OXIDATION OF ORTHO AMINOBENZYL ALCOHOL: A CONCISE KINETIC STUDY

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ABSTRACT

The foremost objective of the present work is to get a deep insight into the kinetics of ortho aminobenzyl alcohol (OABAlc) to develop a simple, efficient, and cost-effective method for its detection in contaminated water samples. This work deals with the silver catalyzed oxidation of OABAlc by potassium persulphate. The rate of oxidative reaction was determined by kinetic spectrophotometric method with absorption maxima of the reaction mixture at 440 nm, at constant pH and temperature of the solution. The effect of substrate, oxidant, catalyst, pH, temperature, ionic strength, and dielectric constant in this reaction has also been studied. During the investigation of thermodynamic parameters, the activation energy was found to be 58.92 kJ/mol, activation entropy = -53.61, activation enthalpy = 56.25 kJ/mol, and free energy = 73.43 kJ/mol. The results manifest first-order kinetics of the reaction concerning substrate, oxidant, and catalyst at optimum pH 7.0 and 40°C temperature. To explore further application and importance of OABAlc, a study on various aspects of the oxidation reaction is carried out in the presence of Ag (I) as a catalyst and a strong oxidant potassium persulphate to get deep insight into the chemical aspects of the compound and to deduce the mechanism of reaction under study.

Keywords: Oxidation, Kinetics, Ortho Aminobenzyl alcohol, Potassium Persulphate, Silver Nitrate, Absorption Maxima, Thermodynamic Parameters.

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INTRODUCTION

The formation of aldehydes, ketones, and other nitrogen-based heterocycles from benzyl alcohols and their derivatives are known for their industrial importance.¹⁻⁴ The carbonyl compounds so formed are absorbed in the synthesis of varied high-grade chemicals and agro-based products.⁵ The oxidation products of alcohols are widely used as a substrate in both research and industries due to its usage in various pharmaceutical preparations, which tends to be significant and versatile intermediates for the synthesis of new chemicals required to prepare soaps, perfumes, dyes, etc.⁶⁻⁹ Benzyl alcohol and its derivatives, particularly aminobenzyl alcohols have a wide range of applications in organic chemistry and drug synthesis.¹⁰ The mono-substituted benzyl alcohols and their derivative compounds, especially aminobenzyl alcohols, are a class of protean intermediates used in pharmaceutical and medicinal chemistry. OABAlc has vast synthetic applicability. They are naturally occurring alkaloids present in the leaves of plants with their traditional medicinal activities.¹¹ Despite the above-mentioned applications, the toxicity of OABAlc towards humans and the environment cannot be overlooked. The harmful impact of OABAlc is characterized by serious skin allergy, headache, fatigue, dizziness, dyspnea, rapid heart rate, and blue-colored skin emanating from the lack of proper oxygenation in blood and ultimately leading to death.¹² OABAlc and its derivatives might become a part of the wastewater streams originating from pharmaceuticals manufacturing units that are involved in the production or usage of OABAlc¹³⁻¹⁶ eventually turning detrimental to flora and fauna of the environment in a general and aquatic ecosystem in specific.

In this regard, many traditional methods have been reported on the selective oxidation of aminobenzyl alcohols, these reactions are synthetically advantageous, but they require aggressive reaction conditions,

use of stoichiometric reagents, difficulties in workup procedures and are also prone to undergo over oxidation.

The production of amino carbonyl derivatives from their respective OABAlc remains a daunting task and their methodologies are not widely investigated owing to the reaction between oxidant and amino groups that leads to a substantial decrease in the yield of a viable product. Therefore, it is still extremely desirable and stimulates us further to form practical catalytic systems for the alcohol oxidation without affecting the other oxidizable functional groups like amino, alkyne, and hydroxyl, etc., under normal reaction conditions.

To investigate the behavior of OABAlc, the Indirect Friedlander method has been documented in which OABAlc has been reacted with ketones catalyzed by transition-metal complexes obtained from ruthenium,¹⁷⁻¹⁹ palladium,²⁰ iridium,^{21, 22} rhodium,²³ and copper.²⁴ Different methods have been developed from time to time, making use of transition metals viz: manganese, cobalt, nickel, iron,²⁵ iodine reagents, etc. Various advanced oxidation processes (AOPs) and in-situ chemical oxidation (ISCO), have been applied to quickly oxidize the broad range of pharmaceuticals from wastewaters and soil samples.^{26, 27} Many other oxidants are used to remove contaminants, including hydrogen peroxide (H_2O_2), permanganate (MnO_4^-), persulphate, ozone (O_3), and Fenton process ($\cdot OH$). Among all of these oxidants, both persulphate salt such as PDS and PMS has good performance in wastewater treatment to oxidize the contaminants present in water samples. On the other hand, PDS has accrued attention due to its conjoint properties (i.e., hydrogen peroxide, ozone) in the ISCO technique to transform groundwater adulterants into less toxic chemical species.

