

Study of Catalysed Oxidation of Some 2-alkanones by N-bromoisonicotinamide in aqueous acetic acid

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Abstract: The catalysed oxidation kinetics of two-alkanones (2-butanone and 2-pentanone) by N-bromoisonicotinamide in aqueous acetic acid medium leads to afford corresponding diones. The reaction was found to be of first-order with respect to oxidant and complex behaviour was exhibited by enolic ketone and phosphotungstic acid. The reaction exhibited fractional-order kinetic by H⁺ ion dependence. The solvent effect has been analysed for ion-dipole interactions. A suitable mechanism for the reaction was suggested which agrees with the measured kinetic and thermodynamic parameters.

Keywords: 2-butanone, 2-pentanone, N-bromoisonicotinamide, phosphotungstic acid, kinetics.

1. INTRODUCTION

In the last two decades, the oxidation of various organic compounds, extensively studied by heteropoly Keggin type phosphotungstic acid.^[1] (H₃PW₁₂O₄₀)⁻³. It is thermally stable consumes small reaction time and requires small quantity of reagent. As per surveyed literature, PTA has been employed for the oxidation of several organic compounds- (amines,^[2] alcohols,^[3] hydroxy acids^[4] and halo-oxime^[5] etc.).

N-bromoisonicotinamide (NBIN), a halo-oxidant, is stable, economically cheap and eco-friendly, widely used in biotechnology.^[6] and oxidative studies of alcohols,^[7] amino acids,^[8] and unsaturated acids.^[9]

2-alkanones possess carbonyl groups, exhibit a variety of properties such as tautomerism, inductive effect, and polarity largely in numerous inorganic and organic reactions. Owing to this nature, kinetics of oxidation of alkanones by different oxidants have been investigated involving SeO₂,^[10] NDC,^[11] NCSA,^[12] CAT^[13].

The reactivity are often markedly affected by change in the carbon skeleton and introduction of additives. The survey of literature reveals that there seems to be no work documented on the above entitled reactions. In this article, we report here the hitherto unreported results of PTA catalysed oxidation of 2-butanone and 2-pentanone by NBIN in aqueous acetic acid medium.

2. EXPERIMENTAL

Materials : All the reagents employed in the kinetic investigations were of analytical grade. The solution of PTA was prepared in distilled water and mineral acid, used in the study less than pH8. The synthesized sample of NBIN is dissolved in acetic acid^[14] (B.D.H.) and its purity was checked iodometrically. The commercial samples of 2-butanone, 2-pentanone were used as such received. All the stock solutions were kept in the dark until needed.

Kinetic procedure

The kinetic investigation was conducted at pseudo first-order condition [NBIN] << [2-alkanone] in a highly equipped thermostat (±0.1°C). In a kinetic run, the NBIN, acetic acid, PTA were taken in a calculated proportion of solution in a stoppered conical flask whereas alkanone contained in another flask separately placed in the water bath maintained at their experimental temperatures for half an hour. After, thermal equilibrium was reached, both the solutions were mixed and kinetics of the reaction was monitored for unreacted [NBIN] iodometrically at different intervals of time. The values of rate constant (k_{obs}) were computed by using integration and graphical methods. The reproducibility of the results was observed within ±4%.

4. Results and Discussion

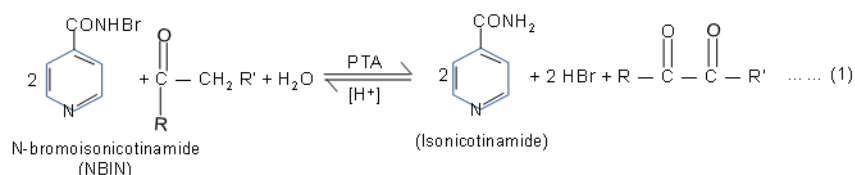
Phosphotungstic acid catalysed oxidation of 2-alkanone viz. 2-butanone, and 2-pentanone by NBIN was probed in aqueous acetic acid medium and results are presented here.

Stoichiometry and product analysis

The stoichiometry of the reaction was determined under stated reaction conditions of the experiments by varying amount of [NBIN] largely in excess over [2-alkanones]. The estimation of unreacted NBIN showed that 1 mole of 2-alkanone

reacts with 2 moles of NBIN as conform in the reaction equation (1). The oxidative products diones were analysed by spot test, and forming their Nickel dioxime salt complex, and 2,4-DNP derivatives.

