

“Kinetics and mechanism of oxidation of mandelic acid by N-bromoanisamide”

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Abstract

The kinetics of the oxidation of the mandelic by N-bromoanisamide has been studied in 40% acetic acid medium in the presence HClO_4 and of $[\text{Hg}(\text{OAc})_2]$. The reactions exhibit a first order rate dependence with respect to oxidant and fractional order with respect to substrate. The reaction rate decreases slightly with increasing the concentration of $[\text{H}^+]$ and retarded by the addition of anisamide, (as one of the oxidation product of oxidant). The decrease in dielectric constant of the medium decreases rate of the reaction. Increase in ionic strength, by the addition of sodium perchlorate has no effect on the rate constant. The effect of temperature on the reaction has been investigated in the temperature range 308-323 K. The activation parameters were calculated and a possible operative mechanism was proposed.

Keywords: mandelic acid; oxidation; mechanism; N-bromoanisamide.

Introduction

N-halo compounds are commonly used for oxidation of various organic compounds such as alcohols, aldehydes amino, acids keto-acids and hydroxy acids etc. The kinetics of α -hydroxy acids has been studied with N-halocompounds like N-bromoacetamide^{1,2} N-bromosucciniamide³, N-bromophthaliamide^{4,5} N-bromobenzamide⁶ N-Chlorosaccharin^{7,8} N-halosulphonamides⁹⁻¹¹ (brommine-B chloamine-B, chloramine-T) and other oxidants¹²⁻¹⁶. As similar to other N-halo compounds, N-bromoanisamide also a potent oxidant. Only few works have been done on N-bromoanisamide as an oxidant in acidic medium. We now report the kinetics and mechanism of oxidation of mandelic acid by N-bromoanisamide. Mandelic acid is the smallest α -hydroxy acid among compounds which have aromatic group. It is excreted well in urine & used as antiseptic ingredient particularly against urinary tract infections. Mandelic acid and its derivatives are used to apply the dual activities as an antibacterial agent and as antiaging agent.

Materials and Method

All the reagents employed in the kinetic investigation were of analytical grade. Double distilled water employed in kinetic run. To prevent photochemical effect, the freshly prepared solution of N-bromoanisamide was stored in brown colored bottle and its strength was checked iodometrically.

Kinetic Measurement:-

The reaction was studied at constant temperature 35°C ($\pm 0.1^{\circ}\text{C}$) under the pseudo-first order condition $[\text{MA}] \gg [\text{NBA}]$ in 40% aqueous acetic acid medium. The reaction was initiated by addition of requisite amount of NBA to reaction mixture containing substrate, mercuric acetate, perchloric acid. The Progress of reaction was monitored by measuring unconsumed NBA iodometrically using 1% starch as an indicator.

Stoichiometry And Product Analysis:-

The stoichiometry of the reaction was ascertain by equilibrating the reaction mixture containing an excess of [NBA] >> [MA], HClO₄, mercuric acetate in 40% acetic acid at 35⁰C for 48h. The unconsumed oxidant (NBA) was determined iodometrically, and it was found that one mole of mandelic acid consumed one mole of NBA. Thus the ratio of consumption of substrate to oxidant is 1:1



Bezaldehyde was found as the end product of oxidation, and identified by the spot test and 2:4 dinitrophenylhydrazine method.

Results and Discussion

The oxidation of mandelic acid by N-bromoanisanide was kinetically probed at several initial concentrations of the reactants in acid media. The salient features obtained are discussed. The rate constant k_1 calculated, under the pseudo-first order condition [MA] >> [NBA] at constant HClO₄, [Hg(AcO)₂], solvent composition and temperature, results are given in (Table-1) Plots of log(a-x) vs. time were linear, indicating a first order dependence of rate on [NBA]. The values of k_1 calculated from these plots are unaltered with variation of oxidant, conferring the first order dependence on [NBA].

Table-1: Effect of NBA on the reaction rate at 35⁰C in presence of 40% acetic acid
HClO₄ = 0.01 M; Mandelic Acid = 3.5 x10⁻² M; Temp. = 308K
[Hg(AcO)₂] = 0.002M; Solvent; AcOH-H₂O = (v/v) 40%

NBA × 10 ⁻³ M	k × 10 ⁻³ min ⁻¹
2.5	4.055
3.5	4.055
4.5	4.053
5.5	4.057
6.5	4.051
7.5	4.052

The rate constants (k_1) have been found to increase with increase in the concentration of mandelic acid and plots of k_1 vs. [MA] was linear with slope less than unity, indicating fractional order dependence with respect to mandelic acid. (Table-2)

Table-2: Effect of Substrate, HClO₄, CH₃COOH on the reaction rate
NBA = 4.5 x10⁻³ M; [Hg(AcO)₂] = 0.002M; Temp. = 308 K

