"KINETICS STUDY ON OXIDATION OF P-NITRO BENZALDEHYDE BY ISOQUINOLINIUM BROMOCHROMATE IN AQUEOUS ACETIC ACID MEDIUM"

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Abstract

Kinetics study on oxidation of p-Nitro Benzaldehyde by isoquinolinium bromochromate in aqueous acetic acid medium has been investigated in water-HOAc medium. The reaction is of pseudo first-order in [IQBC], fractional order in [p-nitrobenzaldehyde] and first order in [H$^+$] ion. The velocity of the reaction increases with increase the Dielectric constant of medium and solvent polarity. Effect of temperature has been studied and thermodynamic parameters are calculated and a suitable mechanism has been suggested.

Key words: **IQBC; Kinetics study; fractional order; Di electric constant of medium; thermodynamic parameters**

INTRODUCTION

Chemical kinetics provides information about the rate of reaction on possible pathways, by which the reactants are transformed into products. Thus, the fundamental of objective of the study of the kinetics of chemical reaction is to unfold the mysteries of chemical processes. In chemical equilibria, only the initial and final stages of the reactions are considered, while thermodynamics describes the energy relations between the reactants and products. In chemical kinetics, the rate and mechanism of a chemical reaction is to determine the overall stoichiometry

of the reaction and to identify any side-reaction. This study involves the determination of the effect of changes in the concentrations of reactant and product species. One reason for studying the rates of the reaction is to predict how quickly a reaction mixture approaches equilibrium. Another is that the study of reaction rates leads to an understanding of the mechanism of a reaction and analysis into a sequence of elementary steps.

Halo chromates [4-10] have been used as mild and selective oxidizing reagent in synthetic organic chemistry. Varieties of compounds containing chromium (VI) have proved to be versatile reagents capable of oxidizing almost every oxidizing functional group. The kinetics and mechanism of oxidation of Cr (VI) has been well studied, chromic acid being one of the most versatile available oxidizing reagents, reacting with diverse substrates. The development of newer chromium (VI) reagents for the oxidation of organic substrates continues to be of interest. A number of new chromium containing compounds like pyridinum bromochromate[11] , quinolinium chlorochromate[12], 2,2'-bipyridinium chlorochromate[13], pyridinium fluorochromate[14], quinolinium fluorochromate[15], quinolinium bromochromate[16], quinolinium dichromate [17], pyridinium fluorochromate[18] , imadazolium fluorochromate [19] have been used to study the kinetics and mechanism of oxidation of various organic compounds. In the present work, I have chosen new chromium (VI) oxidizing reagent isoquinolinium bromochromate (IQBC) which was prepared and characterized. The IQBC has been found to be stable and an efficient solid reagent, which can be easily prepared in good yield. It act as an efficient brominating reagent for hydroxylated aromatic compounds as well as good oxidizing reagent for the conversion of alcohols to carbonyl compounds in good to excellent yield. The synthesized isoquinolinium bromochromate is ideal reagent, with number of specification including higher yield, mild conditions and easy preparation. The results obtained with isoquinolinium bromochromate are satisfactory and suggest that the reagent has few advantages over the existing chromium (VI) reagents.

The Structural formula of isoquinolinium bromochromate (IQBC)
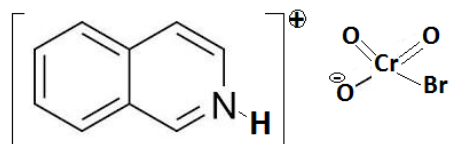
Since, most of the reagents developed so far suffer from at least one of the drawbacks such as high acidity, photosensitivity, instability, hygroscopic, low selectivity, long reaction time and

need for Large excess of reagent. To overcome these disadvantages, we have synthesized isoquinolinium bromochromate (IQBC) as a new mild, efficient and stable reagent, which is able to work as both an oxidizing agent and a brominating reagent.

