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Kinetic Study of Acetophenone by N-Bromoisonicotinamide

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ABSTRACT

Kinetics oxidation of acetophenone by N-Bromoisonicotinamide In aqueous acetic acid medium, in the presence of [H^+] ion, have been studied in the 35^0 C range. The problems to be solved in the establishment of the rate of reaction and different factors such as concentrations of oxidant, reactants, reaction medium, etc., and interpretation of the provided further support to the proposed mechanism, intermediate possible complex, and product formation in the reaction. The reactions were found to be first-order concerning [NBIN] and fractional or zero order of the reaction concerning [substrate] and[H^+]. The rate decreases with increases in the dielectric constant of the medium. The plot is linear with a negative slope. Activation parameters were evaluated.

Keywords: Kinetics, Mechanism, P-substituted acetophenone NBIN, Activation parameters Perchloric Acid.

INTRODUCTION

This research paper describes the kinetic study of the oxidation of acetophenone by N-Bromoisonicotinamide in aqueous acetic acid medium. N- Bromoisonicotinamide is known to be a versatile reagent as an oxidant uses in kinetic studies. The Nature of the substrate, oxidant, and the experimental work condition. This compound has many advantages like as well as low cost, easy handling, low toxicity, and mild nature with stability [1]. The kinetic oxidation of acetophenone by NBIN [2]. The perchloric acid has been used as a source of [H^+] in the reaction medium [3].The kinetics deals with the study of such oxidation reactions through elucidation of their mechanisms and hence the investigations of reaction kinetics in chemical reactions are important aspects in chemistry [4].

Compounds have been extensively employed as oxidizing reagents for organic compounds [5]. kinetics, and mechanisms of oxidation reactions involving these reagents in the recent past [6]. With the above facts, we have reported for the first time, the result investigation on the kinetic and mechanism aspects of acetophenone by NBIN in an aqueous acetic acid medium at 308K. the objective of the present work is mainly to unfold the mechanistic image of the NBIN kinetic studies and to know the relative reactivityof acetophenone substance towards NBIN in aqueous acetic acid medium.

MATERIALS AND METHODS

The contents of preparation of various solution of reagents such as oxidant, substrates etc. required in kinetic studies of the oxidation of acetophenone by NBIN. The details are being mentioned in the following sections :

N-BROMOISONICOTINAMIDE;Oxidant N-bromoisonicotinamide is a compound of biological importanceand was prepared as method suggested by Balasubramaniyan[7]It was prepared by passing slow stream of bromine gas into a suspension of iso-nicotinamide in presence of sodium hydroxide and acetic acid at low temperature. The precipitated NBIN was filtered off; the process of repeatedly passing of Br_2 gas was stopped when no more precipitate is obtained. It is recrystalised from carbon tetra chloride and hexaneThe solution of N-bromoisonicotinamide was prepared by dissolving its weighted quantity in 100% acetic acid (B.D.H.) and kept in black paper wrapped bottle to save it from the action of diffused day light which alters appreciably its concentration.

The standardization of N-bromoisonicotinamide was carried by taking 1 ml of its solution in conical flask to which 10ml of 2% KI solution followed by 5 ml of 2N H_2SO_4. The liberated iodine was titrated against standard $Na_2S_2O_3$ solution using starch solution as an indicator iodometrically[8]

Preparation of substrate solution; Three substrate acetophenone of analytical grade have been used as such obtained after distillation. The solution was prepared of desired concentration by calculating their molecular weight and specific gravity.

Preparation of $CuSO_4$, $K_2Cr_2O_7$ and COOH; The standard solution of $CuSO_4.5H_2O$ (B.D.H) sample by dissolving its required amount of in distilled water followed by addition of 2-3 drops of glacial acetic acid. The standard solution of $K_2Cr_2O_7$ was prepared by dissolving its weighted quantity in distilled water as standard solution. The standard solution of oxalic acid $(COOH)_2$. $2H_2O$ AR sample was prepared by dissolving its definite amount in distilled water.

Preparation of H_2SO_4 solution; Stock solution of H_2SO_4 of appropriate strength was prepared by diluting the calculated volume (from specific gravity) of acid with distilled water and finally its concentration was determined by titrating it against standard solution hydroxide solution using phenolphthalein as an indicator.

Preparation of NaOH and Sodiumthiosulphate ($Na_2S_2O_3\,5H_2O$) solutions

The weighted quantity of NaOH (B.D.H.) sample is dissolved in distilled water standardized by oxalic acid using phenolphthalein as an indicator. The sodium thiosulphate solution was also made by dissolving its weighted quantity of AR sample and standardized against standard copper sulphate solution using KI and starch idometrically.

