MECHANISTIC STUDY OF OXIDATION OF 2-ALKANONES BY ISOQUINOLINIUM BROMOCHROMATE IN ACIDIC MEDIUM

Khushboo Trivedi[1], M. U. Khan[1] , K.N.Sharma[3]

[1]Department of chemistry, Govt. Model Science College, Rewa-486001 (M.P.) India.

[2]Retd. P.G.Principal,Govt. College, Budhar, Shahdol, (M.P.) India.

[3] Department of Chemistry, Govt.Girls P.G. Rewa (M.P.)-486001, India.

ABSTRACT

Kinetics and mechanistic study of oxidation of 2-butanone and 2-pentanone have been studied in binary solvent mixtures of water and acetic acid with isoquinolinium bromochromate in presence of sulphuric acid. The oxidation follow first-order kinetics with respect to [oxidant] and [H^+], whereas order falls one to zero at higher concentration of substrate. The reaction is acid catalysed. The acceleration of rate was observed with rise in percentage composition of acetic acid, while primary salt showed negligible effect. Added catalysts $CuSO_4$ and $MnSO_4$ affect the rate of reaction. The enolic form of ketonic species actively participates in stoichiometric ratio 1:1 in the formation of complex at transition state. Activation parameters were evaluated and suitable mechanism was proposed. The rate law in consistent with the observed kinetic results has been discussed.

Key Words : Probe, estimation, appropriate, acceleration, dominancy.

INTRODUCTION

Now-a-days a halochromate isoquinolinium bromochromate (IQBC) has been used as a mild and selective, eco-friendly oxidizing reagent in the oxidation of alcohols,[1,2] anilines,[3] phenols.[4] The survey of literature pertaining to the oxidation of 2-alkanones show little kinetic information on the IQBC oxidation in aqueous acetic acid medium in presence of sulphuric acid (H_2SO_4). Although the 2-alkanones viz. 2-butanone, and 2-pentanone exhibited variety of chemical reactions with different oxidants namely SeO_2,[5] BAT[6], NCSA[7] etc. at 2- Carbon atom of the keto functional

group. The ambiguity always exists as reported that the attack of participating activated species of IQBC occur at enolic or keto position of the 2-alkanones. This prompted me to probe the kinetic and mechanism of IQBC led oxidation of 2-butanone and 2-pentanone in aqueous acetic acid medium.

EXPERIMENTAL

The entire chemical used during the investigation were either B.D.H., E-Merck or S-Merck of extra pure quality except where specifically mentioned. The glass apparatus used were made of either Pyrex or coring glasses.

Isoquinolinium bnromochromate was prepared by chromium trioxide (10g, 0.1 mol.) was dissolved in distilled water (15 ml) and cooled to 0^0C. To this solution was added hydrobromic acid (17ml, 48%) slowly with vigorous stirring, then isoquinoline (13ml, 0.1 mol) was added drop wise for 10 minutes. The reaction mixture was cooled for 2-3 hrs and filtered. The resulting yellow orange needles were dried and recrystallised.

The 2-butanol and 2-pentanol were distilled under reduced pressure[8] using a trace of zinc dust. The standard solution of sodium thiosulphate was prepared and standardized iodometrically daily before use. The kinetic measurements were initiated under the condition [2-alkanones] >> [IQBC]. The solutions of oxidant IQBC and 2-alkanones were placed in a reaction vassel in a thermostat maintained at experimental temperatures with an accuracy of $\pm$ 0.1^0 C. When the equilibrium of temperature is reached, the solutions were mixed and aliquot of definite volume was withdrawn immediately and was quenched with ice-cold water. The amount of unreacted IQBC was estimated iodometrically[9] with the standard solution of sodium thiosulphate using starch as an indicator.

The experimental data were fed into the integrated form of equation for pseudo first-order reaction. The values of rate constant obtained were found fairly constant within the experimental error $\pm$ 3%.

RESULTS AND DISCUSSION

The kinetic data has been obtained for the effect of concentration of oxidant (IQBC) at fixed concentration of other reactants and temperature. The linear plots of log (a-x) vs. time, suggested first-order kinetics with respect to [oxidant].