MATERIALS AND METHODS

Isoquinolinium bromochromate was prepared by the following method: Chromium trioxide (10 g, 0.1 mol) was dissolved in water (15 ml) and cooled to 0 ºC. To this solution was added hydrobromic acid (17 ml, 48%) slowly with vigorous stirring; then, isoquinoline (13 ml, 0.1 mol.) was added drop wise during 10 min. The reaction mixture was cooled for 2-3 h and filtered. The resulting yellow orange needles were dried and re-crystallized.

The solution of IQBC so obtained was prepared by dissolving its weighed quantity in 100% CH_3COOH (B.D.H.) and kept either amber colored flask or black paper wrapped around it to save it from the action of diffused day light which alters appreciably its concentrations.

The standardization of IQBC was done by taking one ml of its solution in conical flask to which 10 ml of 2% KI solution followed by 5ml of 2N H_2SO_4 added to it. The liberated iodine was titrated against standard sodium thiosulphate (hypo) solution using starch solution as an indicator

Preparation of substrate's solution

The p-Nitro Benzaldehyde for kinetics of oxidation studies was used analytical grade. The solutions of substrate under investigation were prepared in requisite volume of glacial acetic acid-water mixture.

KINETIC STUDIES

Preliminary experiments for the oxidation of p-nitrobenzaldehyde with Isoquinolinium bromochromate were conducted to choose the appropriate conditions of concentration of the reactants and temperature under which these oxidation proceeds with measurable rate. It has been observed that in the presence of $HClO_4$, the oxidation of the substrate proceeds at a measurable rate. The kinetic study of each system undertaken was carried out by integration and Ostwald's isolation methods . In each set of reaction, concentration of substrate was taken in large excess over the concentration of oxidant.

PROCEDURE

The known volume of oxidant, acetic acid and $HClO_4$ acid were taken in a conical flask while substrate and rest amount of water were in another conical flask. These two-stopper flasks were placed at experimental temperature in a thermostat of sensitivity $\pm$ 0.1^{0}C. After the equilibrium of the temperature, the both solutions were mixed and aliquot was withdrawn immediately and was quenched. The amount of un-reacted Isoquinolinium bromochromate was estimated iodometrically with the help of standard solution of sodium thiosulphate using starch as an indicator. The titre value at zero time was taken as "a".

The aliquots were withdrawn at regular intervals and were estimated for un-reacted Isoquinolinium bromochromate. These readings are the values of (a-x) at time "t". The experimental data were fed into the integrated form of equation for first-order reactions. The values of pseudo first-order rate constant obtained from the rate equation –

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

The effect of $[HClO_4]$ on the oxidation of la was determined by adding different concentrations of $HClO_4$. The effect of isoquinoline was also investigated. Different compositions of binary solvent mixtures of acetic acid-water were used to study the effect of variation of dielectric constant of the medium.

STOICHIOMETRY AND PRODUCT ANALYSIS

Stoichiometry and end-product analysis: stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of N-chlorobenzamide over p-nitrobenzaldehyde and Perchloric acid, for 24 hrs. at 308K. The un-reacted oxidant (Isoquinolinium bromochromate) was determined by iodometrically. The estimated amount of

un-reacted Isoquinolinium bromochromate showed that 3 moles of p-nitrobenzaldehyde consumes one mole of Isoquinolinium bromochromate.
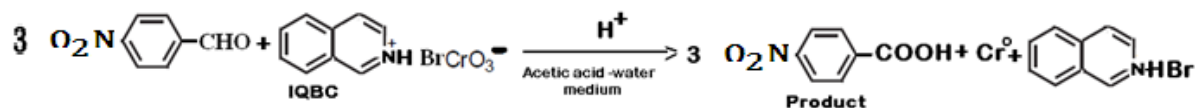
The reaction of p-Nitro Benzaldehyde with IQBC showed an induction period. The presence of free radicals in the system understudy was tested qualitatively by addition of 1-2 ml of acrylonitrile (monomer) in about 5-6 ml of the reaction mixture employing trapping method. The non-occurrence of turbidity and white precipitate clearly indicates the absence of free radicals in the system [31-32]. P-Nitro Benzoic acid is formed as the end-product, which was identified by their melting point and existing conventional methods.