The addition of acrylonitrile, in an atmosphere of nitrogen to the reaction mixture did not affect the rate, indicating that free radicals, is unlikely present in the reaction, that is, absence of free radicals in the reaction pathway did not play any role in reaction mechanism.



where, $\text{R} = \text{R}' - \text{CH}_3$ for 2-butanone,

and $\text{R} = -\text{CH}_3$ and $\text{R}' = -\text{CH}_2\text{CH}_3$ for 2-pentanone respectively.

The increase in [NBIN] did not affect the rate of reaction. The first-order plots of $\log [\text{NBIN}]$ versus time were linear. The computed k_{obs} derived from the slopes of the plot remained unaffected by the five-fold changes in [IQBC]. This study established the first-order dependence of the rate on [NBIN] in both the cases.

The effect of five-fold variation of concentration of 2-alkanones enhance the reaction rate initially showing first-order kinetics at low concentration of substrate but refused to obey first-order at their higher concentration (Table 1). The plots of k_{obs} versus concentration of 2-alkanones for different initial concentrations of substrate (Fig. 1) results non-linear curve with slopes less than unity indicate existence of complex at the transition state.

Table 1: Dependence of rate on [2-alkanone]

$10^3 \times [\text{NBIN}] \text{ (mol dm}^{-3}\text{)} = 3.33 \text{ (1, 2)} ; [\text{H}^+] \text{ (mol dm}^{-3}\text{)} = 0.0015(1), 0.00166 \text{ (2)} ;$

$10^5 \times [\text{PTA}] \text{ (mol dm}^{-3}\text{)} = 2.50 \text{ (1, 2)} ; \text{CH}_3\text{COOH-H}_2\text{O} \%, \text{ (v/v)} = 20 \text{ (2), 25 (1)} ; \text{Temperature K} = 303(1), 308 \text{ (2)}$

$10^2 \times [\text{2-alkanone}]$ (mol dm ⁻³)	$10^4 k \text{ (s}^{-1}\text{)}$	
	2-butanone (1)	2-pentanone (2)
1.00	2.27	-
1.25	-	1.91
1.50	3.14	-
2.00	3.92	2.78
2.50	-	3.18
3.33	5.40	3.86
4.00	5.79	4.49
5.00	6.20	5.12

The reaction is not much sensitized by H^+ ions. The plots of $\log k$ vs. $[\text{H}^+]$ were linear with fractional-order dependence of the rate on $[\text{H}^+]$ for each reaction follows $k_{\text{obs}} = a + b [\text{H}^+]$. The rate of oxidation was collected for 10% to 40% acetic acid and water mixture the rate remarkably increased with decrease in dielectric constant of the medium (D) showing dipole type of interaction between the oxidant and the substrate.

The dependent of rate with five-fold concentration of PTA catalyst studied on the reaction (Table 2), shows the ability to form complexes with the enolic substrate and reacting species of oxidant NBIN at experimental conditions. Plots of k vs. $\log [\text{PTA}]$ (Fig.2) shows fractional-order kinetics in respect of [PTA]. PTA does not fully catalyse the reaction, as heteropoly Keggin type catalyst releases proton and causes slow protonation of oxidant. The outer sphere of this catalyst overlaps with the enolic ketone in the form of tungstated frame work. The addition of Cl^- ions of the form of NaCl at constant condition and ionic strength, did not alter the rate of oxidation. The rate of reaction was examined by addition of reductant product, isonicotinamide which shows almost negative effect on rate discarding the non-participation in reaction mechanism.

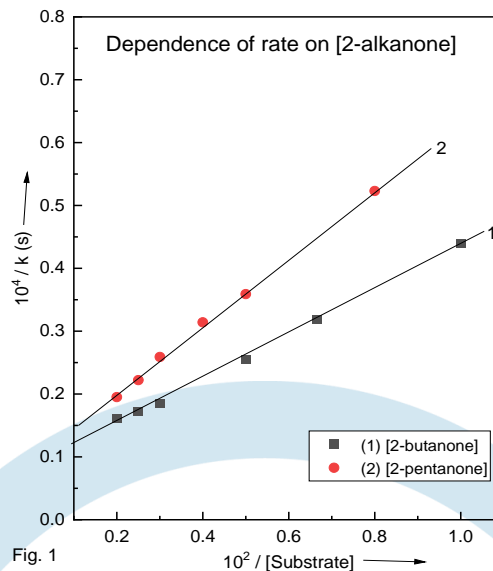


Fig. 1

Plot of $1/k_{\text{obs}}$ vs. $1/[\text{substrate}]$

$10^3 \times [\text{NBIN}] (\text{mol dm}^{-3}) = 3.33 (1, 2)$;

$[\text{H}^+] (\text{mol dm}^{-3}) = 0.0015 (1), 0.00166 (2)$;