Preparation of Indicator;0.1 % Phenolphthalein (indicator was dissolved in absolute alcohol similarly fresh solution of starch $(C_6H_{10}O_5)n$ H_2O is prepared by taking its suspension solution in boiling water.

Preparation of miscellaneous solution; The other solutions, needed in present study viz, NaCl, KCl, isonicotinamide were also prepared and standardized by usual methods as mentioned in literature. The study of the effect of binary solvent (acetic acid and water (v/v) was prepared of different compositions. The solution of acrylonitrile was prepared by the standard method for the detection of free radical formation if present in the detection.

Methodology; A number of preliminary experiments were set up for each reaction under probe to choose the appropriate conditions to proceed the reactions smoothly.

Measurement of kinetics; Preliminary set of experimental were installed for the study of the reactions. In kinetic study calculated amount of oxidant N-bromoisonicotinamide was taken in a reaction pyrex flask. The solutions of unsaturated acids, H_2SO_4 and CH_3COOH with rest volume of water were taken in another pyrex flask both the flasks were equilibrated at the experimental temperature in a thermostat with an accuracy ($\pm 0.1^0$C). When both the solution attains same temperature 35^o and 40^o were mixed stop watch was on the mixture was shaken well. Reading at zero time was taken by withdrawing 2.0 ml aliquot, immediately the transferred in conical flask quenched with ice cold water and were estimated Iodometrically^2 for unconsumed N-bromoisonicotinamide, the process is repeated at definite intervals of time for seven-eight readily till reaction is completed about 80%. The observed data was utilized for calculating the values of rate constant by graphical isolation and integration methods.

Integration method; The values of pseudo first-order rate constant obtained from the integration rate equation

$$k = \frac{2.303}{t} \log \frac{a}{(a - x)}$$

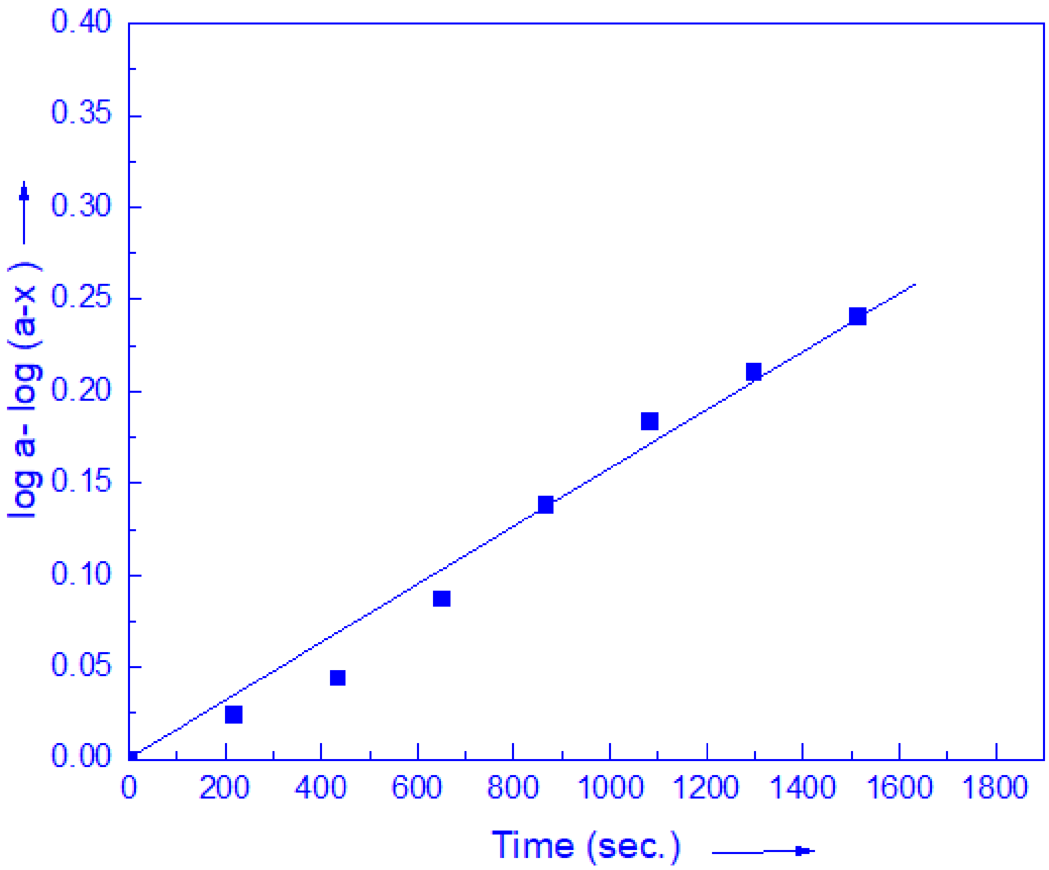
Were found fairly constant within the experimental error suggested that each reaction obeys first-order kinetics