RESULTS AND DISCUSSIONS

The experimental kinetic data have been collected for variant concentrations of oxidant (IQBC) at fixed concentration of other reactants and temperature. The linear plots of log (a-x) vs. Time, suggested that the first-order rate dependency with respect to oxidant. The value of first-order rate constant evaluated from the plot is excellently in good agreement with those calculated from first-order rate equation. (Table.1)

The values of first-order rate constant increases with increase in concentration of p-Nitro Benzaldehyde. The reaction follows first order kinetics at lower concentration of p-Nitro Benzaldehyde which tends towards zero-order at higher concentration; this evidence indicated that formation of complex during the reaction between substrate and oxidant. (Fig.1) Reactions are fully acid catalyzed. The plot of k_1 vs. [HClO$_4$] is obtained linear with the positive unit slope and passing through origin, confirming that the order with respect to HClO$_4$ acid is one. (Fig.2) Reaction rate increases with rising in binary percentage composition of the solvent of the medium i.e. acetic acid-water; The presence of free radicals in the system understudy was tested qualitatively by addition of 1-2 ml of acrylonitrile (monomer) in about 5-6 ml of the reaction mixture employing trapping method. The non-occurrence of turbidity and white precipitate clearly indicates the absence of free radicals in the system.

Various activation parameters namely temperature coefficient, energy of activation (Ea) , frequency factor (A), enthalpy of activation ($\Delta H^{\#}$), free energy of activation ($\Delta G^{\#}$), and entropy of activation ($\Delta S^{\#}$) for each reaction are calculated for p-Nitro Benzaldehyde –IQBC system

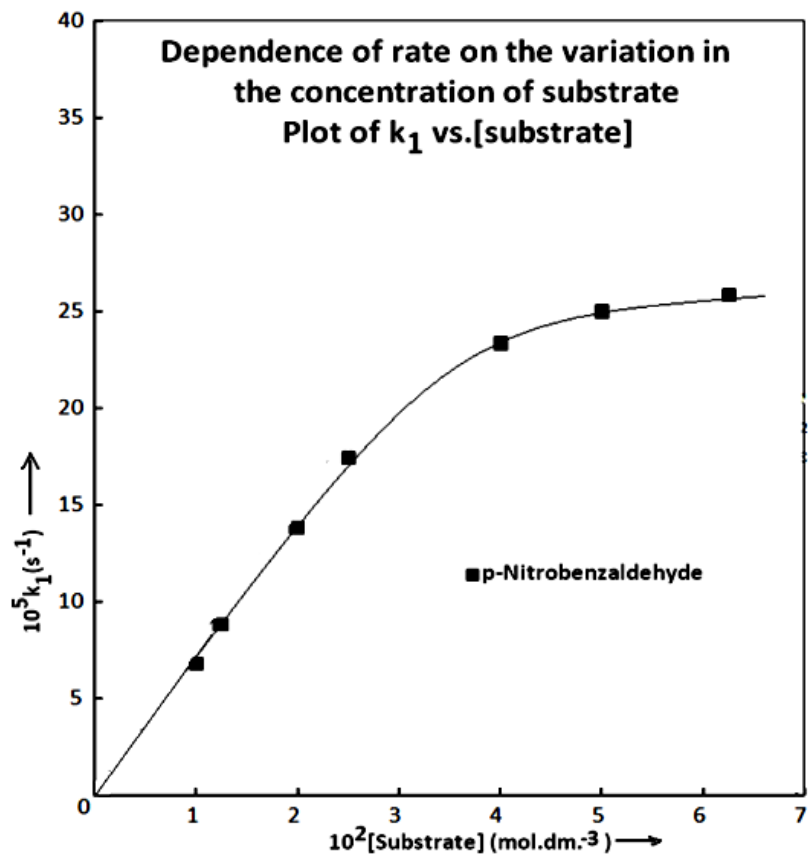(Table:2) and according to the reaction mechanism, rate equation and order of reaction have been discussed.