Potassium persulphate has also emerged as a strong oxidant for oxidizing environmental contaminants into less toxic species. It is also known as potassium peroxydisulphate or KPS. It is also found to be efficacious in degrading organic pollutants, particularly for the aromatic pollutants category. It is known to be the best choice due to its low cost and easy availability. Persulphate ions are outstanding and multiskilled oxidizing agents used mainly for oxidation of synthetic, natural, organic, and inorganic substances in aqueous and neutral solutions and are also used for polymerization. In photo-oxidative removal of some organic compounds gives the best results in comparison to other persulphate salts under natural pH. It dissociates into the water by forming sulphate anion, which shows slow rate kinetics of organic pollutants. Therefore, to increase the rate of reaction, many transition metal catalysts i.e., Fe, Ag, Cu, Zn, Mn, and Ti are known to activate this oxidant to generate sulphate radicals ($SO_4^{\cdot -}$), facilitating through one-electron transfer process²⁸ and potassium persulphate can also be activated by thermally and photo-chemically activation processes to generate these sulfate radicals for progressing the chemical reaction systemically. In some cases, it has been documented in the literature that Ag (I) produces Ag (II), sulfate radical anion, and sulfate anion with the combination of potassium persulphate. The sulphate radicals so generated react freely with a broad range of organic contaminants present in groundwater and soils to give rise to additional reactive species like hydroxyl radicals, hydrogen peroxide, etc., which are important degradation processes for various pollutants present in water and soils.²⁹

In our present work, we used potassium persulphate as an oxidizing agent because of its low cost, ease in its availability, and simple handling to oxidize OABAlc. The oxidation of alcohols by this oxidant shows slow rate kinetics. To overcome this problem, Ag (I) in the form of $AgNO_3$ has been used as a catalyst to activate Potassium persulphate under neutral pH.

The main purpose of this work was the investigation of the oxidation of OABAlc to analyze the kinetic and thermodynamic behavior of reaction under normal reaction conditions. This method was carried out in simple operational conditions and found to be eco-friendly in all conditions.

EXPERIMENTAL

Material and Methods

Reagent grade OABAlc was purchased from Sigma Aldrich chemicals and its solution was prepared in acetone. Potassium persulphate and Ag (I) (Merck, India) were used and the solution was prepared in triply distilled water. Ammonium nitrate and ammonium hydroxide were used to make a buffer for running the kinetic experiments. The reaction mixture is formed by the addition of potassium persulphate solution, OABAlc, buffer, and catalyst. The kinetic reaction was studied in ammonia buffer with almost

stable pH during the entire process. For this above process, a buffer made from ammonium nitrate and ammonium hydroxide was used for obtaining the desired pH.

Buffer Preparation

Ammonia buffer was prepared using the previously reported method. For this preparation, 1M of ammonium nitrate and 1M of ammonium hydroxide were used for the kinetic experiment. To run the experiments, the ammonium nitrate was dissolved in triply distilled water in a 250 ml volumetric flask. Then standardize the ammonium nitrate solution with ammonium hydroxide to set the pH of the reaction mixture by using SYSTRONICS- Digital pH meter-335.

Preliminary Investigation

When the reactants were mixed, the solution turned light yellow initially changing to dark color later on. It finally gives the product on keeping for a longer time duration. Surprisingly, when we kept the reaction mixture at room temperature, the silver mirror formation was observed on the inner surface of the Erlenmeyer flask, which was further confirmed by using tollens reagent (silver mirror on the test tube) as a preliminary investigation in the laboratory. The silver mirror on the flask indicates the presence of aminobenzaldehyde in the reaction mixture as a reaction intermediate. The absorption maxima of the reaction mixtures are in the visible region, while the UV-VIS spectra of potassium persulphate and Ag (I) indicate no absorption in the visible region. The absorbance of the sample was recorded as a function of time. The kinetic experiments were carried out at temperature regulation of reaction mixture in a thermostat water bath with a precision of $\pm 0.1^{\circ}\text{C}$. The kinetics of Ag (I) catalyzed, the oxidation reaction of OABAlc was studied in basic buffer at pH 7.0 and temperature 40°C . Under all the conditions and concentrations, the reaction showed first-order dependence concerning substrate, oxidant, and catalyst.

