

Kinetics and Mechanism of OsO₄ Catalysis in Acid Bromate Oxidation of Substituted 2-Azachalcones in Aqueous CH₃COOH-H₂SO₄ Medium

Naseem*, Satla Gangakishan, S. Sharath Kumar Goud and E Venkata Ramana

Physical Chemistry Laboratory,
Department of Pharmaceutical Chemistry,
Telangana University-503322, Nizamabad, TS, INDIA.
email: gangakishan33@gmail.com

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ABSTRACT

The kinetic and mechanism of OsO₄ catalysis in acid bromate oxidation of substituted 2-Azachalcones have been studied in 50% (V/v) acetic acid - water – sulphuric acid medium at various temperatures. The reaction follows zero order kinetics in [Bromate] and [H⁺] fractional order in [substrate] and first order dependence on Os(VIII) catalyst. Varying the H⁺ the rate of the reaction is not altered. The Michaelis-Menten's plot (1/k_{obs} against 1/[S]) gives a positive intercept on y-axis support for the formation of the complex between the oxidant and substrate. A linear plot is observed with a positive slope by plotting of log k versus 1/D is suggesting that the reaction between two neutral molecules. The more negative value (-1.17) of ρ⁺ indicates the reaction is facilitated by more electron density at the reaction centre, and the rate of the reaction is increased by electron donating substituents and is decreased by the electron withdrawing substituents. Therefore, the different substituted 2-Azachalcones reactivity studied is *p*-OCH₃ > *p*-CH₃ > H > *p*-Cl. Thermodynamic activation parameters are evaluated. The products of Os(VIII) catalysis oxidation of 2-Azachalcone are identified as 1-picolinoyl-2-arylethane-1,2-diol. Based on the above arguments the plausible mechanism proposed for the Os(VIII) catalyzed acid bromate oxidation of 2-Azachalcone.

Keywords: Kinetics, catalyst, Azachalcones, mechanisms, oxidation.

INTRODUCTION

2'-Azachalcones, has a unique structure consisting of two aromatic rings are joined by a three-carbon α, β- unsaturated carbonyl system and whole molecule is in conjugation.

Oxidation of Phenyl styryl ketones or chalcones was studied by using different oxidants in all these reactions either the >C=C< or the >C=O group of the chalcone is attacked.

During the oxidation the reactive site (>C=O) of the 2-Azachalcone is attacked by bromate¹, and in chalcones attacked by N-chloronicotinamide², Pyridinium chlorochromate³, TCICA⁴, bromate⁵. The >C=C< group of the chalcone was attacked by the different oxidants like Os(VIII)⁶, Cr(VI)⁷, epoxidation⁸, bromination⁹. Potassium bromate is a powerful oxidizing agent has been used to oxidize different compounds in both medium. Scanning of literature revealed that no work is reported on the Os(VIII) catalysed acid bromate oxidation kinetics of 2-Azachalcones. The kinetic and mechanism of OsO₄ catalysis in acid bromate oxidation of substituted 2-Azachalcones in acetic acid - water – sulphuric acid medium has been studied to investigate the reactive species of the substrate and oxidant, and to find site of attack, and evaluation of activation parameters, to elucidate a possible mechanism.

EXPERIMENTAL

Materials

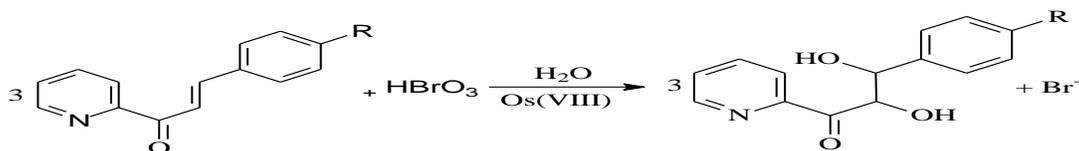
AR, BDH grade chemicals were used. Substrate used as a 2-azachalcones, Claisen-Schmidt condensation procedure is followed to preparation of substituted/ unsubstituted 2-Azachalcones¹⁰. The stock solution of 2-Azachalcones was prepared in pure acetic acid (AR, BDH). Stock solution of OsO₄ (Aldrich) was standardized using the method of Houricichi and Osmu¹¹. Conductivity water was used throughout the course of investigation.