The reactions follow first-order kinetic at lower concentration of 2-alkanones which tends toward zero-order at higher concentration, showing limiting value of rate constant which is confirmed by the formation of complex between substrate and IQBC species (Table 1). The double reciprocal plot of k^{-1} versus $[substrate]^{-1}$ exhibited state line intercepting Y-axis with positive slope (Fig. 1).The first-order constant increases linearly with an increase in $[H^+]$. The reaction velocity increases with successively increasing composition of acetic acid, that is, the rate slightly accelerated with decreases in dielectric constant of the medium (Table 2).

Table: 1

Dependence of rate on the variation of the concentration of 2-alkanones

10^3 [IQBC] (mol^{-1} dm^3) = 2.50 (1, 2) ;
10^3 [H$^+$] (mol^{-1} dm^3) = 1.0 (1, 2);
HOAc-H$_2$O %, (V/V) = 20 (1, 2) ;
Temperature K = 303 (1), 308 (2)

[2-alkanone] $\times 10^2$ (mol. dm^{-3})	2- butanone (1)	2- pentanone (2)
	$\longleftarrow 10^4 \, k_1 \, (s^{-1}) \longrightarrow$	
1.00	1.73	-
1.25	2.11	1.41
2.00	3.75	2.61
2.50	3.92	2.92
3.33	-	3.42
4.00	5.15	3.82
5.00	5.61	4.23

1. 2-butanone (CH$_3$–CH$_2$–C(=O)–CH$_3$); 2. 2-pentanone (CH$_3$–CH$_2$–CH$_2$–C(=O)–CH$_3$)

Dependence of rate on the concentration of 2-alkanones

$10^{-4} / k_1 (s)$ →

$(CH_3–CH_2–CH_2–C–CH_3)$

$(CH_3–CH_2–C–CH_3)$

$10^2/[Substrates]$ (mol dm^{-3}) →
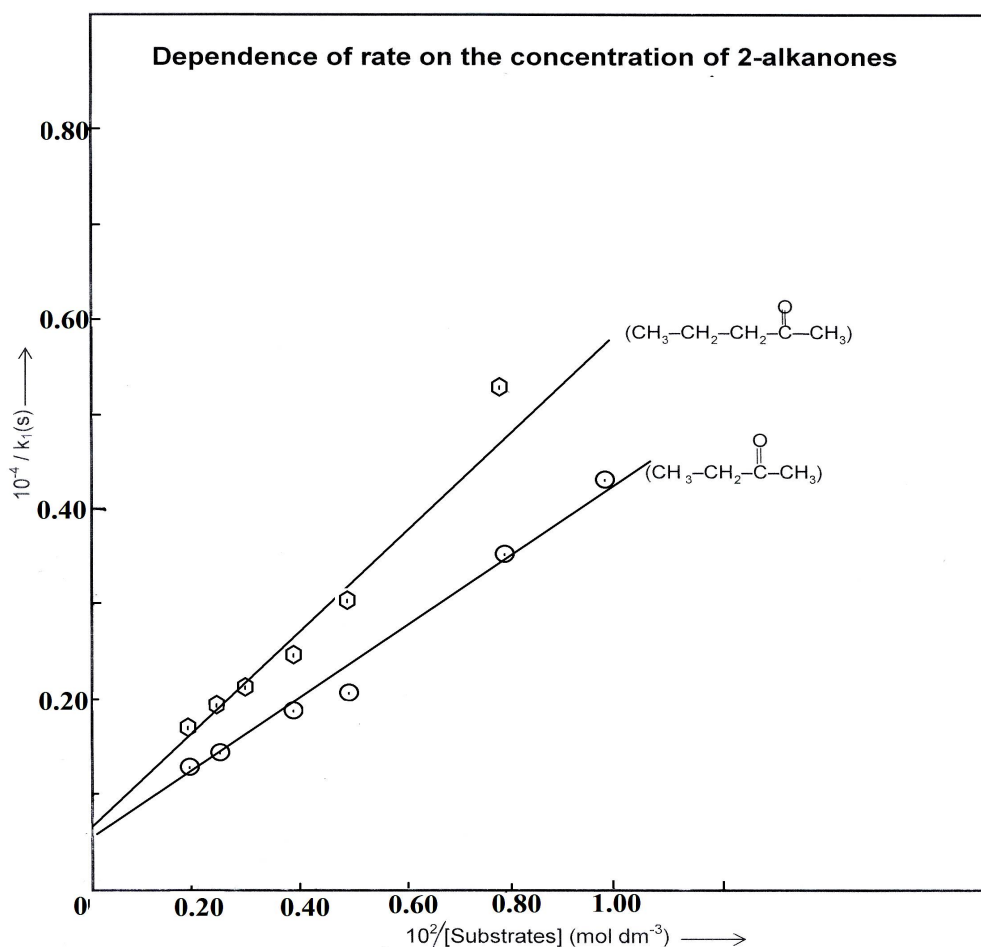
Fig. 1   [IQBC] x10^{-3} (mol dm^{-3}) = 2.50 (1, 2) ; [H$^+$] x10^{-3} (mol dm^{-3}) = 1.0 (1, 2);
HOAc–H$_2$O % (v/v) = 20 (1, 2); Temp. K = 303 (1), 308 (2)