$10^5 \times [\text{PTA}] (\text{mol dm}^{-3}) = 2.50 (1, 2)$;

$\text{CH}_3\text{COOH-H}_2\text{O} \%, (\text{v/v}) = 20 (2), 25 (1)$;

Temp. K = 303 (1), 308 (2)

Table 2: Dependence of rate on [PTA]

$10^2 \times [\text{2-alkanone}] (\text{mol dm}^{-3}) = 2.0(1), 2.50(2)$; $10^3 \times [\text{NBIN}] (\text{mol dm}^{-3}) = 3.33 (1, 2)$; $[\text{H}^+] (\text{mol dm}^{-3}) = 0.0015(1), 0.00166 (2)$; $\text{CH}_3\text{COOH-H}_2\text{O} \%, (\text{v/v}) = 20 (2), 25 (1)$; Temperature K = 303(1), 308 (2)

$10^5 \times [\text{PTA}]$ (mol dm^{-3})	$5 + \log$ [PTA]	2-butanone		2-pentanone	
		$10^4 k$ (s^{-1})	$4 + \log k$	$10^4 k$ (s^{-1})	$4 + \log k$
1.00	0.0000	1.70	0.2304	1.36	0.1335
1.50	0.1760	2.56	0.4082	1.95	0.2900
2.00	0.3010	3.40	0.5314	2.62	0.4183
2.50	0.3979	3.92	0.5932	3.18	0.5024
3.33	0.5224	4.74	0.6757	3.86	0.5865
4.00	0.6020	5.55	0.7442	4.41	0.6444

The rate of enolization of 2-alkanones under investigation was determined by halogenation method that shows rate of enolization was found much faster than the rate of oxidation. More over HOBr was assumed as a main profile of reacting species of oxidant.

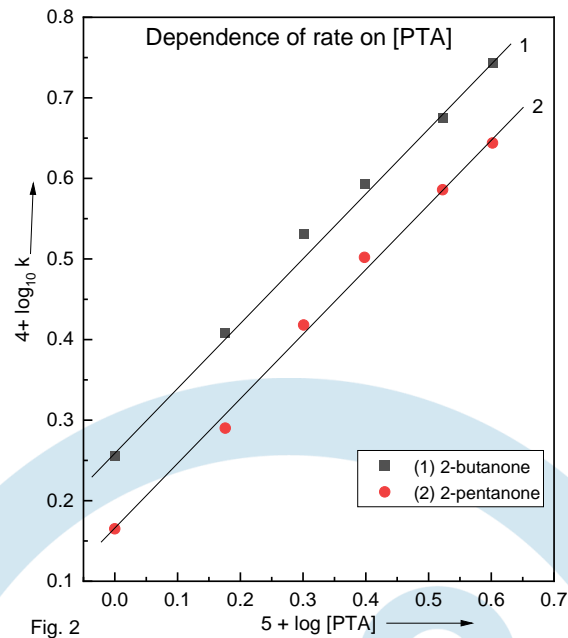


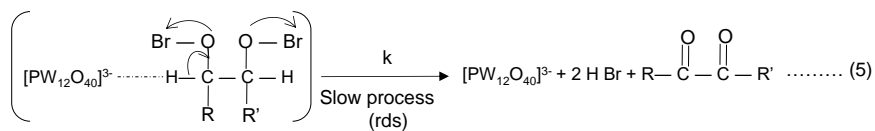
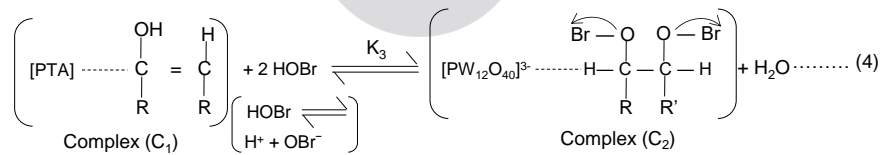
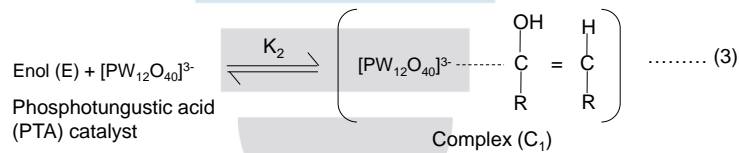
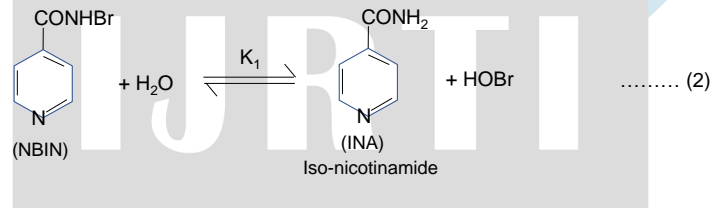
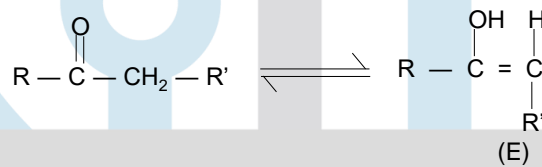
Fig. 2

