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Kinetic and Mechanistic Study on the Oxidation of Indole-3-Propionic Acid in Acetic Acid Medium

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Abstract

Kinetic investigation on the oxidation of IPA in an acidified solution of potassium bromate in the presence of $Hg(OAC)_2$ as a scavenger, have been studied in the temperature range of 303-323K. Increase in the concentration of H^+ ion showed first order. The influence of $Hg(OAC)_2$, ionic strength and oxidant on the rate was found to be insignificant. The reaction was found to be of zero order each in concentration of IPA and $KBrO_3$. The various thermodynamic parameters were calculated form rate measurements at 303, 308, 313, 318 and 323K respectively. A suitable mechanism in conformity with the kinetic observations has been proposed and the rate law is derived on the basis of the observed data. The product γ-spirolactone was confirmed from the IR and NMR spectral analysis.

Keywords: Kinetics, oxidation, potassium bromate, IPA.

Introduction

Potassium bromate has been used as an oxidant in acidic media[1-4]. The product of bromate oxidation is bromide which can be safely recycled, thus making bromate oxidations environmentally being compared to metal ion oxidations. Although bromate itself a strong oxidizing agent, having a redox potential of 1.45 V[5]. Bromate oxidations sometimes even involve oscillation reactions[6-8]. Hence, the chemistry of bromate ion in an aqueous acid medium is of considerable interest, given its importance in mechanistic chemistry[9].

Tryptophan derived indole compounds have been widely investigated as antioxidants. Indole-3-propionic acid (IPA) one of these compounds, is a deamination product of tryptophan[10]. IPA has a combination of properties which renders it particularly useful for preventing the cytotoxic effect of amyloid beta proteins on cells for treating any fibrillogenic disease, and for protecting cells from oxidative damage. The main objectives of the present study are to ascertain the reactive species of the substrate and oxidant elucidate a plausible mechanism, identify the oxidation products and evaluate the kinetic and thermodynamic parameters of the product.

Material and Methods

All chemicals and reagents used in the work were of analytical grade and used without further purification. An aqueous solution of potassium bromate (Merck), $NaClO_4$ were prepared by dissolving the weighted samples in double distilled water. Sodium per chlorate was used to maintain the ionic strength of the medium. IPA is used as received. Mercuric acetate (E. merck) was dissolved in acetic acid.

Kinetic Measurements: The requisite volume of all reagents, including substrate, was thermostated at 303-323K to attain equilibrium. A measured volume of $KBrO_3$ solution, maintained separately at the same temperature, was poured rapidly into the reaction vessel and the progress of the reaction was followed by assaying, aliquots of the reaction mixture of $KBrO_3$ iodometrically, using starch as an indicator after suitable time intervals. The unused bromate reacts with KI in acid solution in accordance with the equation.

$$BrO_3^- + 6I^- + 6H^+ \rightleftharpoons Br^- + 3I_2 + 3H_2O \quad (1)$$

All the reactions were carried out under the condition of using tenfold excess of (IPA) over [Bromate]. The pseudo first order rate constants (s^{-1}) were computed from linear plots of log [bromate] against time ($r^2 \geq 0.98$) up to 80% completion of reaction. The rate constants (K) were reproducible within 5%. Freshly prepared solutions of IPA in acetic acid were used to avoid any possible side reactions. The scavenger mercuric acetate of concentration (0.001 $moldm^{-3}$) was added through the reaction which will remove the bromine ions formed during the course of the reaction. Duplicate kinetic runs were reproducible with ±5%.

Test for free radicals: There was no induced polymerisation of acrylonitrile monomer, ruling out the possibility of free radical formation during the course of the reaction[11].

Product Analysis Stoichiometry: The stoichiometry of the reaction was determined by equilibrating reaction mixtures of various [Bromate]/[IPA] ratios at 30^0C for 24 hrs keeping all the other reagents constant. Estimation of unconsumed [bromate] revealed that 3 moles of IPA consumed 4 moles of bromide[12].

The final product also identified by UV, FT-IR, and NMR spectral and elemental analysis. The IR spectrum was recorded using KBr pellets and ^{1}HNMR by the solvent DMSO.