The plot of log k_1 versus 10^3/D was obtained linear with positive slope in each alkanones (Fig.2). The addition of Cl⁻ ions in the form of NaCl, almost show negligible salt effect. Metal cations Cu^{++} ions used as catalyst show acceleration in the reaction velocity while Mn^{++} ions retard the rate of oxidation. The study rules out the presence of free radicals when tested qualitatively by addition of 1-2 ml of acrynitrile monomer. Stoichiometric determination[10-13] indicated 1:1 mole ratio for substrate and oxidant (IQBC).
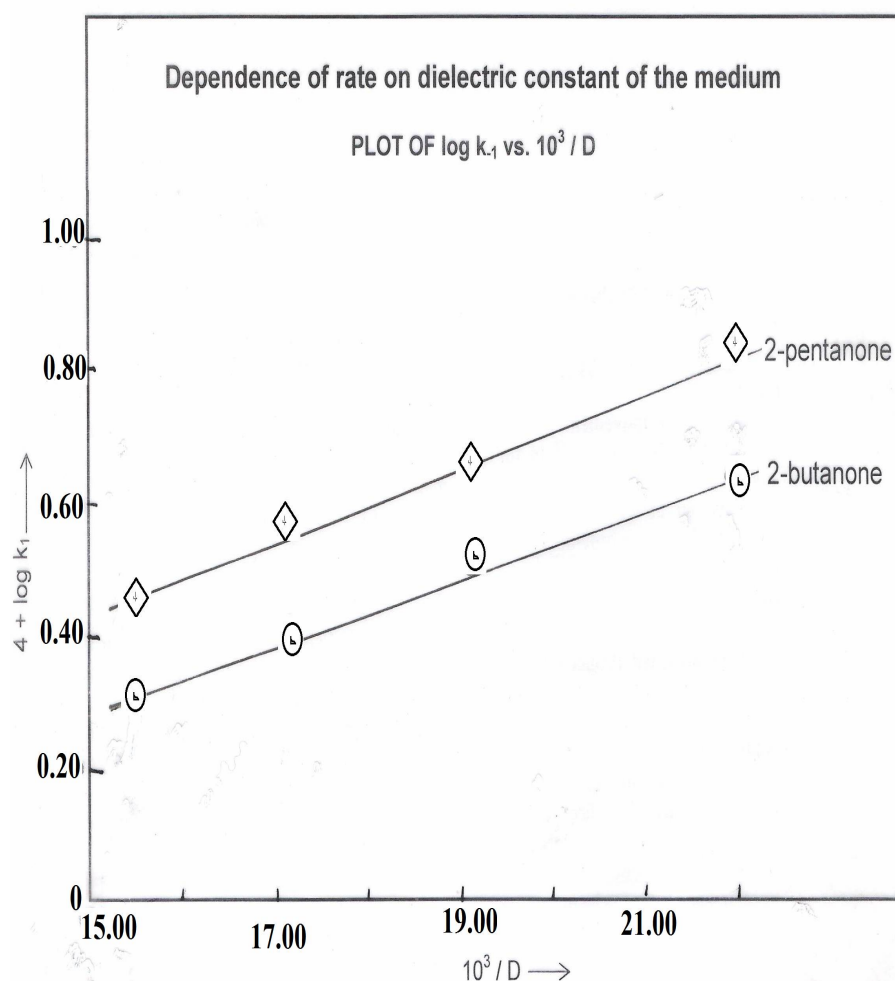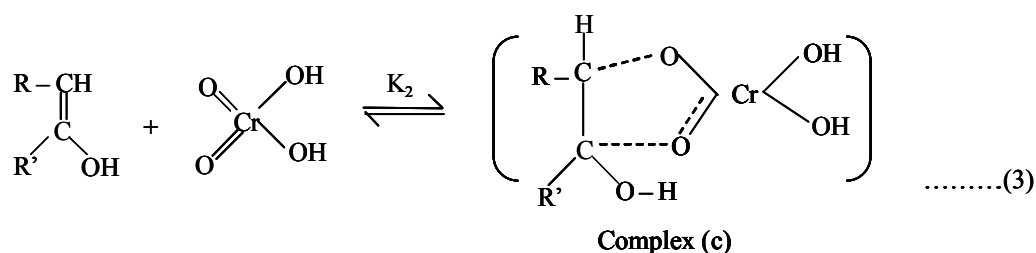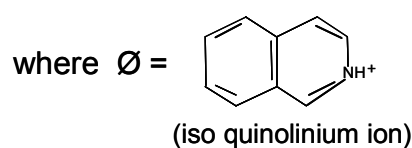
Fig. 2 10^2x[Substrate] (mol dm^{-3}) = 2.0 (1), 2.5 (2) ; 10^3x[IQBC] (mol dm^{-3}) = 2.50 (1,2) ; 10^3 [H$^+$] (mol dm^{-3}) = 1.0 (1, 2) ; Temp. K = 303 (1), 308 (2)