Kinetic Experiments for Ag (I) catalysed Oxidation of OABAlc with Potassium Persulphate

The reaction mixture was prepared for the determination of absorption maxima to analyze the order concerning substrate, oxidant, and catalyst. The impact of different parameters like ionic strength, pH, dielectric constant, and temperature was also observed.

The order of reaction was determined w.r.t. OABAlc and the rate of reaction was studied by varying it in the concentration range 1.0×10^{-2} to $2.5 \times 10^{-2}\text{M}$ for which the amount of oxidizing agent was kept the same, i.e., $1.0 \times 10^{-3}\text{M}$ with constant pH and temperature, in ammonia buffer medium. In the variation of OABAlc, the reaction kinetics was found of the first-order. The rate of reaction was calculated by the plane mirror method and the value of k_{obs} was calculated from Guggenheim method.³⁰ The graph plotted by the Guggenheim method was found to be linear with a negative slope.

To determine the order concerning oxidant, the rate of reaction on the variation of the oxidant was studied by varying it in the concentration range 4.0×10^{-3} to $5.5 \times 10^{-3}\text{M}$ with the substrate being constant i.e. 4.0×10^{-4} at constant pH and temperature. In the variation of oxidant, the kinetics of the reaction was found to follow the first-order.

To find the impact of variation of catalyst, the rate of reaction on the variation of Ag (I) was studied by varying it in the concentration range of 3.0×10^{-4} to $6.0 \times 10^{-4}\text{M}$ in which concentration of substrate and oxidant was kept constant with fixed pH and temperature. Kinetics of reaction was observed to follow first-order concerning Ag (I) on studying the variation of Ag (I).

The temperature effect on the rate of oxidation of OABAlc was studied in the range of 40 to 55°C . OABAlc, Ag (I), and oxidant were kept at $4.0 \times 10^{-4}\text{M}$, $3.0 \times 10^{-4}\text{M}$, and $4.0 \times 10^{-3}\text{M}$ respectively. The data so drawn was used to calculate the thermodynamic parameters associated with the reaction under study.

For further investigation of the solvent interactions on the rate of reaction, acetone was used as a reaction solvent which acts as a binary mixture with water in the reaction mixture. In this experiment, the substrate was kept at $4.0 \times 10^{-4}\text{M}$, catalyst at $3.0 \times 10^{-4}\text{M}$, and oxidant at $5.0 \times 10^{-3}\text{M}$ while keeping other conditions unchanged. The amount of acetone was varied from a range of 4 to 16% to determine the results.

To examine the effect of ionic strength NaNO_3 (sodium nitrate) was used as ionic salt, which determines the ionic strength of the reaction mixture. In this kinetic run, the concentration of OABAlc, catalyst, and

oxidant was $4.0 \times 10^{-4}\text{M}$, $3.0 \times 10^{-4}\text{M}$, and $5.5 \times 10^{-3}\text{M}$, respectively. The Na^+ ions were taken from its nitrate part and the concentration of NaNO_3 ions was altered in between 2.0×10^{-3} to $8.0 \times 10^{-3}\text{M}$.

Formulae used to calculate the Thermodynamic Parameters for Kinetics of Oxidation Reaction

To investigate the thermodynamic parameter of reaction, different methods were used, which are as follows. In 1989, Arrhenius suggested a simple reaction relation between the rate of reaction and the temperature of the reaction. Arrhenius equation was used to calculate the effect of change of temperature on the rate constant and the reaction rate as well. We plotted the graph between $\log k_{cat}$ and $1/T$ to show the effect of temperature on reaction rate constant which follows the Arrhenius equation:

$$\log k_{cat} = [-E_a/2.303 RT] + \text{Constant} \quad (1)$$

Where, E_a = the activation energy in kJ/mol, R = Gas constant (1.987×10^{-3}), T = temperature of reaction.

