

KINETICS AND MECHANISTIC STUDY OF ETHANE 1, 2-DIOL BY ISOQUINILIUM BROMOCHROMATE IN ACETIC ACID MEDIUM

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Abstract

In proposed work, we have analyzed kinetics and mechanistic study of oxidation of Ethane 1,2-diol by isoquinolium bromochromate in aqueous acetic acid medium. This kinetic and mechanistic study was carried out at 298⁰ k and reaction follows first order kinetics at low concentration of Ethane 1, 2-diol with trend towards zero order at its higher concentration with respect Isoquinolium bromochromate and the reaction is acid catalyzed. In proposed studies the formation of complex has been observed and rules out the involvement of free radicals in mechanism. Thermodynamic parameters were computed and a suitable mechanism with kinetic results has been proposed.

Key words:

Complex, kinetic, reaction, Effect, Ethane 1,2-diol and oxidation .

Introduction

Study of the kinetic of reaction is one of the important tools to help a chemist to a reaction such kinetics studies are important from the industrial point of view too since a complete understanding of kinetic behavior of reaction enables a chemist to work out a reaction. Franclin¹ introduced the electron transfer reaction which has created a new era in the field of chemical kinetics.

In present work we explored the kinetic and mechanism of oxidation of Ethane 1,2-diol by Isoquinolium bromochromate in aqueous acetic acid medium because it is an ecofriendly, cheap, non-hazardous and easily synthesized in chemical laboratories and available in market. The oxidation of aniline by Isoquinolium bromochromate in aqueous acetic acid was carried out by Vibhut² etal., Patwari etal.³ has been carried out oxidation of alcohols by Isoquinolium bromochromate in aqueous acetic acid leads to the formation of corresponding aldehyde and ketones.

The present kinetic of reactions involving de-electronation, electronation i.e. redox system. In these reaction electrons⁴ are transferred from reductant to oxidant. A very interesting and effective oxidant for the oxidation of organic compounds of these reagents is well known in several couples.⁵⁻⁷ Isoquinolium bromochromate has been reported as an oxidant in the oxidation of some alcohols, hydroxyl acid, ketones and phenols.

However most of these reagents have been developed so for suffer from at least one of the drawbacks such as high acidity photosensitivity, instability, low sensitivity, and long reaction time and need excess of reagent. To overcome these Isoquinolium bromochromate which is mild efficient, stable reagent which works as both oxidizing as well as brominating reagent.

Material and method

All the chemicals employed in this investigation were of analytical grade. The solution of Ethane 1,2-diol have been prepared in requisite amount of acetic acid water mixture of appropriate compositions. To prevent photochemical effect the freshly prepared solution of Isoquinolium bromochromate was stored in an amber color bottle. The purity of reagent was confirmed by spectral and elemental analysis.

The standardization of -Isoquinolium bromochromate was carried out by chromium trioxide (10 g, 0.1 mol) was dissolved in water (15 ml) and cooled to 0° C. 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 hours and filtered. The resulting yellow orange needles were dried and recrystallised. The purity of reagent was confirmed by spectral and elemental analysis.

Result and Discussion

The reaction follows first-order kinetics with respect to Isoquinolium bromochromate. The summarized result of the aforementioned variation are reported in table -I for Ethane 1,2-diol under investigation. The reactions are acid catalyzed. The plot of K_1 VS $[H_2SO_4]$ and K_1 VS $\log[H^+]$ is linear with unit slope exhibiting first order with respect to H_2SO_4 for Ethane 1,2-diol. Furthermore the value of K_2 (Table-I) does not show constancy.

The effect of neutral salt such as NaCl, KCl etc. show slightly decreasing effect on the rate of the all reaction overall its effect is insignificant on reaction velocity. Addition of catalyst $[Mn^{++}]$ retards the reaction velocity where as catalyst $[Cu^{++}]$ accelerate the reaction rate.

H_2CrO_4 have been reported as the active species. The stoichiometric studies of Ethane 1,2-diol - Isoquinolium bromochromate system at experimental temperature have been investigated separately. It was found that for each mol of substrate 1 mole of oxidant is consumed.

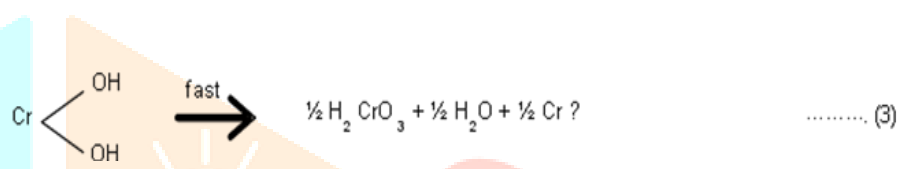
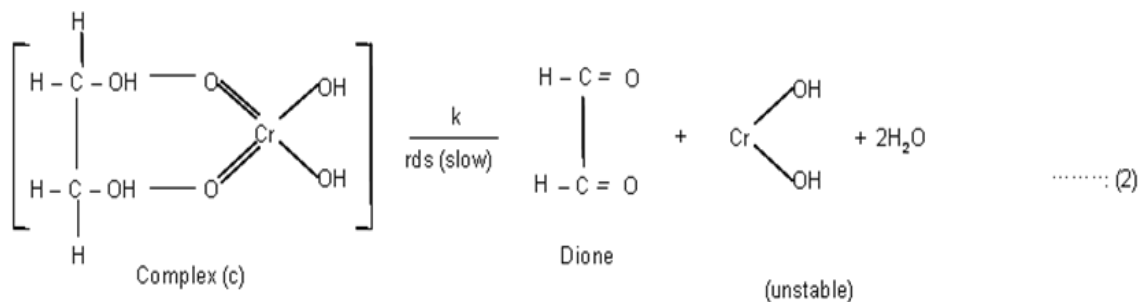
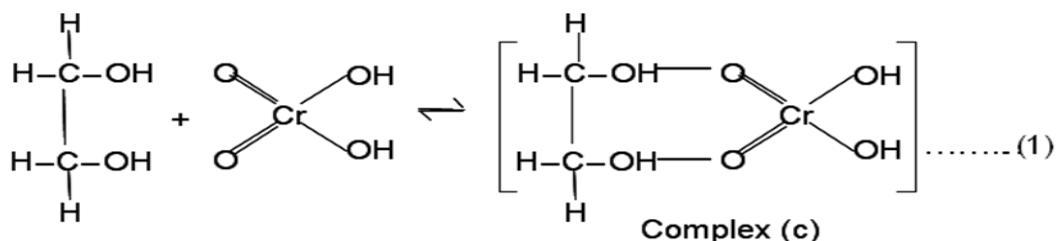
Waters et al.⁸ (1953) and Hinshelwood⁹ have also been reported such a consumption of oxidant in the oxidation of Ethane 1,2-diol with alkaline $KMnO_4$ and $Ce(IV)$. The oxidation products corresponding Ethane 1,2-diol were identified for each oxidation as dione¹⁰ qualitatively and chromatographically and also by existing methods.