KINETIC MEASUREMENTS

All the experiments were carried out under pseudo-first conditions, using the conditions of [acid] >> [2-Azachalcone] > [bromate] > [Catalyst]. The amount of unreacted bromate was estimated by iodometric method by studying the reaction up to 80% completion. Pseudo first order rate constants were calculated from the linear plots of log C_t versus time.

Stoichiometry

The stoichiometry of the reaction was studied with varying amounts of bromate over 2-Azachalcone keeping all other reagents constant. The unreacted bromate was estimated by iodometrically, and revealed that three moles of 2-Azachalcone consumed one mole of bromate. The products of Os(VIII) catalysed oxidation were identified as 1-picolinoyl-2-arylethane-1,2-diol.



RESULTS AND DISCUSSION

Order with respect to Bromate.

The effect of bromate on the reaction has been studied by varying initial [bromate] in the range is $2.0 \times 10^{-3} \text{ M} - 10.0 \times 10^{-3} \text{ M}$, by keeping the concentrations of substrate, acid and other constituents are constant. The evaluated pseudo-first order rate constants by plotting of $\log C_t$ versus time. The pseudo-first order rate constants were found to be dependent on initial bromate concentration, confirming zero order dependence in [bromate].

Order with respect to Substrate

Effects of substrate on the reaction studied by changing the concentration of substrate from 0.05 to 0.20 mol dm^{-3} keeping all other constituents are constant. By the plotting of $\log [\text{substrate}]_t$ versus time can evaluate the pseudo first order rate constants. The order in substrate was found to be unity in simple 2-Azachalcone but fractional order follows in substituted ones. (**Table: 1**). The Michaelis-Menten's plot ($1/k_{\text{obs}}$ versus $1/[S]$) (**Fig: 1**) give a positive intercept on Y-axis indicating that a formation of the complex between the substrate and the oxidant.

Table: 1 Effect of varying [Substrate] on the acid bromate Os (VIII) catalysed oxidation of 2-Azachalcones at 303K, [Bromate] = 0.01 mol dm^{-3} ; $[\text{H}_2\text{SO}_4] = 10.0 \text{ mol dm}^{-3}$; [Os (VIII)] = $1.0 \times 10^{-3} \text{ M}$; $[\text{Hg}(\text{OAc})_2] = 0.1 \text{ mol dm}^{-3}$; HOAc – H₂O = 1:1 % (v/v).

| $10^1 \times [2'\text{-Azachalcone}] \text{ M}$ | $10^4 \times k' \text{ (s}^{-1}\text{)}$ | | | |
|---|--|----------------------------|---------------------------|--------------|
| | H | <i>p</i> -OCH ₃ | <i>p</i> -CH ₃ | <i>p</i> -Cl |
| 0.5 | 1.84 | 12.90 | 3.24 | 0.918 |
| 1.0 | 3.22 | 23.18 | 5.14 | 1.80 |
| 1.5 | 5.08 | 32.9 | 9.36 | 2.35 |
| 2.0 | 7.87 | 43.7 | 12.12 | 3.12 |
| **S (Slope) | 1.02 | 0.86 | 0.96 | 0.86 |