Fig. I

Dependence of rate on the variation in the concentration of substrate Plot of k_1 vs.[substrate]

p-Nitrobenzaldehyde

[IQBC]   = 2.50×10^{-3} (mol.dm^{-3})
HOAc-H$_2$O = 30% (v/V)
[H$^+$]   = 2.00×10^{-3} (mol.dm^{-3})
Temp.   = 313 K

Dependence of rate on variation in the concentrations of Perchloric acid

Plot of k_1 vs.$[H^+]$ Ion
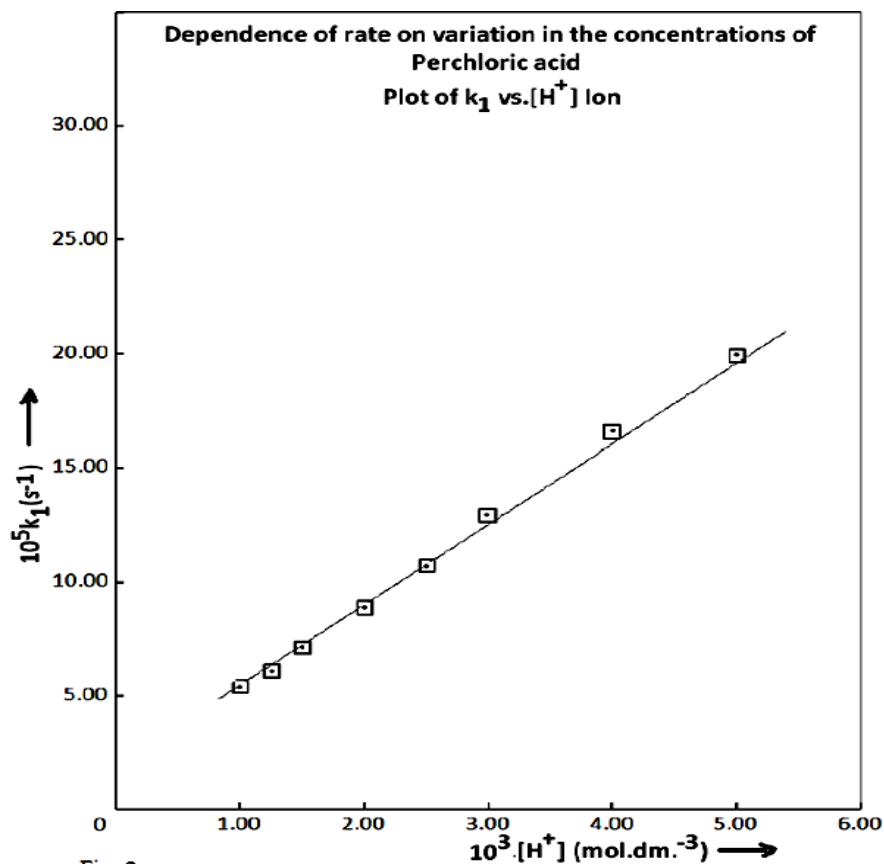
Fig. 2

[IQBC]	:	2.50×10^{-3} (mol.dm.$^{-3}$)
[p-nitro Benzaldehyde]	:	1.25×10^{-2} (mol.dm.$^{-3}$)
HOAc-H$_2$O	:	30%(v/V),
Temperature	:	313 K.

Reactive species of oxidant

Before going into details of the mechanistic path of the reactions, it would be most appropriate at this stage to ascertain the actual reacting species of IQBC in aqueous acetic acid medium. There are various types of species of IQBC present in the aqueous solution, which may bring about the oxidation, some are H_2CrO_4, $HCrO_4^-$ and $BrCrO_3^-$. On dilution, the equilibrium shift to left converting more of $Cr2O7^{2-}$ into $HCrO_4^-$. Hence if the rate of a reaction decreases, on increasing the acid concentration then $HCrO_4^-$ ought to be oxidizing species. Further $Cr_2O_7^{2-}$ is also not oxidizing species because reaction in presence of $Cr_2O_7^{2-}$ is found to be much shower than in the presence of chromic acid under the similar conditions.