The aldehydes and ketones were also reported by various authors and co-workers in their previous works by Carrying similar oxidation of Ethane 1,2-diol with variety of oxidants such as: $NCSA^{11}$, SeO_2^{12} , $KMnO_4^{13}$, $Mn(III)^{14}$, Tl^I bromanine- T^{15} , but most appropriate and authentic methods confirmed diones as the main oxidation products.

Mechanism

In the present study reaction velocity follow nearly first-order kinetics at low concentration of Ethane 1,2-diol which tends towards zero order at its higher concentration. Such kinetic trend of a reaction for organic of substrate accounts for the complex formation with oxidant, as was observed by Michaelis and Menton¹⁶, in enzyme catalyzed reaction. Considering these facts a probable mechanism for the oxidation of Ethane 1,2-diol with Isoquinolium bromochromate could be proposed as per following schemes, using H_2CrO_4 reacting species.

Probable mechanism of oxidation of Ethane 1,2-diol by isoquinolium bromochromate:



The rate law was derived as:

$$k_{obs} = \frac{\text{Rate}}{[\text{Ethane1,2-diol}]T} = \frac{K_1K_2k[S][H^+]}{[IQ]K_1 + K_1K_2[S]}$$

Where,

IQ=Isoquinoline, [S]=Substrate

Table - 1

Dependence of rate on the concentration of Sulphuric acid

10 ² × [Ethane1,2-diol] (mol dm ⁻³)	= 2.50;
10 ² × [substrate] (mol dm ⁻³)	= 2.50;
HOAc-H ₂ O % (v/v)	= 30;
Temperature ^o K	= 298

S.N.	[H ⁺] × 10 ² (mol dm ⁻³)	Ethane1,2-diol
1.	0.50	6.81
2.	1.00	8.22
3.	1.25	8.63
4.	1.50	8.75
5.	2.00	9.32
6.	2.50	9.87

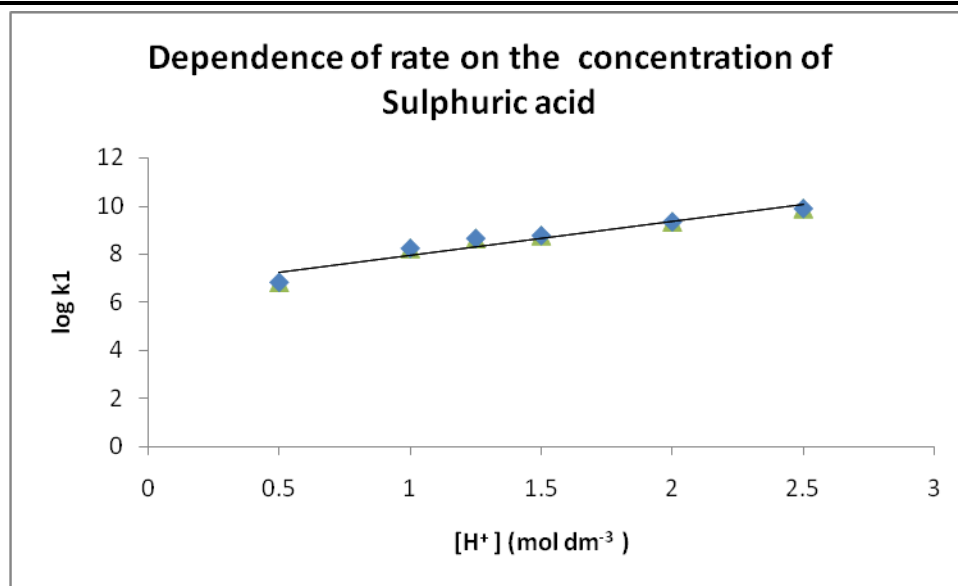


Fig .01: Plot of K_1 VS $\log[H^+]$

Conclusion

Kinetic studies employing Isoquinolium bromochromate as an oxidant and allied aspects of its reactions lead us to conclude that the activity of Isoquinolium bromochromate is much limited and needs to be explored in a broad way. It possesses vital potentiality and displays interesting behaviors at moderate condition of temperature.

This work can better and suitably be utilized in biology and pharmacodynamics, chemical engineering electro chemistry, geology Inorganic mechanist engineering organic chemistry and physics.

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