The main oxidation products diones, were identified by spot test. Considering the above statements regarding the enolic species of 2-alkanones and other kinetic findings, the following scheme of mechanism for the reactions is proposed:

MECHANISM

$$R-CH_2,\ R'-C=O \ \underset{}{\overset{H^+}{\rightleftharpoons}}\ R-CH,\ R'-C-OH \qquad \ldots\ldots\ldots\ldots (1)$$

(keto) (enol)

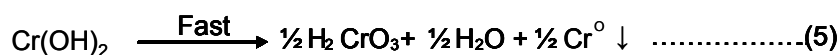$$\emptyset HCrO_3 Br + H_2O \ \overset{K_1}{\rightleftharpoons}\ H_2CrO_4 + \emptyset + HBr \qquad \ldots\ldots (2)$$
(IQBC)

where ∅ =

(iso quinolinium ion)

$$\ldots\ldots\ldots (3)$$

Complex (c)
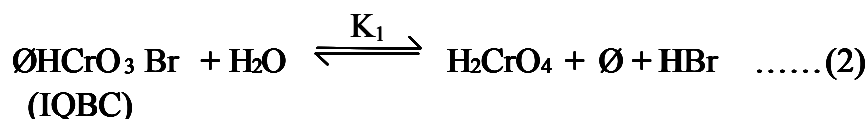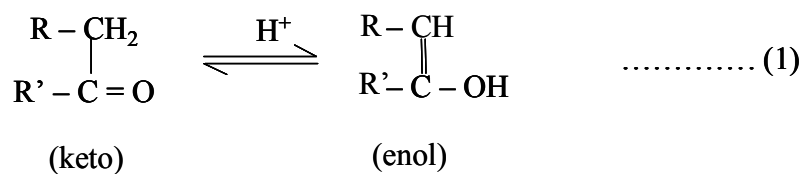
where R = R' = $-CH_3$