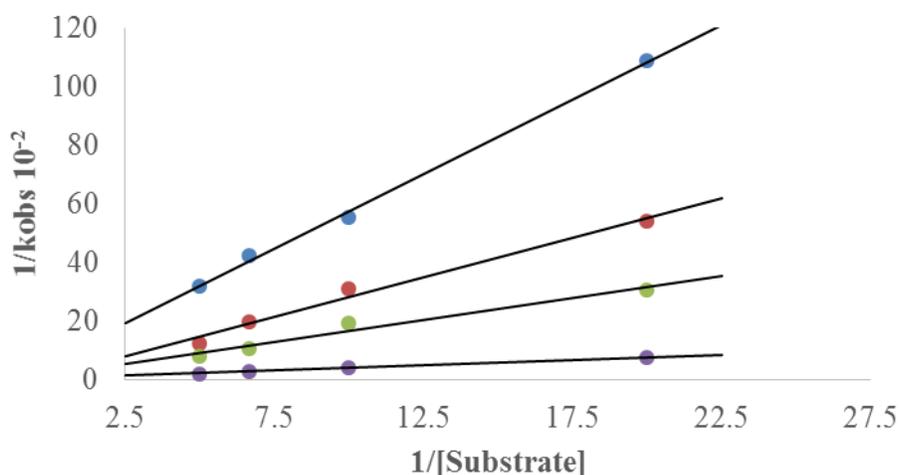


Fig: 1 Michaelis-Menten's plot $1/k_{\text{obs}}$ versus $1/[S]$

Order with respect to Acid

The effect of acid on the reaction rate was studied by varying the [acid] from 2.50M to 10.0M keeping other constituent's constant. Plot of $\log k$ versus $\log [H^+]$ has been used to determine the order of the reaction. It was observed that the rate of the reaction is does not altered with an increase in the concentration of Sulphuric acid. Suggesting that zero order dependence on [Acid].

Effect of Dielectric Constant

To understand the effect of dielectric constant (D) on the reaction rate has been studied by varying acetic acid–water composition. By decreasing the dielectric constant value the rate of reaction was increased understanding by plotting of $\log k$ versus $1/D$ (**Table: 2**). Positive slope of the plot indicates reaction between two neutral molecules.

Table: 2 Effect of varying solvent composition on the acid bromate oxidation of 2-Azachalcones at 303K, [Substrate] = 0.1mol dm⁻³; [Bromate]= 0.01mol dm⁻³; [H₂SO₄] = 10.0mol dm⁻³; [Hg (OAc)₂] =0.1mol dm⁻³

| 2-Azachalcone | 10 ⁴ x k' s ⁻¹ at % (v/v) of acetic acid | | | |
|----------------------------|--|--------------|--------------|--------------|
| | 30 *(54.4) | 40 (48.0) | 50 (41.5) | 60 (34.4) |
| -H | 0.79 | 0.82 | 1.07 | 1.75 |
| <i>p</i> -OCH ₃ | 5.56 | 8.90 | 13.5 | 23.22 |
| <i>p</i> -CH ₃ | 1.32 | 1.78 | 2.48 | 4.20 |
| <i>p</i> -Cl | 0.37 | 0.49 | 0.58 | 0.92 |

Effect of [Catalyst]

Effect of the [catalyst] on the rate of reaction has been studied in the range of 5×10⁻⁴ to 20×10⁻⁴ mol dm⁻³. The rate of reaction enhances with increase in Os(VIII) concentration (**Table: 3**). The plot of $\log k_c$ versus \log [catalyst] shows a unit slope value indicating the order with respect to catalyst follows first order kinetics. The Michaelis-Menten's plot of $1/k_{obs}$ versus $1/[catalyst]$ was also linear with a positive intercept indicating that the formation of complex between catalyst and Os (VIII). [**Fig: 2**]

Table: 3 Effect of varying [Catalyst] on the acid bromate Os (VIII) catalysed oxidation of 2-Azachalcones at 303K, [Bromate] = 0.01 mol dm⁻³; [H₂SO₄] = 10.0 mol dm⁻³; [Substrate] =0.1 M; [Hg (OAc)₂] =0.1 mol dm⁻³; HOAc – H₂O = 1:1 % (v/v)}.