IR and NMR data: The identity of this product γ-spirolactone oxindole was confirmed from its ^{1}H NMR and FT-IR spectra. FT-IR (KBr) 3426.27, 1711.22 and 1634 cm^{-1}, ^{1}H NMR (DMSO) ppm = 2.4-3.6 (m, 4H), 6.9-7.4 (m, 5H, ArH, NH).

Results and Discussion

Effect of oxidant and Substrate: The rate of oxidation of IPA by acid bromate is first order with respect to IPA and bromate table- 1, 2. The plots of log [$KBrO_3$] versus time for various concentration of [IAA] are linear.

Table-1
Effect of oxidant on reaction rate

Oxidant x 10^{-3} M	1	2	3	4
K x 10^{-4} min^{-1}	7.177	7.204	7.216	7.177

Table-2
Effect of concentrations of IPA on the reaction rate

IPA x 10^{-2} M	2	2.5	3	3.5	4
K x 10^{-4} min^{-1}	4.65	5.71	6.09	7.72	9.44

Effect of H^+ ion: At constant [$KBrO_3$], [substrate], ionic strength and the rate of the reaction increases linearly with increase in [H^+] acid. The plot of log K against log [H^+] is linear with a slope of unity. This establishes that the reaction is first order with respect to hydrogen ion.

Effect of μ: The variation of the reaction has negligible influence on the reaction rate. This indicates the reaction between the neutral molecules or a neutral molecule and anion.

Effect of temperature: The reaction was carried out at four different temperatures to study the effect of temperature on the rate of the reaction. It was observed that, the rate of the reaction increase with an increase in temperature table-3. The thermodynamic parameters like energy of activation (E_a), enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$) and free energy of activation ($\Delta G^{\#}$) were calculated by determining values of K at different temperatures figures-1, 2 and table- 4.

Table-3
Effect of temperature on the reaction rate

Temperature K	303	308	313	318	323
K_2 x 10^{-2} sec^{-1}	1.61	2.30	3.50	6.00	8.60

Table-4
Thermodynamic parameters for the oxidation of IPA

Energy of activation [Ea] KJ mol^{-1}	70.25
Enthalpy of activation [$\Delta H^{\#}$] KJ mol^{-1}	67.685
Entropy of activation [$\Delta S^{\#}$] KJ mol^{-1}	-184.273
Free energy of activation [$\Delta G^{\#}$] KJ mol^{-1}	123.51