In the present investigation, it has been found that the rate increases, on increasing the acid concentration, then protonated form of $H_3CrO_4^+$ ought to be the oxidizing species.

<div align="center">Table.1</div>

[p-Nitro Benzaldehyde]	=	$1.25 \times 10^{-2} (mol.dm^{-3})$
$[H^+]$	=	$2.00 \times 10^{-3} (mol.dm-3)$
$HOAc-H_2O$	=	30% (v/V)
Temp.	=	313 K

$[IQBC]10^3 \ (mol.dm.^{-3})$	$k_1 \times 10^5 (s^{-1})$
1.00	8.90
1.25	8.86
2.00	8.84
2.50	8.84
4.00	8.85
5.00	8.85

<div align="center">**Table: 2**</div>
<div align="center">**Thermodynamics parameters**</div>

Substrate	Ea kJ/mol.	A (s^{-1})	$\Delta H^{\#}$ kJ/mol.	$-\Delta G^{\#}$ kJ/mol.	$-\Delta S^{\#}$ JK/mol.
p-NO$_2$. C$_6$H$_4$-CHO	61.83 ±0.51	3. 12X10^5 ±0.98	58. 03 ±0.56	88. 32 ±0.77	108. 08 ±0.29

MECHANISM

In view of the above experimental kinetic data, facts and finding, a suitable mechanism has been proposed for the oxidation of p-nitrobenzaldehyde – IQBC system as:
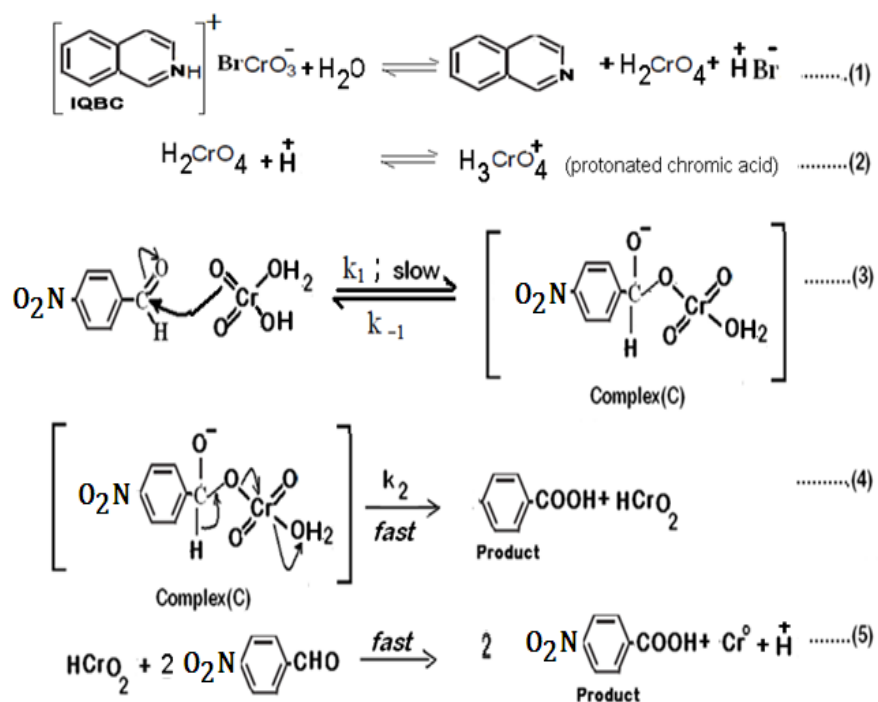
Rate Expression

$$k_{obs} = k_1 \text{ [p-NO}_2 \text{ Benzaldehyde][H}_2\text{CrO}_4\text{][H}^+] \cdots \cdots \cdots (6)$$

The derived rate equation (6) explains all the experimental facts, which are in good agreement with our experimental kinetic data i.e. the observed first order kinetic in [oxidant], and [H$^+$] ion and fractional order kinetics in [substrate] etc.

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