| 10 ³ x [Catalyst] M | 10 ⁴ x k' (s ⁻¹) | | | |
|--------------------------------|---|----------------------------|---------------------------|--------------|
| | H | <i>p</i> -OCH ₃ | <i>p</i> -CH ₃ | <i>p</i> -Cl |
| 0.5 | 1.10 | 10.3 | 3.13 | 0.68 |
| 0.75 | 2.07 | 14.9 | 4.08 | 1.31 |
| 1.0 | 3.22 | 23.18 | 5.40 | 1.80 |
| 2.0 | 4.72 | 40.01 | 12.09 | 2.96 |

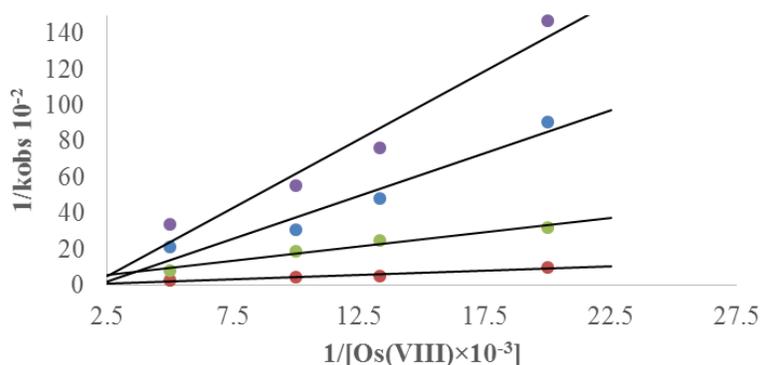


Fig: 2 The Michaelis-Menten's plot of $1/k_{obs}$ versus $1/[Catalyst]$

The Effect of structure on Reactivity and Relationships

Hammett's plot (**Fig: 3**) ($\log k$ versus σ^{+11}) is used to understand the effect of substituents on 2-Azachalcone system. A linear plot is observed with a negative slope (ρ^+) which is -1.17 indicates the reaction Centre is facilitated by high electron density. From the Hammett's plot the 'negative ρ^+ ' value also confirms that electron-donating substituents accelerate the rate of the reaction and electron-withdrawing substituents retard the rate of the reaction. Supporting the proposed mechanism in which electrophilic attack by Os(VIII) on to the $>C=C<$ in a single step resulting to formation of a complex between substrate and catalyst. Therefore, the order of reactivity with substituents of 2-Azachalcones follows: $p-OCH_3 > p-CH_3 > H > p-Cl$.

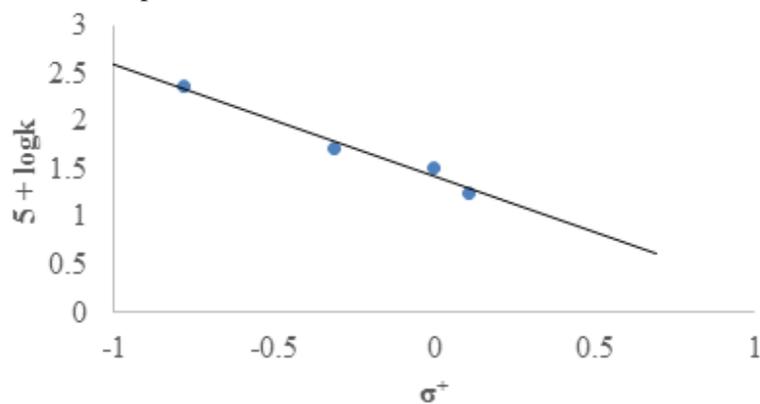


Fig: 3 Effect of substituents on k' in the 2-Azachalcone- Os(VIII)-bromate system