Typical Kinetic Runs;acetophenone by N-bromoisonicotinamide (NBIN) have been studied in aqueous acetic acid medium. The rate constant was determined by employing graphical, integration and Oswald's dilution methods. The typical kinetics runs pertaining to the oxidation of the substrates as representative sets have been mentioned in the following ways:

Typical kinetic run for the influence of concentration of oxidant, N-bromoisonicotinamide (NBIN) on reaction velocity
[acetophenone] = 2.50×10^{-2} (mol dm^{-3});
[NBIN] = 2.50×10^{-3} (mol dm^{-3});
HOAc-H_2O = 30% (v/v);
Temp. =313 K

S. No.	**Time (sec)**	**Vol. of $\frac{N}{1000}$ hypo (ml)**	**10^4 k_1 (s^{-1})**
1.	0	5.0	-
2.	600	3.95	3.92
3.	1200	3.20	3.71
4.	1800	2.50	3.85
5.	2400	1.95	3.92
6.	3000	1.55	3.90
7.	3600	1.25	3.85
8.	4200	1.00	3.83

Average $k_1 = 3.85 \times 10^{-4}$ (s^{-1}) Graphical $k_1 = 3.83 \times 10^{-4}$ (s^{-1})



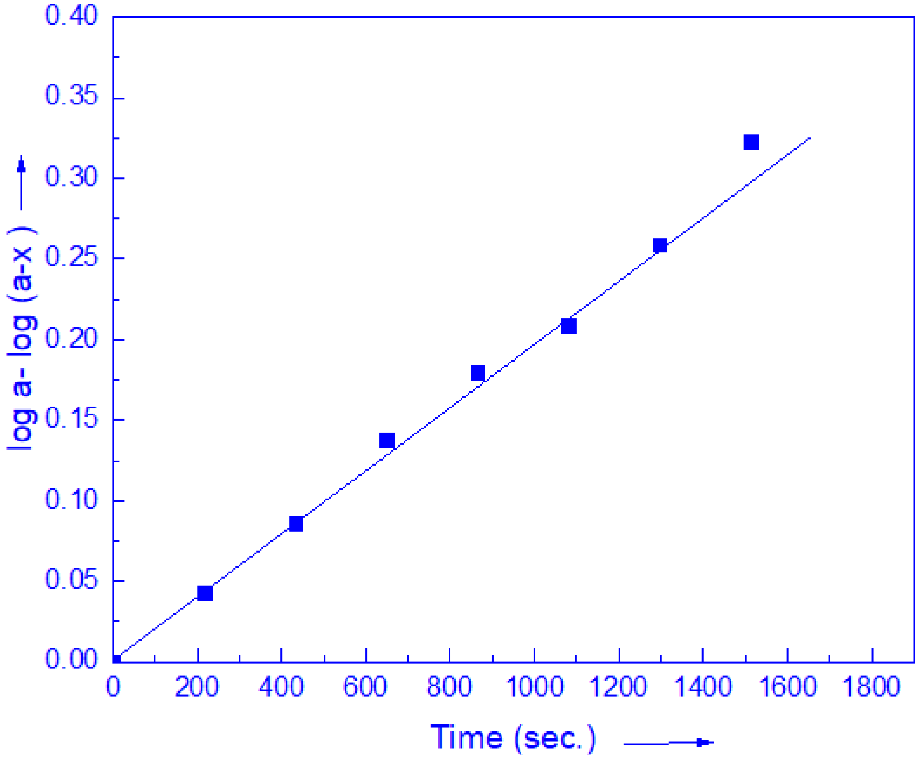
Typical kinetic set for the influence of concentration of acetophenone (substrates),
[acetophenone] = 2.00×10^{-2} (mol dm^{-3});
[NBIN] = 2.50×10^{-3} (mol dm^{-3});

Vol. of $\frac{N}{1000}$ hypo (ml)

