slope of plot log k Vs. log $[H^+]$ indicates that it obeys first-order kinetics with respect to H^+ ions and shows that reaction is acid catalysed.

It was observed that the reaction velocity of substrate increases with rise in the percentage composition of acetic acid constant in the reaction mixture (Table 2). The linear plot of log k vs. 1/D with positive slop is the evidence of this effect.

The study completely rules out the existence of free radicals based mechanism. They addition of foreign catalysts $CuSO_4$ indicates an increase in rate whereas $MnSO_4$ shows decreasing trend in rate of reaction. The rate of reaction is unaffected by added primary salts. This indicates that rate determining steps involves either neutral species or anion and a neutral, molecule. The observed stoichiometric measurement showed mole ratio 1:1 for IQBC and 3-methyl-2 butanone under study. The 3-methyl-2-oxobutanal was isolated as the oxidation product of the reaction, which is characterized by formation of 2:4 dinitrophyenyl hydrazines (M.P. 168^0 C).

- **Mechanism For 3-Methyl-2-Butanone**

Considering the observed kinetic findings, a mechanism for an attack of reacting species H_2CrO_4 of oxidant IOBC at enolic substrate may therefore be postulated in the slow process as:

(1)

(2)

where Ø = (iso quinolinium ion)

(3)

(4)

(5)
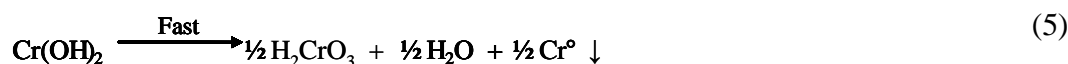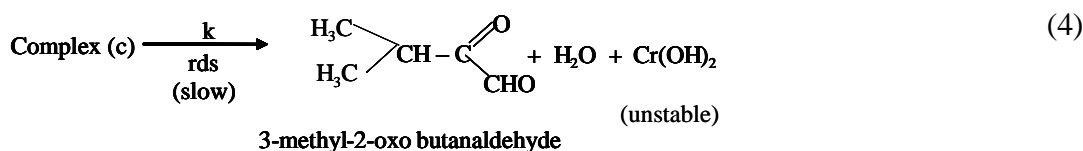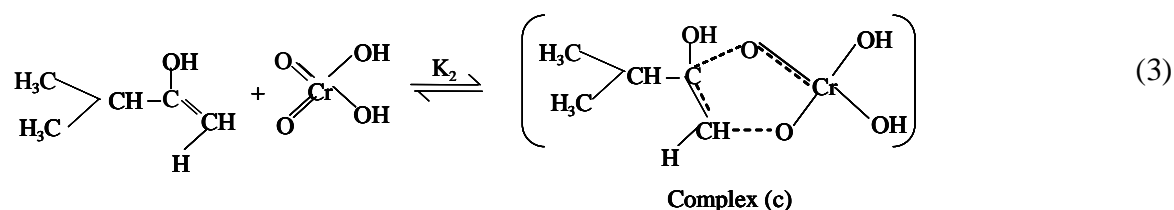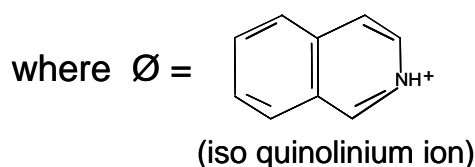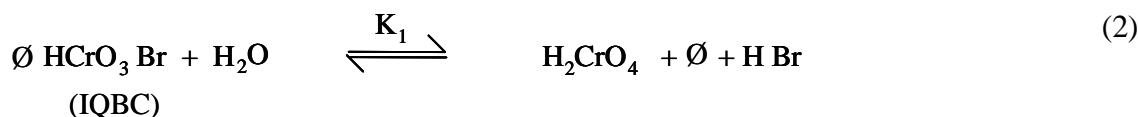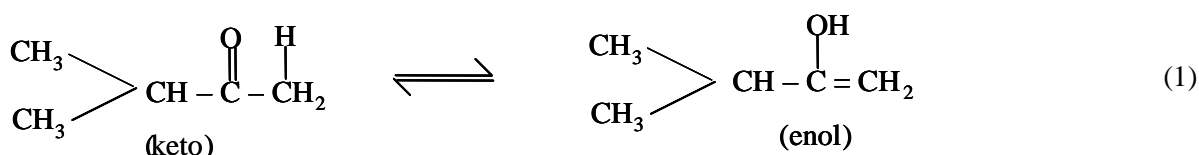
Applying steady state condition with reasonable approximation the mechanism leads to the following rate law:

$$k_{obs} = \frac{K_1 K_2 k [E] [H+]}{[IQ] K_1 + K_1 K_2 [E]} \qquad (6)$$

The formulated mechanism is also supported by the moderate value of energy of activation and other thermodynamic activation parameters. The validity of rate law was tested by making some assumptions. The intercept on Y-axis of double reciprocal plot drawn between $1/k_{obs}$ Vs. $1/[substrate]$ explains clearly the first to fractional-order as illustrated in complex mechanism of the reaction.

Table1. *Effect of variation of [3-methyl-2-butanone] on reaction rate*

$[IQBC] = 2.50 \times 10^{-3}$ (mol dm^3);

$[H^+] = 1.0 \times 10^{-3}$ (mol dm^3);

HOAc-H$_2$O = 20 %, (V/V);

Temperature K = 308 K

Sr. No.	[3-methyl-2- butanone] $\times 10^2$ (mol dm^{-3})	10^4 k$_1$ (s^{-1})
1.	1.25	1.16
2.	2.00	1.63
3.	2.50	1.79
4.	3.33	2.46
5.	4.00	2.65
6.	5.00	2.87

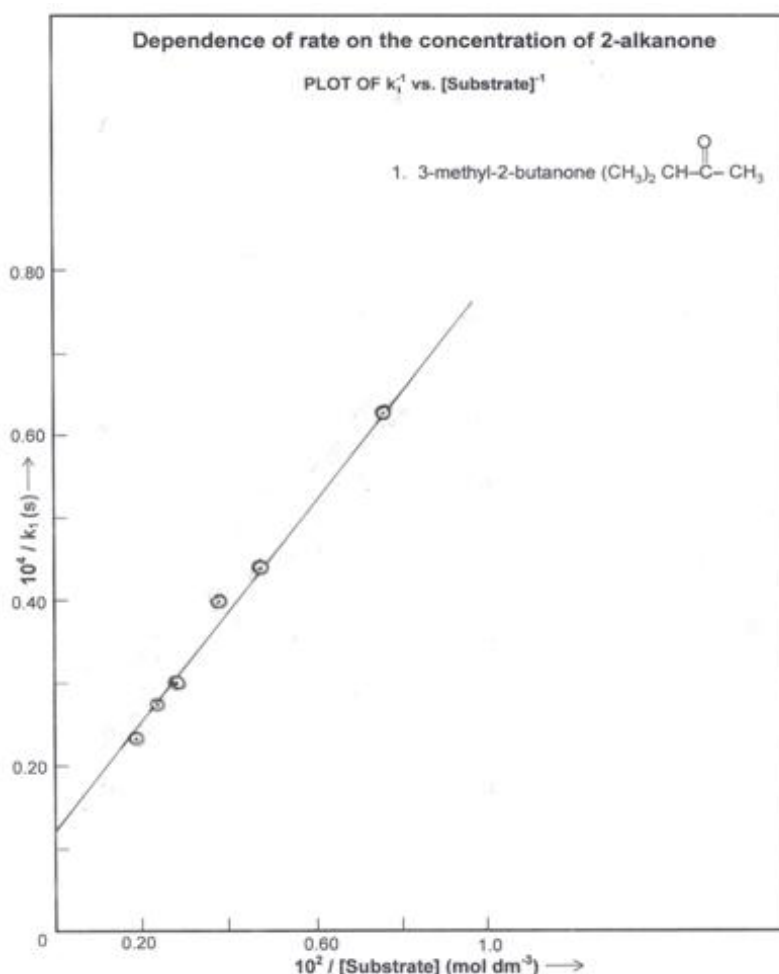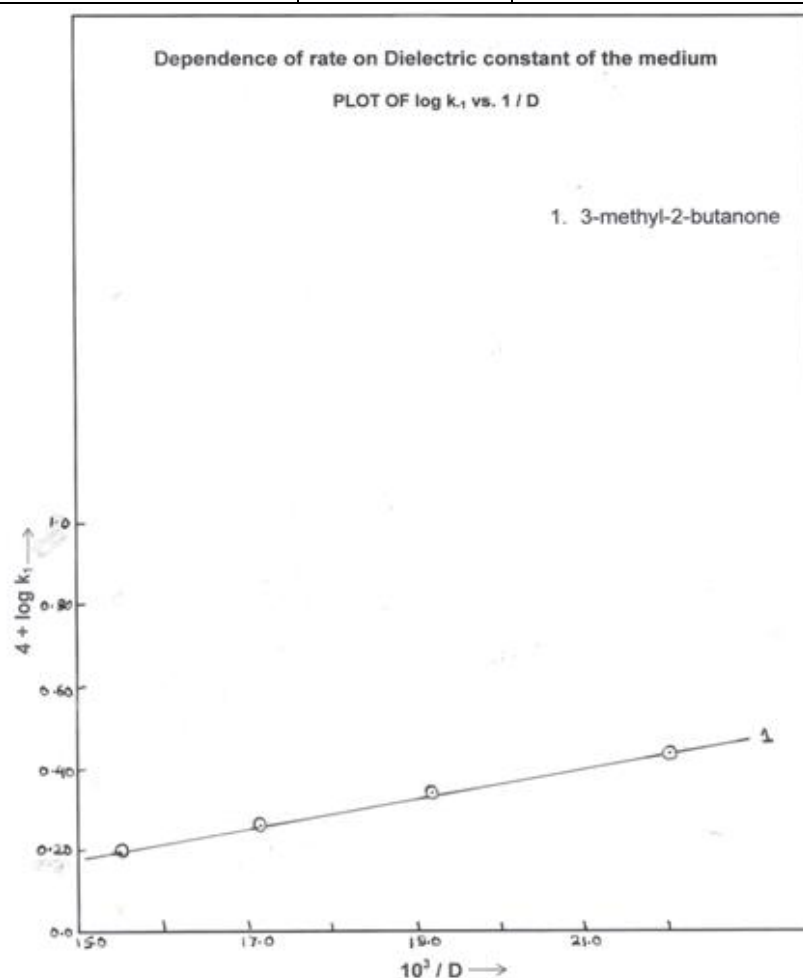**Fig1.** *[IQBC] = 2.50 × 10^{-3} (mol dm^3); [H$^+$] = 1.0 × 10^{-3} (mol dm^3); HOAc-H$_2$O = 20 %, (V/V); Temperature K = 308 K*

Table2. *Dependence of rate on Dielectric constant of the medium*

[3-methyl-2- butanone] = 2.50×10^{-2} (mol dm^3);

[IQBC] = 2.50×10^{-3} (mol dm^3);

[H$^+$] = 1.0×10^{-3} (mol dm^3) ;

Temperature = 308 K

Sr. No.	HOAc-H$_2$O % (v/v)	$\dfrac{10^3}{D^*}$	$k_1 \times 10^4$ (s^{-1})
1.	10	15.50	1.52
2.	20	17.17	1.79
3.	30	19.15	2.25
4.	40	21.98	2.71

Fig2. *[Substrate] = 2.0×10^{-2} (mol dm^{-3}); [IQBC] = 2.50×10^{-3} (mol dm^3); [H$^+$] = 1.0×10^{-3} (mol dm^3) ; Temperature = 308 K*

4. CONCLUSION

IQBC is a mild efficient economically cheap reagent containing Cr(VI) is able to work as both and oxidizing and Brominating agent. The mechanism of oxidation was explained through the formation of reacting species H_2CrO_4 and enol form of ketone precursor prior to rate rds altransition state. The validity of rate law was tasted by rate expression. The order of ketone changed from unity to a fraction at its higher concentration.

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