Evaluation of thermodynamic activation parameters and temperature effect

The rates of acid bromate Os(VIII) catalysed oxidation of 2-Azachalcones has been studied at different temperatures (303K-328K). Activation energy E_a was calculated from the

slopes of Arrhenius plot (**Fig-4**), E_a is useful to evaluation of activation parameters such as ΔH^\ddagger , ΔS^\ddagger , ΔG^\ddagger (**Table: 4**). Large negative ΔS^\ddagger values are observed, indicating the contention that the activated complexes are actually addition complexes of the Os and substrate. The slope of the Exner's 1^2 plot (**Fig: 4**) was found to be 0.982 ($r^2 > 0.95$). The isokinetic temperature β can be calculated using the following equation.

$$\beta = T_1 T_2 (b-1) / (b T_2 - T_1)$$

In the present study it was found to be 397K, which is greater than the experimental range. The value of β is similar to the slope (393K) of Exner's plot. The above and below values of ΔG^\ddagger values more or less same for all the substituted 2-Azachalcones indicating that a probably similar mechanism is operative in all these cases as shown in **scheme 1**.

Table: 4 Activation parameters for the Os(VIII) catalysed oxidation of 2-Azachalcones by acid bromate at 303K, [Substrate] = 0.1mol dm⁻³; [Bromate] = 0.01mol dm⁻³; [Os (VIII)] = 1.0 x 10⁻³ M; [H₂SO₄] = 10.0mol dm⁻³; [Hg (OAc)₂] = 0.1mol dm⁻³; HOAc – H₂O = 1:1 (v/v).

| 2'-Azachalcone | 10 ⁴ x k(s ⁻¹) | 5+logk | E _a (kJ/mole) | ΔG [‡] (kJ/mole) | ΔH [‡] (kJ/mole) | -ΔS [‡] (J/K mole) |
|----------------------------|---------------------------------------|--------|--------------------------|---------------------------|---------------------------|-----------------------------|
| -H | 3.22 | 1.508 | 36.94 | 73.60 | 34.35 | 129.56 |
| <i>p</i> -OCH ₃ | 23.18 | 2.36 | 23.35 | 68.66 | 20.76 | 158.1 |
| <i>p</i> -CH ₃ | 5.14 | 1.71 | 34.84 | 72.43 | 32.25 | 132.63 |
| <i>p</i> -Cl | 1.80 | 1.255 | 57.05 | 75.02 | 39.53 | 117.64 |

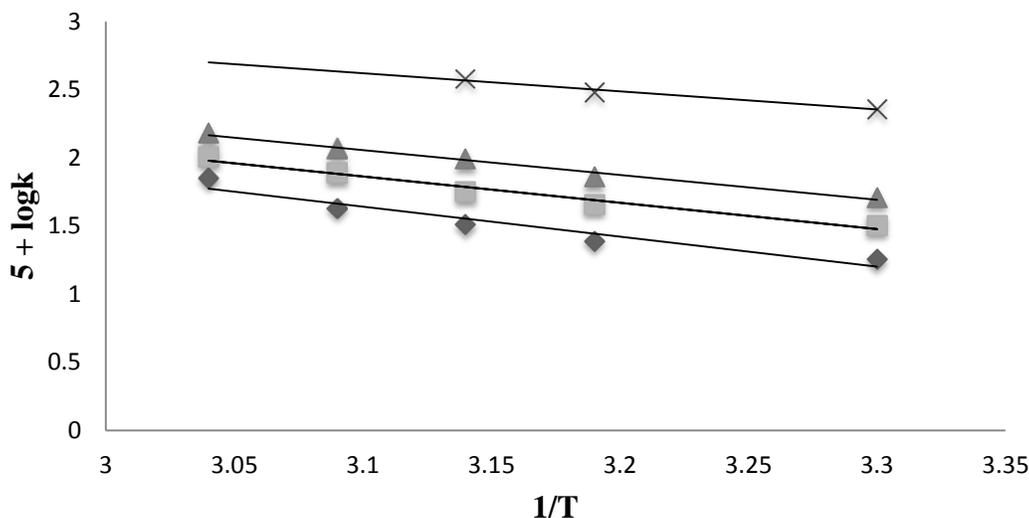
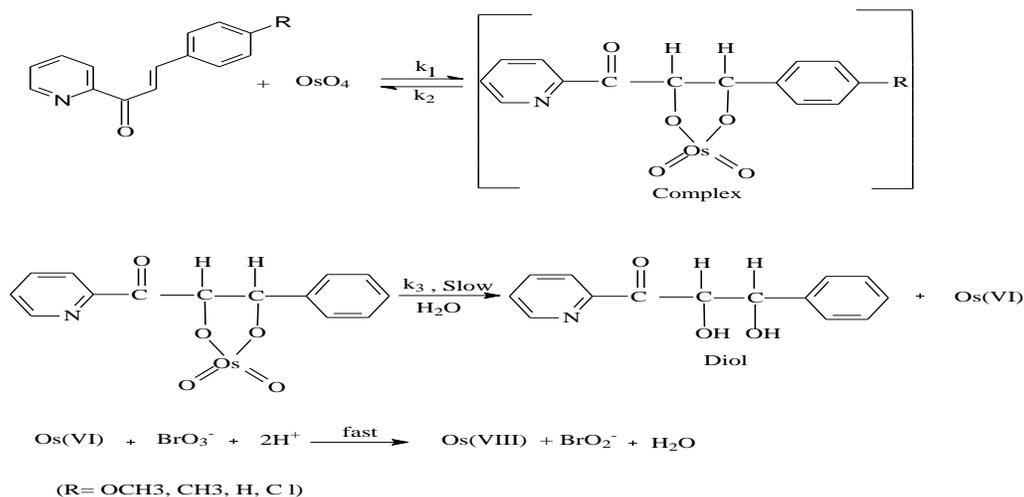