HOAc-H_2O = 30% (v/v);
Temp. = 313 K

S. No.	**Time (sec)**		**10^4 k_1 (s^{-1})**
1.	0	5.0	-
2.	600	4.05	3.51
3.	1200	3.25	3.59
4.	1800	2.55	3.74
5.	2400	2.15	3.51
6.	3000	1.65	3.69
7.	3600	1.40	3.53
8.	4200	1.15	3.49

Average $k_1 = 3.58 \times 10^{-4}$ (s^{-1}) Graphical $k_1 = 3.56 \times 10^{-4}$ (s^{-1})



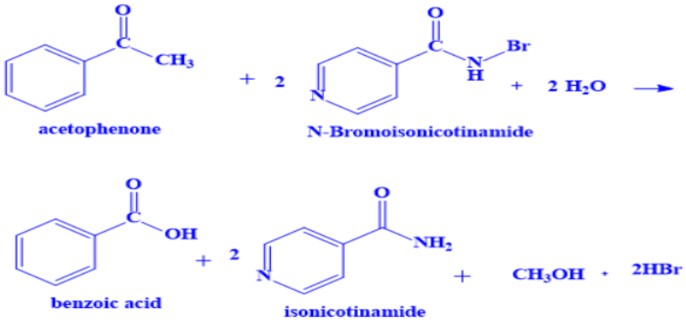
Above Tables for the typical runs, representing various conditions for each of the substrate indicate that the pseudo first-order rate constant calculated from the integrated first-order rate equation is constant. The plots of log a /(a-x) versus time are obtained linear passing through origin the graphical values of rate constant obtained from the plot of log a /(a-x) vs. time are in good agreement with the calculated values. It is, therefore, concluded that the oxidation of substrates by NBIN obey first-order kinetics under the experimental conditions.

STOICHIOMETRY AND PRODUCT ANALYSIS

The oxidation between N-bromoisonicotinamide (NBIN) and acetophenone was investigated for the stoichiometry and product analysis. In stoichiometry, the reactions were performed by taking the greater ($\approx 10^{-15}$ times) concentration of oxidant (NBIN) than the concentration of substrate. In the set of experiment, requisite amount of the oxidant and substrate were taken separately in conical flasks and calculated amount was added to the substrate solution. Both the flasks were kept in a thermostat at the experimental temperature. After attaining the identical temperature, the solution was mixed together and immediately aliquot was withdrawn at zero times and was estimated for unreacted NBIN, iodometrically. This observed result gives the initial concentration of NBIN. The aliquots were withdrawn periodically till a constant titrate value was obtained.

Stoichiometry and product analysis

The stoichiometric investigations of every reaction under test have been resolved independently and it was discovered that one mole of oxidant, expended one mole of substrate for complete oxidation of the reaction. The stoichiometric condition for the reaction might be spoken to as :

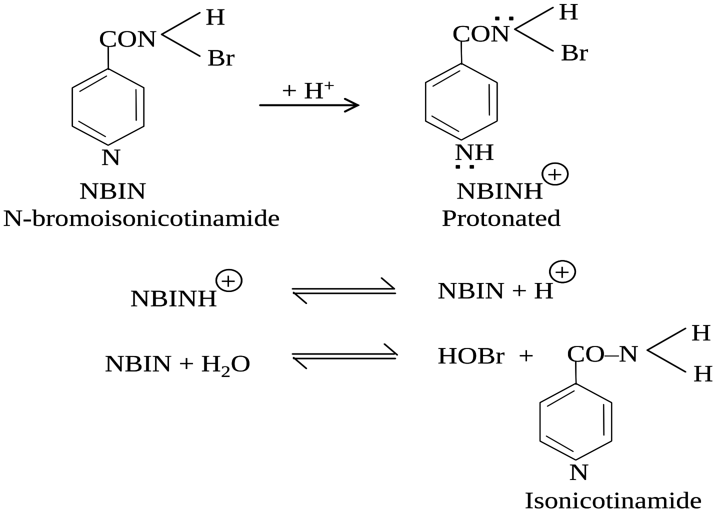


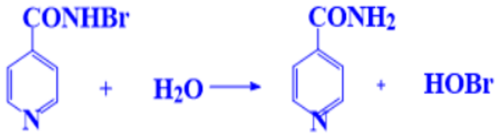
Stoichiometry of the reaction was learned by equilibrating the response blend containing an overabundance of N-bromoisonicotinamide (NBIN) over acetophenone , with HCl corrosive in 30 % acidic acid for 24 hrs. at 308 K. The un-responded oxidant was dictated by iodometrically. The assessed measure of unreacted N-bromoisonicotinamide (NBIN). Demonstrated that one mole of certain acetophenone devours one mole of N-bromoisonicotinamide (NBIN). acetophenone was found as the primary result of oxidation.