for 2-butanone and

R = $-CH_3$ and R' = $-CH_2 CH_3$

for, 2-pentanone

Complex (c) (unstable) $\ldots\ldots\ldots (4)$

$$Cr(OH)_2 \ \overset{Fast}{\longrightarrow}\ \tfrac{1}{2} H_2 CrO_3 + \tfrac{1}{2} H_2O + \tfrac{1}{2} Cr^o \downarrow \qquad \ldots\ldots\ldots\ldots (5)$$
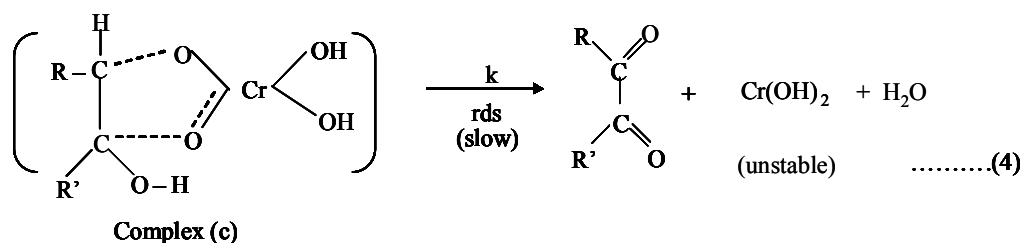
In present investigation, the powerful remote cationic electrophilic is H_2CrO_4 which interact with the enolic form of substrate in the slow process.

The transfer of electron takes place from substrate to active species of IQBC during the formation of complex, which is electron deficient species.

Rate law

Taking into consideration the various step involved in the proposed scheme of mechanism, the rate law could be derived as follows:

Since,   Rate $=$ k [complex]   ....(6)

$$\text{Rate} \ = \ \frac{K_1 \, K_2 \, k \, [E] \, [IQBC] \, [H^+]}{[IQ]} \qquad \text{............(7)}$$

Further

$$[IQBC]_T \ = \ [IQBC] \ + [H_2 \, CrO_4] \ + \ [complex] \qquad \text{............(8)}$$

Substituting the value of [IQBC] from $[IQBC]_T$ in above equation, we get, rate equation

$$\text{Rate} \ = \ \frac{K_1 \, K_2 k \, [E] \, [IQBC]_T \, [H^+]}{[IQ] \, K_1 + K_2 \, K_1} \qquad \text{............(9)}$$

Applying steady state condition with reasonable approximation yield the final rate law :

$$k_{obs} \ = \ \frac{\text{Rate}}{[IQBC]_T} \ = \ \frac{K_1 \, K_2 \, k \, [E] \, [H^+]}{[IQ] \, K_1 + K_1 \, K_2 [E]} \qquad \text{............(10)}$$

The rate law (10) apparently accounts for the first-order kinetics with respect to [IQBC] and [H^+] and fractional order with respect to enol form of substrates which is obvious from the rate law equation which appears in the expression.

REACTIVITY: In the present investigation, the observed order of reactivity among 2-alkanones was found as.

$$CH_3 - CH_2 \ - \overset{\displaystyle \overset{O}{\|}}{C} - CH_3 \ > \ CH_3 - CH_2 \ - CH_2 - \overset{\displaystyle \overset{O}{\|}}{C} - CH_3$$

    2-butanone   2-pentanone
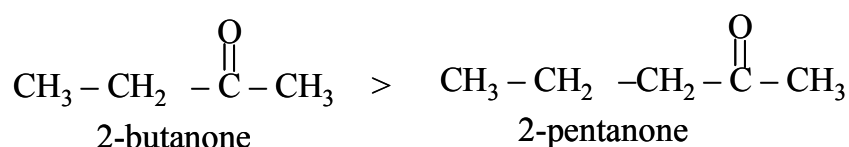
It is quite obvious from the study that 2-butanone exhibits fastest rate among the 2-alkanones which may be attributed side[14] reaction.