Fig: 4 Effect of temperature on k' in the 2-Azachalcones-Os(VIII)-bromate system



Scheme: 1.

From the above mechanism and investigations derived the following rate law

$$-\frac{d[\text{BrO}_3^-]}{dt} = k [\text{Complex}] \quad (1)$$

$$[\text{Complex}] = \frac{K [\text{Substrate}] [\text{Os(VIII)}]}{1 + K [\text{Substrate}] + K [\text{Os(VIII)}]} \quad (2)$$

From equation 1 and 2 $[\text{Substrate}] = [2\text{-Azachalone}]$

$$-\frac{d[\text{BrO}_3^-]}{dt} = \frac{k K [\text{Substrate}] [\text{Os(VIII)}]}{1 + K [\text{Substrate}] + K [\text{Os(VIII)}]} \quad (3)$$

$$[\text{Os(VIII)}] \llll [\text{Substrate}]$$

equation 3 can be written as

$$-\frac{d[\text{BrO}_3^-]}{dt} = k' = \frac{k K [\text{Substrate}] [\text{Os(VIII)}]}{1 + K [\text{Substrate}]} \quad (4)$$

Reciprocals of this equation can be written as

$$\frac{1}{k'} = \frac{1}{k K [\text{Substrate}] [\text{Os(VIII)}]} + \frac{1}{k [\text{Os(VIII)}]} \quad (5)$$

The above rate law explains well first order dependence on Os(VIII) and fractional order dependence on [substrate].

CONCLUSION

The kinetic and mechanism of Os(VIII) catalysed acid bromate oxidation of substituted 2-Azachalcones follows zero order kinetics in [Bromate] and [H⁺] fractional order in [substrate] and first order dependence on Os(VIII) catalyst. Isokinetic temperature was determined more negative value of ρ^+ support the rate of reaction is accelerated by electron donating substituents and is retarded by the electron withdrawing substituents. Following order is *p*-OCH₃ > *p*-CH₃ > H > *p*-Cl. The products of oxidation of 2-Azachalcone are identified as 1-picolinoyl-2-arylethane-1,2-diol. Activation parameters and effect of substituent have been used to suggest the possible mechanism of 2-Azachalcone.

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