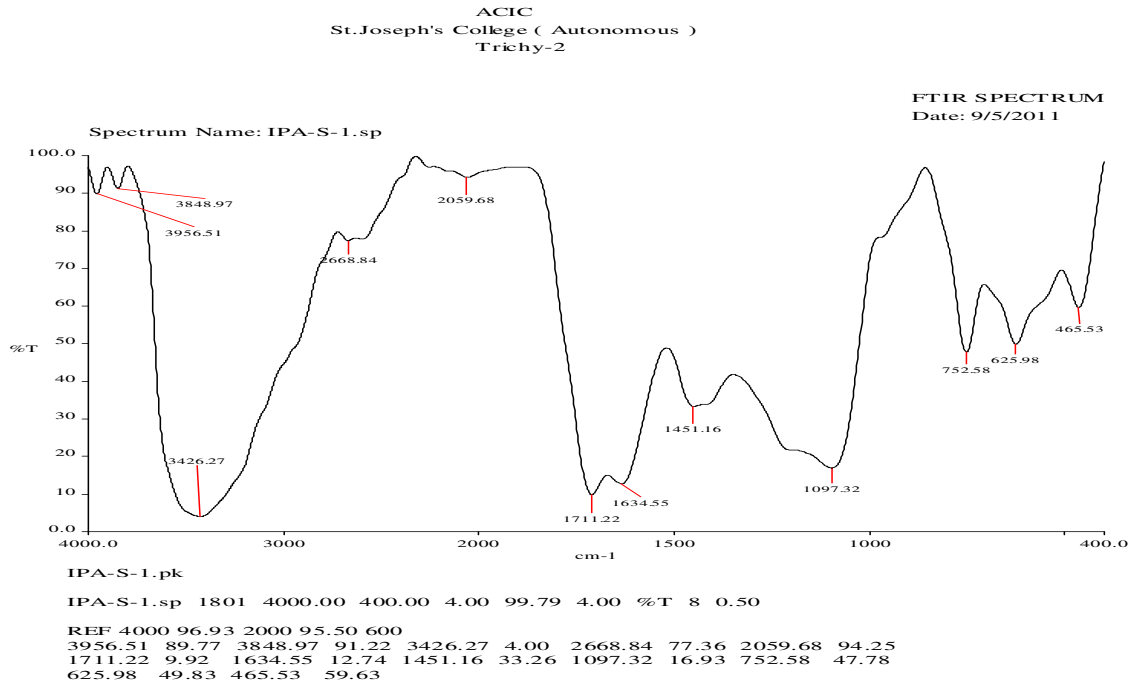


Figure-1
IR spectra of the product γ spirolactone

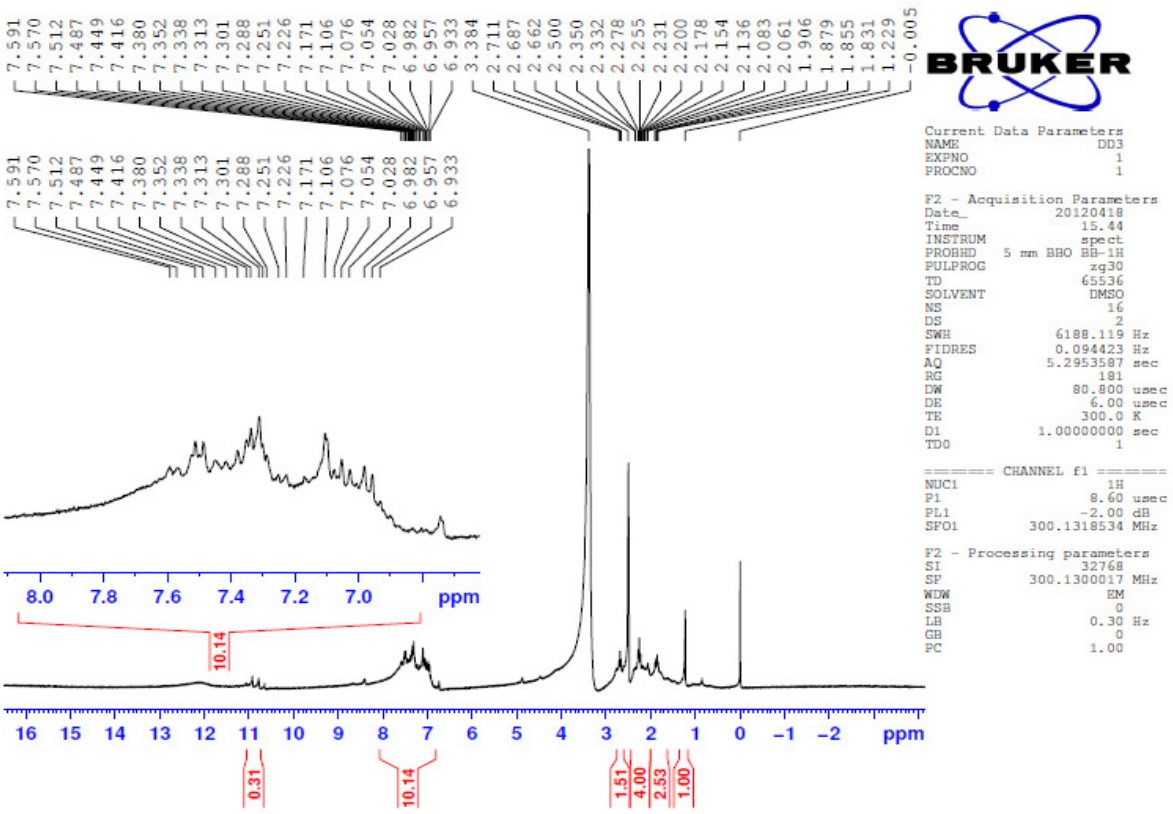


Figure-2
NMR spectra of the product γ spirolactone

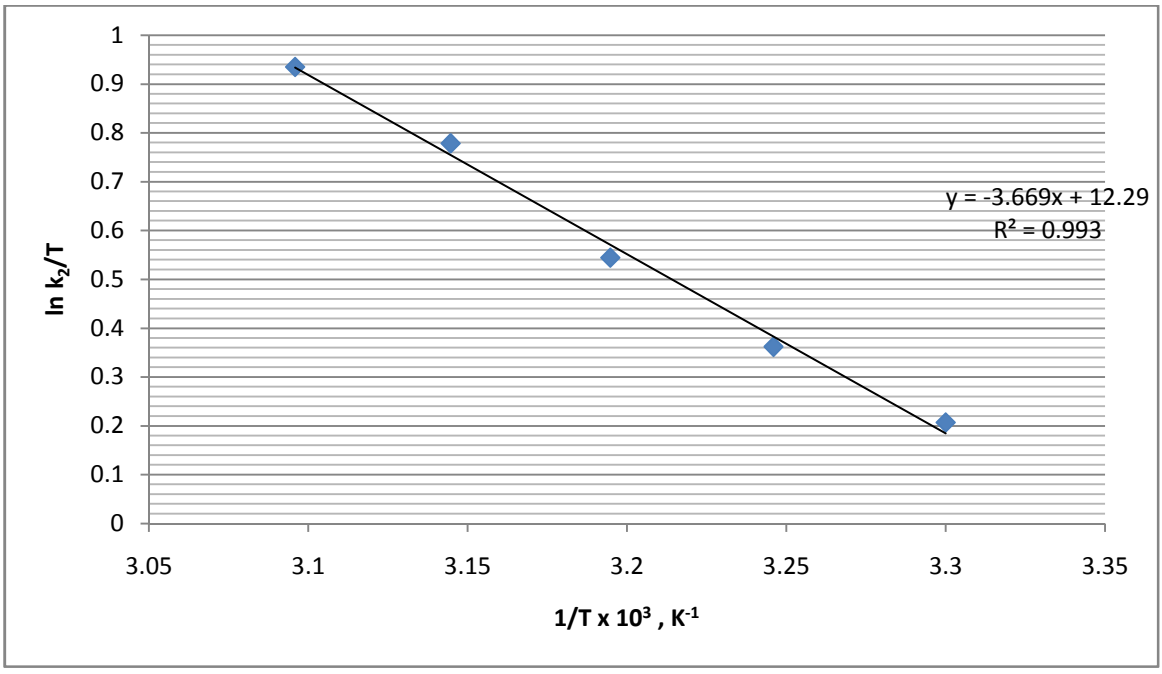


Figure-3
Arrhenius plot for the oxidation of IPA

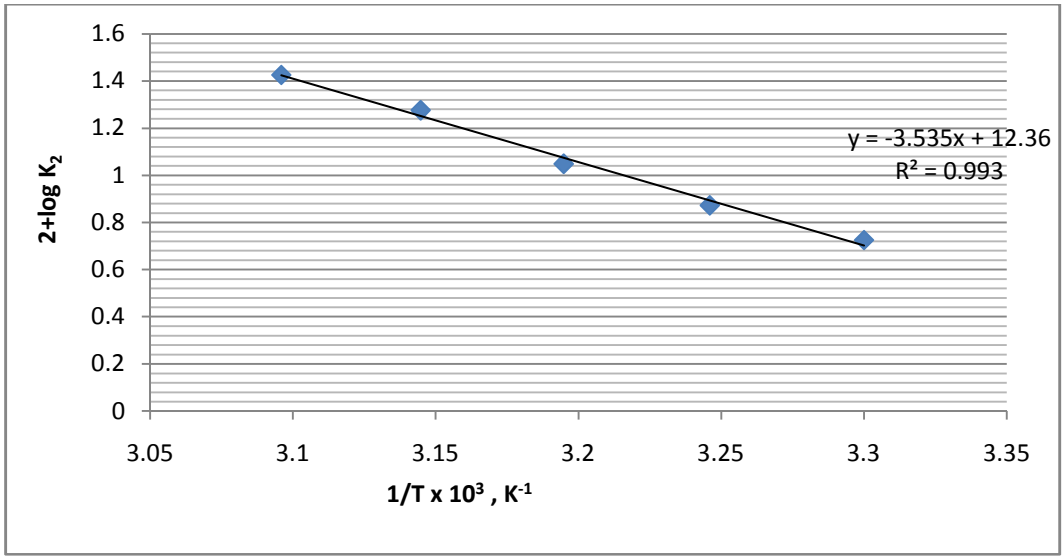
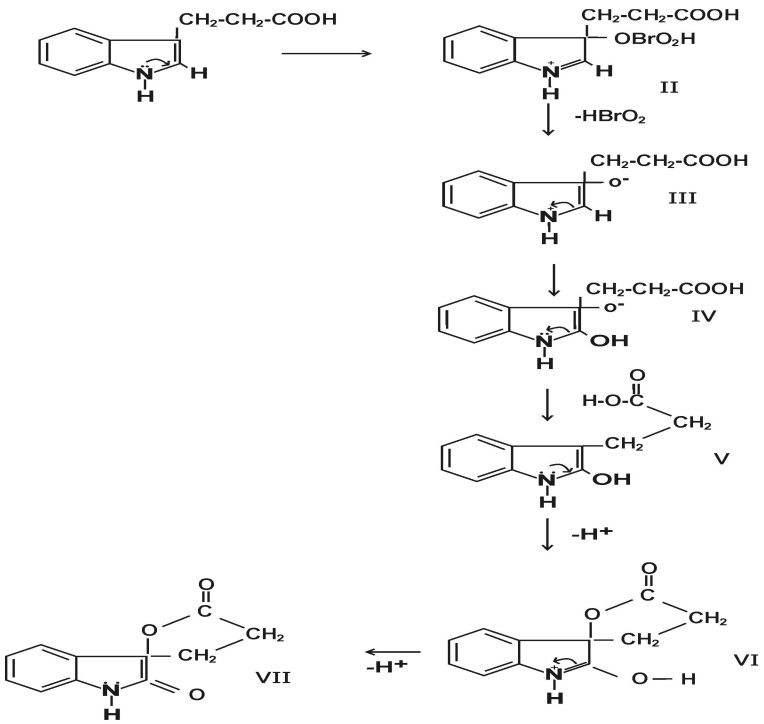


Figure-4
Eyring plot for the oxidation of IPA



Scheme-1

The reaction is independent of potassium bromate concentration. This shows that reaction is first order with respect to change in concentration of oxidant. It is also seen that on variation of ionic strength (μ) $NaClO_4$ and Hg (OAC) $_2$ the rate of the reaction does not change showing negligible effects of these reagents. From the Arrhenius plot the value of energy of activation (E_a) is calculated. Hence the large negative value of entropy of activation ($\Delta S^{\#}$) obtained is attributed to the severe restriction of solvent molecules around the transition state of higher charge and cyclic nature of the intermediate[13, 14].

Based on the above data a possible mechanism shown below has been proposed for the oxidation of IPA by $KBrO_3$.

$$H^+ + BrO_3^- \longrightarrow KBrO_3 \quad (2)$$
$$HBrO_3 + H^+ \longrightarrow H_2 + BrO_3^- \quad (3)$$

Considering the reactive species of potassium bromate as BrO_3^- ions, the rate of the reaction can be written in terms of loss of concentration of bromate ion with time (ie) -d $[BrO_3]$/dt

Rate equation = $-d[BrO_3]/dt = K_1K_2K[H^+][IPA][BrO_3^-]$

Conclusion

IPA - Bromate reaction in the presence of bromo complexing metal ions, does not route through the mechanism suggested in oscillation reactions. Acid bromate oxidises the IPA into an intermediate, which subsequently decomposes into products. It is supported by the results obtained from the IR, NMR and UV Visible spectral studies.

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