The accumulation of electron density on α–carbon atom is partially enhanced by electron donating influence of –CH$_3$ group (+I effect). It is relatively more sterically hindered because of bigger –CH$_3$ than –CH$_2$ CH$_3$ group and thus increasing content of enol occurs due to exhibiting of probably hyperconjugative effect. Consequently rate of reaction increases in 2-alkanones. Moreover the electron deficient species is formed at the transition state which is stabilized by existing hyperconjugation. The (+ I) effect, pushing driving force towards a bond sufficient enough to cleavage the C–H bond and eliminating proton, ultimately resulting the complex. The similar views have also been reported earlier by a couple of authors who carried out oxidation of alkanones with KMnO$_4$[15] and alkaline hexacynoferrate(III)[16] oxidation of ketones.

2- butanones experiences grater hyperconjugation in compared 2-pentanone and therefore 2-pentanone shows slower rate than 2-butanone.

The above mechanism has been supported by the activation parameters. The values of energy of activation of 2-butanones (60.53 kJ mol^{-1}) is less than the value of (61.68 kJ mol^{-1}) for 2-pentanone, which is measure of above order of reactivity of compound. These are well in accordance with the reactivity trends. The high value of $-\Delta S^{\#}$ suggests, the rigid complex forming ability of IQBC with 2-alkanones in the transition state.

The rupture of C–H was also reported in the studies due to loss of translational and rotational freedom of the process. The value of free energy $\Delta G^{\#}$ approximately lies between (82.44 to 87.45 kJ mol^{-1}) indicating the prevalence of same type mechanism. Overall the reactions are enthalpy controlled.

REFERENCES

1	Patwari, S.B., Khansole, S.V., and Vibhute, Y.B.	:	Bulletin of the Catalysis Society of India, 2009, **8**, 114-120.
2	Khansole, S.V., Patwari, S.B., and Vibhute, Y.B.	:	Chinese Chemical Letters, 2009, **20**, Issue:3, 256-260.
3	Patwari, S.B., Khansole, S.V., and Vibhute, Y.B.	:	J. Iran. Chem. Soc., 2009, **6**, No. 2, 399-404.
4	Khansole, S.V., and Vibhute, Y.B.	:	Journal of the Indian Chemical Society, 2009, **86**, Issue 12, 1343-1346.
5	Tiwari, S., Khan, M.U., Tiwari, B.M.L., Tiwari, K.S. and Valechha, N.D.	:	Oxid. Commun., 1999, **22**, No.3, 416-423.
6	Singh, B., Singh, D., Chand, R., and Singh, A.K.	:	J. Indian Chem. Soc., 1987, **64**, 741.
7	Khan, S., Khan, M.U., Singh, S.K., Gupta, H.D. and Singh, P.K.	:	Asian J. Chem., 2007, **15**, No.2, 5267-5270.
8	Tiwari, A.K.S., Sharma, V.K., Sharma, K., Tiwari, A. and Gupta, O.P.	:	Oxid. Commun., 1999, **22**, No.4, 591-598.
9	Singh, B., Singh, D., Chand, R., and Singh, A.K.	:	J. Indian Chem. Soc., 1987, 64, 741.
10	Koshta, S.P., and Koshta, S.	:	Int. J. of Nanotechnology U.S.A., 2004.
11	Singh, S.Kr., Gupta, O.P., Khan, M.U., Gupta, H.D. and Singh, S.K.	:	Oxid. Commun., 2010, **33,** No.4, 891-897.
12	Singh, S.K., Gupta, H.D., Khan, M.U., and Baghel, S.K.	:	Orbital Elect. J. Chem., 2010, **2**, No.2.
13	N.M.I., Alhaji and S. Sofia lawrence mary	:	E. Journal of Chem., 2011, **8(4)**, 1472-1477.
14	Riley, H.L., Moreley, J.F. and Friend, N.A.	:	J. Chem. Soc., 1932, 1875.
15	Radhakrishnamurti, P.S. and Devi, S.	:	Indian J. Chem., 1977, **15**, 524.
16	Radhakrishnamurti, P.S.	:	Indian J. Chem., 1972,**10**, 496.