Plot of log k₁₀ vs. log [PTA]

10² x [2-alkanone] (mol dm⁻³) = 2.0(1), 2.50(2) ;
 10³ x [NBIN] (mol dm⁻³) = 3.33 (1, 2) ;
 [H⁺] (mol dm⁻³) = 0.0015(1), 0.00166 (2) ;
 CH₃COOH-H₂O %, (v/v) = 20 (2), 25 (1) ;
 Temperature K = 303(1), 308 (2)

Reaction mechanism

The mechanism of the PTA catalysed oxidation of 2-alkanones may be postulated as :



The rate law was derived as :

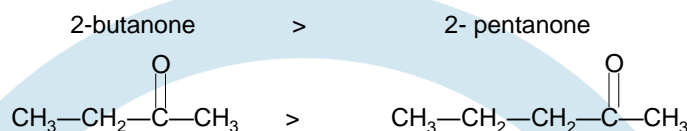
$$k_{obs} = \frac{k K_1 K_2 K_3 [E][PTA]}{[INA] + K_1 + K_1 K_2 K_3 [E][PTA]} \dots (6)$$

The reciprocal of equation (6) gives equation (7)

$$\frac{1}{k_{obs}} \times [PTA] = \frac{1}{[E]} \left\{ \frac{[INA]}{k K_1 K_2 K_3} + \frac{1}{k K_2 K_3} \right\} + \frac{1}{k} \dots (7)$$

The above equation explains the complex behaviour of the reaction between PTA, substrate and oxidant and other kinetic facts.

The order of the reactivity was observed as:



The above order of reactivity may be explained based on steric, inductive, hyper conjugative effects. Both the ketones

have a common part of the $\text{CH}_3\text{-C(=O)-CH}_2\text{R}$ which operates reducing steric and hyperconjugative effect^[15] and is responsible for leading above order of reactivity.

In PTA catalysed reaction, loss of water molecule occurs and simultaneous protonation affect the electron density on carbon atom. This enhance +I effect of CH_3 group consequently steric hinderance occurs and increasing enolic content takes place, +I effect pushing driving force towards bond sufficient enough to cleavage the $\alpha\text{-C-H}$ bond and eliminating proton ultimately resulting the complex. 2-pentanone shows slightly slower rate than 2-butanone due to enhanced positive inductive effect of $(\text{-CH}_2\text{CH}_3)$ chain. This increases the electron density on the carbon which subsequently check the loss of proton.

Considering the thermodynamic parameters it is expected to have lower value of energy of activation (E_a), for more reactive compound (Table 3) .

Table 3 : Activation parameters for the phosphotungstic acid catalysed reaction of 2-alkanones by N-bromoisonicotinamide

S. No.	2-alkanone	E_a (kJ mol^{-1})	ΔH^\ddagger (kJ mol^{-1})	ΔG^\ddagger (kJ mol^{-1})	ΔS^\ddagger ($\text{JK}^{-1} \text{mol}^{-1}$)
1	2-butanone	55.31	45.87	84.45	-126.26
2	2-pentanone	58.08	53.87	86.98	-106.61

The high negative value of entropy ΔS^\ddagger reduces the randomness of the molecule and enhance ability to form complexes with PTA. This value is sufficient to restrict translational and protectional freedom that causes ultimately fission of $\alpha\text{-C-H}$ bond. The small value of ΔH^\ddagger also support the polar nature of transition state.^[16] The Gibbs free energy (ΔG^\ddagger) are found almost same for both the ketones showing similar mechanism operating in the ketones. Based on thermodynamic parameter, it was concluded that reaction was enthalpy controlled.

Conclusion

In the present investigation, the Keggin type heteropoly catalyst PTA, forms a ternary complex between enolic ketone and HOBr reacting species of NBIN in pre-equilibrium state, which decomposed to form diones. The stoichiometry was assigned 1:2 and order of reactivity was discussed. The reaction was observed of first-order with respect to NBIN and fractional-order each with ketones and H^+ ions. The proposed mechanism was supported by the activation parameters and physical properties measured.

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Conflict of Interest

The authors declare conflict of no interest whatsoever.

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