The activation energy (E_a) was calculated by the following formula:

$$E_a = 2.303 R \frac{[T_1 \times T_2]}{[T_2 - T_1]} \times \log[(k''_{cat})/(k'_{cat})] \quad (2)$$

Where, k'_{cat} and k''_{cat} were calculated overall rate constants at temperature T_1 and T_2 , respectively.

Other thermodynamic parameters were given below.

Frequency factor (A) in $\text{dm}^3/\text{mol-s}$ was calculated by the following formula:

$$k_{cat} = A \cdot e^{(-E_a/RT)} \quad (3)$$

Free energy of activation ($\Delta F^\#$) in kJ/mol was calculated by the following formula:

$$\Delta F^\# = \Delta H^\# - (T\Delta S^\#) \times 10^{-3} \quad (4)$$

Enthalpy of activation ($\Delta H^\#$) in kJ/mol was calculated by the following formula:

$$\Delta H^\# = E_a - RT \quad (5)$$

Where, E_a = activation energy, T = Temperature, $R = 1.987 \times 10^{-3}$.

The entropy of activation ($\Delta S^\#$) in J/k-mol was calculated by the following formula:

$$k_{cat} = (k_b T/h) \cdot e^{(-E_a/RT)} \cdot e^{(\Delta S/R)} \quad (6)$$

Where, k_b = Boltzmann constant and h = Planck's constant.

Formulae used to Calculate the Value of Rate Constant and Overall Rate Constant

Rate constant (k_{obs}) - The value of k_{obs} was calculated by the following formula:

$$k_{obs} = [(A_2 - A_1)/(T_2 - T_1)] \times 2.303 \quad (7)$$

Where A = Absorbance and T = temperature of reaction sample.

The overall rate constant (k_{cat}) - the value of k_{cat} was calculated by the following formula:

$$k_{cat} = k_{obs} / [\text{highest concentration of set} \times \text{catalyst concentration}] \quad (8)$$

RESULTS AND DISCUSSION

UV-VIS Analysis

A reaction mixture was prepared in an iodine flask to determine the absorption maxima of the reaction mixture at different conditions and concentrations. The absorbance of the sample was recorded on a UV-VIS Double Beam Spectrophotometer-2203 as a function of time by plotting the graph to find out the λ_{max} of the reaction mixture. During the investigation of λ_{max} of the reaction mixture, it was found to be 440 nm. The graph for λ_{max} of reaction sample was plotted between absorbance and wavelength with time is shown in Fig.-1.

FT-IR (Fourier Transform Infrared) Spectroscopy to Identify the Product

FT-IR is a technique used to characterize different functional groups, molecules, and gases present in a reaction mixture by scanning the sample between the frequency ranges from 4000-400 /cm.

The absorption peaks in FTIR spectra was 3500.0, 3213.0, 2745.0, 2397.0, 1689.55, 1408.5, 1382.3, 1347.3, 1082.2, 830.6, 618.9, 452.9 /cm compared with literature data. In this analysis, the peaks at 2745.0 /cm frequency for C-H and 1689.55 /cm for C=O with stretching frequency indicates the existence of -CHO (aldehyde) group in the reaction sample. The peak 3213.0 and 3500.0 /cm is for N-H and 1082.2 /cm with C-N Stretching frequency signifies amino (-NH₂) group was also present. The functional groups like -CHO and -NH₂ confirm the presence of ortho aminobenzaldehyde in the reaction mixture as a reaction product.

Whereas other peaks like 2397.0/cm show O=C=O stretching for CO₂, and 1408.5 with O-H bending indicates -COOH (carboxylic acid) group, and a peak at 1347.3 was observed with O-H stretching which indicates -OH group was also found to be present in the sample. The FTIR data of the product is shown in Fig.-2.

Fig.-1: UV-VIS Absorption Spectra of Ag (I) catalyzed Oxidation of OABAlc with Potassium Persulphate. Conditions: [OABAlc] $\times 10^4 = 4.0\text{M}$, [KPS] $\times 10^3 = 5.0\text{M}$, [Ag (I)] $\times 10^4 = 3.0\text{M}$, Temp = $40 \pm 0.1^\circ\text{C}$, pH = 7.0, $\lambda_{\text{max}} = 440\text{ nm}$

Fig.-2: FT-IR Spectrum of Ag (I) catalyzed Oxidation of OABAlc with Potassium Persulphate