Preliminary Remarks; oxidation of certain acetophenone by N-bromoisonicotimanide in fluid acidic corrosive medium" manages the oxidation of acetophenone that returns the reaction at quantifiable rate. The trial study unmistakably show that with the exception of acetophenone at 35^{0}C, the pace of oxidation of these mixes were extremely moderate and in this way, the active investigation was turned on at higher temperature than 35^{0}C for example acetophenone both at 40^{0}C .

Mechanism For Oxidation Of Acetophenone; Considering the previously mentioned exploratory realities, a plausible instrument for the oxidation of acetophenone with NBIN be proposed according to following method of plan. The reaction is first-order in [NBIN] and the expansion of isonicotinamide has a slight hindering impact on the rate. Both these components show that HOBr might be the responsive species. It has been accounted for earlier without mineral acids, HOBr is the receptive oxidant species. The active information as condensed at the outset over that the rection pursues first-order kinetic. In its oxidation was discovered that the separate active discoveries in their absolution are comparative. It can, along these lines, be presumed that for the oxidation of acetophenones with NBIN the component could be proposed Experimental conditions, the possible oxidizing species are Br_2, HOBr, H_2OBr^+, and $NBINH^+$ in aqueous solution. The reaction is first order in [NBIN] and the addition of isonicotinamide has a slight retarding effect on therate. Both these factors indicatethat HOBr may be the reactive species. It has been reported earlier in the case of oxidants that, in the absence of mineral acids, HOBr is the reactive oxidant species.

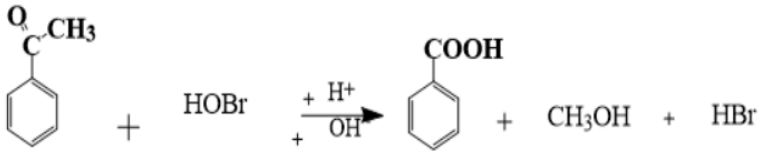
$$CH_3COOH \longrightarrow CH_3COO^- + H^+$$





$$\mathrm{HOBr} + \overset{+}{\mathrm{H}} \rightleftharpoons \mathrm{H_2\overset{+}{O}Br}$$

$$\mathrm{H_2O} \rightleftharpoons \mathrm{H^+} + \mathrm{OH^-}$$



RATE LAW

The rate of the reaction decreases with the increase in [H^+]. This may be explained by assuming equilibrium between unprotonated and protonated oxidant.

$$\mathrm{NBIN} + \mathrm{H^+} \rightleftharpoons \mathrm{NBIN} + \mathrm{H^+}$$

The unprotonated species is involved in the formation of the active oxidant.

$$\mathrm{NBINH^+} \overset{K}{\rightleftharpoons} \mathrm{NBIN} + \mathrm{H^+}$$

$$\mathrm{NBIN} + \mathrm{H_2O} \overset{k_2}{\rightleftharpoons} \mathrm{HOBr} + \text{Isonicotinamide}$$

$$\mathrm{HOBr} + \text{Substrate} \overset{\text{slow}}{\rightleftharpoons} \text{Complex}$$

$$\text{Complex} \overset{\text{fast}}{\rightleftharpoons} \text{Products}$$

Rate = k_2 [NBIN] [H_2O]

Applying equilibrium approximation to step (1)

$$K = \frac{[\mathrm{NBIN}]\,[\mathrm{H^+}]}{[\mathrm{NBINH^+}]}$$

$$K\,[\mathrm{NBINH^+}] = [\mathrm{NBIN}]\,[\mathrm{H^+}]$$

$$[\mathrm{NBIN}]_e = \frac{K\,[\mathrm{NBINH^+}]}{[\mathrm{H^+}]}$$

The rate law shows that the reaction follows first order kinetics with respect to [NBIN] and inverse fractional order kinetics with respect to $[H^+]$.

The pace of the reaction diminishes with the expansion in $[H^+]$. This might be clarified by expecting balance among unprotonated and protonated oxidant. The unprotonated species is engaged with the development of the dynamic oxidant.
Rate = k_2 [NBIN] $[H_2O]$

At the point when 1/k' is plotted against $[H^+]$, a straight line is acquired. The incline of the line is 1/k[NBIN]t. From the estimation of catch and substituting the estimation of k[NBIN]t, the balance steady K is determined. Since $K < [H^+]$. The rate law shows that the response pursues first request energy regarding [NBIN] and converse partial request energy concerning $[H^+]$.

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