Order of Reaction in Case of Substrate, Oxidant, and Catalyst

After analyzing the variation of a substrate, it can be concluded that there is an increase in the rate of reaction with the incremental concentration of substrate (OABAlc > oxidant) and all other constituents and conditions remain constant during the variation, as shown in Fig.-3. On plotting the graph between the rate of reaction (dA/dt) and concentration of OABAlc, the slope comes out to be linear, which indicates first-order reaction with a value of n_1 was 1.0 as shown in Fig.-4. Similarly, during the variation of oxidant, an increased rate of reaction is seen on surging the concentration of oxidant [OABAlc < oxidant] as shown in Fig.-5. Graphical representation between the rate of reaction and concentration of oxidant shows a linear plot which implies the first-order reaction concerning oxidant with a value of n_2 was 1.07 as shown in Fig.-6. In the case of variation of catalyst, the rate of reaction increases with an increase in

the concentration of catalyst as shown in Fig.-7. Graph plotted between the rate of reaction and concentration of Ag (I) shows a straight line and value of $n_3 = 1.0$, which indicates the first-order reaction concerning catalyst also as shown in Fig.-8. Where, n_1, n_2 and n_3 are the order of reaction, respectively. The order of reaction (n) was calculated by using the following formula:

$$n = \frac{\log[(dA/dt)_{i1}] - \log[(dA/dt)_{i2}]}{\log C_1 - \log C_2} \quad (9)$$

Where n = order of reaction, $[(dA/dt)_{i1}]$ and $[(dA/dt)_{i2}]$ was initial rates of reaction corresponding to initial concentrations C_1 and C_2 of reactant. A concise detail of the experimental data of different kinetic experiments has been tabulated in Table-1.

Fig.-3: Variation of OABAlc (Absorbance Vs Time Plot)
Conditions: $[KPS] \times 10^3 = 1.0M$, $[Ag(I)] \times 10^4 = 3.0M$, Temp = $40 \pm 0.1^\circ C$, pH = 7.0, $\lambda_{max} = 440 \text{ nm}$

Fig.-4: Determination of Order with respect to OABAlc.

Fig.-5: Variation of Oxidant (Absorbance Vs Time plots)
Conditions: $[OABAlc] \times 10^4 = 4.0M$, $[Ag(I)] \times 10^4 = 3.0M$, Temp = $40 \pm 0.1^\circ C$, pH = 7.0, $\lambda_{max} = 440 \text{ nm}$.

Fig.-6: Determination of Order with respect to Oxidant

Fig.-7: Variation of Catalyst (Absorbance Vs Time Plot)

Conditions: $[OABAlc] \times 10^4 = 4.0M$, $[KPS] \times 10^3 = 4.0M$, $pH = 7.0$, $Temp = 40 \pm 0.1^\circ C$, $\lambda_{max} = 440\text{ nm}$

Fig.-8: Determination of Order with respect to the Catalyst

Effect of pH on Reaction Rate

The effect of pH is graphically shown in Fig.-9. It was carried out from pH range 6.5 to 9.5. The variation of pH was studied by keeping the concentration of ammonium nitrate fixed and varying the ammonium hydroxide solution. It has been observed that the rate of reaction was found to be maximum at pH 7.5 whereas an increase in the pH results in the decrease of the rate of reaction.³¹ Rate constant and rate attained its maximum value as the pH approaches 7.5. Subsequently above pH 7.5, the rate and rate constant of reaction decreases continuously. Above this pH, ionization of persulphate salt must be at its maximum level, and thus, its sulphate ions completely dissociate into solution losing their stability, and hence, the decreased rate and rate constant was observed. Thus, it was concluded that oxidation of

OABAlc by Potassium Persulphate shows the best kinetics and highest level of oxidation either in a slightly basic or in a neutral medium in our present analysis.

Table-1: Kinetic Data for Silver catalysed Oxidation of OABAlc by Potassium Persulphate

No. of Exp.	[KPS] $\times 10^3$ (mol/dm ³)	[OABAlc] $\times 10^3$ (mol/dm ³)	[Ag (I)] $\times 10^3$ (mol/dm ³)	pH	Acetone % (V/V)	[NaNO ₃] $\times 10^3$ (W/V)	10 ⁴ k_{obs} /sec	$k_{cat} \times 10^{-2}$ dm ⁶ mol ⁻² /sec
1	1.0	10.0	0.30	7.0	-	-	1.02	0.34
2	1.0	15.0	0.30	7.0	-	-	1.54	0.34
3	1.0	20.0	0.30	7.0	-	-	2.05	0.34
4	1.0	25.0	0.30	7.0	-	-	2.66	0.35
5	4.0	0.40	0.30	7.0	-	-	1.62	1.35
6	4.5	0.40	0.30	7.0	-	-	2.03	1.50
7	5.0	0.40	0.30	7.0	-	-	2.32	1.55
8	5.5	0.40	0.30	7.0	-	-	2.66	1.61
9	4.0	0.40	0.30	7.0	-	-	1.62	1.35
10	4.0	0.40	0.40	7.0	-	-	2.17	1.36
11	4.0	0.40	0.50	7.0	-	-	2.65	1.33
12	4.0	0.40	0.60	7.0	-	-	3.29	1.37
13	5.0	0.40	0.30	7.0	4	-	2.32	1.55
14	5.0	0.40	0.30	7.0	8	-	2.19	1.46
15	5.0	0.40	0.30	7.0	12	-	2.04	1.36
16	5.0	0.40	0.30	7.0	16	-	1.92	1.28
17	5.5	0.40	0.30	7.0	-	2.0	2.51	1.52
18	5.5	0.40	0.30	7.0	-	4.0	2.44	1.48
19	5.5	0.40	0.30	7.0	-	6.0	2.37	1.44
20	5.5	0.40	0.30	7.0	-	8.0	2.33	1.41
21	4.0	0.40	0.30	7.0	-	-	1.62	1.35
22	4.0	0.40	0.30	7.0	-	-	2.34	1.95
23	4.0	0.40	0.30	7.0	-	-	3.30	2.75
24	4.0	0.40	0.30	7.0	-	-	4.55	3.79
25	5.5	0.40	0.30	6.5	-	-	2.37	1.44
26	5.5	0.40	0.30	7.0	-	-	2.66	1.61
27	5.5	0.40	0.30	7.5	-	-	2.83	1.72
28	5.5	0.40	0.30	8.0	-	-	2.58	1.56
29	5.5	0.40	0.30	8.5	-	-	2.33	1.41
30	5.5	0.40	0.30	9.0	-	-	2.30	1.40
31	5.5	0.40	0.30	9.5	-	-	2.22	1.35

Variation of Ionic Strength

The influence of ionic strength was studied by using sodium nitrate (NaNO₃)³² as ionic salt with a concentration range from 2.0×10^{-3} to 8.0×10^{-3} M by keeping fixed concentrations of other reaction ingredients at pH 7.0 and 40°C. The rate of reaction decreases with an increase in ionic strength. The plot between $\log k_{cat}$ and ionic strength (μ) is found to be linear with a negative slope which indicates that the rate-determining step is a reaction between ion and dipole. The graph plotted between $\log k_{cat}$ and ionic strength (μ) of the reaction mixture is represented in Fig.-10. The ionic strength of the reaction mixture is calculated by the following formula:

$$\text{Ionic strength } (\mu) = \frac{1}{2} \times \sum (C_i Z_i^2)$$

Where μ = ionic strength, C_i = concentration of Na and NO₃ ions, Z_i = charge on ions.

Effect of Dielectric Constant

The reaction mixtures act as a binary mixture due to the presence of water and acetone together. During the effect of acetone on the reaction mixture, the rate of reaction decreases as the amount of acetone increases.³³

Fig.-9: Variation of pH (k_{cat} Vs pH plot)

Conditions: $[OABAlc] \times 10^4 = 4.0M$, $[KPS] \times 10^3 = 5.5M$, $[Ag(I)] \times 10^4 = 3.0M$, Temp = $40 \pm 0.1^\circ C$, $\lambda_{max} = 440$ nm.

Fig.-10: Effect of Ionic Strength ($\log k_{cat}$ Vs Ionic Strength)

Condition: $[OABAlc] \times 10^4 = 4.0M$, $[KPS] \times 10^3 = 5.5M$, $[Ag(I)] \times 10^4 = 3.0M$, $[NaNO_3] \times 10^3 = 2.0$ to $8.0M$, Temp = $40 \pm 0.1^\circ C$, pH = 7.0, $\lambda_{max} = 440$ nm

The plot of $\log k_{cat}$ vs $1/D$ was found to be linear with a negative slope which reaffirms that the rate-determining step is the reaction between a dipole and anion of persulphate. The dielectric constant (D) was calculated by the following formula:

$$D = [(V_{acetone} \times D_{acetone}) + (V_{water} \times D_{water})] / (\text{total volume of reaction mixture})$$

Where $V_{acetone}$ = the volume of acetone in the reaction mixture, $D_{acetone}$ = the dielectric constant of acetone at $40^\circ C$ temperature. V_{water} is the volume of water in the reaction mixture, and D_{water} is the dielectric constant of water at $40^\circ C$. The graph of dielectric constant with negative slope by plotting the graph between $\log k_{cat}$ and $1/D$ is shown in Fig.-11.

Effect of Temperature

For establishing the impact of varying temperatures on the rate of reaction, the reaction was carried in the temperature range of $40^\circ C$ to $55^\circ C$ at pH 7.0. The presentation of data according to the Arrhenius equation is shown in Table-2.

The activation energy (E_a) was found to be $58.92 kJ/mol$, temperature coefficient (η) as 1.99, Arrhenius factor (A) as $9.19 \times 10^{11} dm^3/mol-s$, activation entropy ($\Delta S^\ddagger$) as $-53.61 J/k-mol$, activation enthalpy ($\Delta H^\ddagger$) as $56.25 kJ/mol$, and free energy of activation ($\Delta F^\ddagger$) as $73.43 kJ/mol$. Thereby by increasing the temperature of the reaction mixture, the rate of reaction increases. A plot of $\log k_{cat}$ vs $1/T$ was found to be linear, which indicates that the Arrhenius equation relating the temperature and specific rate with the

equation- $\log k_{cat} = [-E_a/2.303 RT] + \text{Constant}$. The positive value of enthalpy of activation indicates that the reaction was endothermic³⁴ and the negative value of entropy of activation shows that charged and rigid transition state was formed, which indicates the formation of product. The plot between $\log k_{cat}$ and $1/T$ is shown in Fig.-12.

Fig.-11: Effect of Dielectric Constant on Reaction Rate

Condition: $[OABAlc] \times 10^4 = 4.0M$, $[KPS] \times 10^3 = 5.0M$, $[Ag(I)] \times 10^4 = 3.0M$, Temp = $40 \pm 0.1^\circ C$, pH = 7.0, $\lambda_{max} = 440 \text{ nm}$.

Table-2: Thermodynamic Activation Parameters for Ag (I) catalysed Oxidation of OABAlc by Potassium Persulphate in Ammonia Buffer Medium at $40^\circ C$

Temp. ($^\circ C$)	$k_{cat} \times 10^{-2}$ $dm^6 mol^{-1} s^{-1}$	E_a (kJ/mol)	η Temp. coefficient	$A \times 10^{11}$ ($dm^3/mol \cdot s$)	$-\Delta S^\ddagger$ J/k-mol	$\Delta H^\ddagger$ (kJ/mol)	$\Delta F^\ddagger$ (kJ/mol)
$40^\circ C$	1.35	-	-	9.150083852	50.02268754	56.31333803	73.03025832
$45^\circ C$	1.95	60.86843586	-	9.258678631	52.44584520	56.27176999	73.29829783
$50^\circ C$	2.75	58.72152793	2.03703704	9.248170920	54.81884448	56.23020195	73.56633734
$55^\circ C$	3.79	58.15652829	1.94358974	9.123005278	57.14421851	56.18863391	73.83437680
Mean Values		58.91549733	1.99031339	9.194984673	53.60789894	56.25098597	73.43231758

Where E_a = activation energy, A = frequency factor, $\Delta S^\ddagger$ = activation enthalpy; $\Delta H^\ddagger$ = activation entropy, $\Delta F^\ddagger$ = free energy.

Fig.-12: Arrhenius plot

Conditions: $[OABAlc] \times 10^4 = 4.0M$, $[KPS] \times 10^3 = 4.0M$, $[Ag(I)] \times 10^4 = 3.0M$, pH = 7.0, $\lambda_{max} = 440 \text{ nm}$

CONCLUSION

A cost-effective way to monitor and remove OABAlc from a contaminated sample of water through oxidation is being pursued to develop a comprehensive method by carrying out the reaction under varied conditions of pH, ionic strength, temperature, and dielectric constant alongside the variation in concentration of substrate, oxidant, and catalyst for a meticulous approach. The study has shown that the reaction can be easily executed under normal conditions of temperature, pH with moderate quantities of reagents and instruments been involved as well. Further studies to elucidate the mechanism of the reaction and also to understand the dynamics involved in this reaction are underway.

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