Substrate × 10 ⁻² M	HClO ₄ × 10 ⁻² M	CH ₃ COOH % (v/v)	k × 10 ⁻³ min ⁻¹
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1.5	1	40	2.630
2.5	1	40	3.345
3.5	1	40	4.053
4.5	1	40	4.828
5.5	1	40	5.178
6.5	1	00	5.577
3.5	0.50	40	5.253
3.5	0.75	40	4.549
3.5	1.00	40	4.053
3.5	1.25	40	3.716
3.5	1.50	40	3.061
3.5	1.75	40	2.182
3.5	1	40	4.053
3.5	1	50	3.345
3.5	1	60	2.630
3.5	1	70	1.961

The rate constant k_1 decreased with increase in the concentration of HClO_4 (**Table-2**) this may due to protonation of the substrate. The plot of $\log k_1$ vs. $[\text{HClO}_4]$ is linear with negative slope. The slope being less than unity indicates inverse fractional order dependence on HClO_4 .

Addition of mercuric acetate to the reaction mixture showed an insignificant effect on the rate of reaction, suggesting that mercuric acetate act as a bromide ion scavenger only, in the form of $[\text{HgBr}_4]^{-2}$

Successive addition of anisamide (as one of the oxidation product of oxidant) to the reaction mixture showed decreasing effect on the rate of oxidation of mandelic acid. Addition of NaClO_4 (to study the effect of ionic strength) in the reaction mixture showed an insignificant effect on the rate of oxidation.

In order to find the effect of dielectric constant (polarity) of the medium on the rate, the reaction was studied in aqueous acetic acid mixture of various compositions (**Table-2**). The data clearly reveal that the rate of reaction increase with a decrease in the percentage of acetic acid, i.e., increasing dielectric constant or polarity of the medium leads to the inference that there is a charge development in the transition state involving a more polar activated complex than the reactants. (Laidler KJ 1965 Tata Mc. Graw Hill, New Delhi pp 229)

Effect of Varying Temperature:-

The rate constant was measured at four different temperature and the results are summarized in (**table-3**). Using Arrhenius equation the energy of activation for substrate has been calculated and this value subsequently utilized in computing various activation parameters. (**Table-4**)

Table-3 Effect of Temperature, on the reaction rate
NBA = 4.5×10^{-2} M; Mandelic Acid = 3.5×10^{-2} M; HClO_4 = 0.010 M;
 $[\text{Hg}(\text{AcO})_2]$ = 0.002M; Solvent; AcOH- H_2O = (v/v) 40%

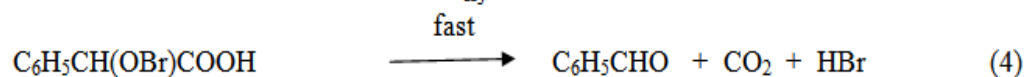
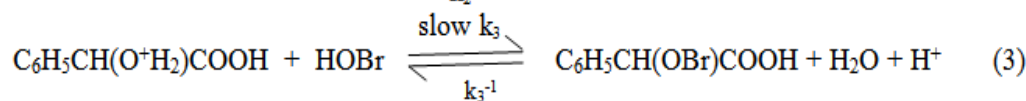
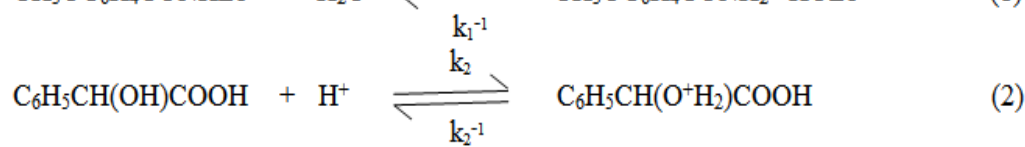
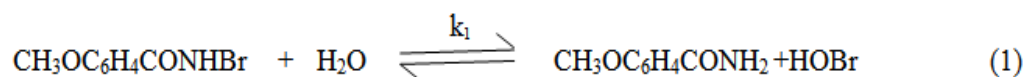
Temperature K	$k \times 10^{-3} \text{ min}^{-1}$
308	4.053
313	5.866
318	8.176
323	12.039

Table-4: Activation Parameters for the oxidation of mandelic acid
NBA = 4.5×10^{-2} M; Mandelic Acid = 3.5×10^{-2} M; HClO_4 = 0.010 M
 $[\text{Hg}(\text{AcO})_2]$ = 0.002M; Solvent; AcOH- H_2O = (v/v) 40%

Substrate	Ea (kJ mol ⁻¹)	ΔH* (kJ mol ⁻¹)	-ΔS* (J K ⁻¹ mol ⁻¹)	ΔG* (kJ mol ⁻¹)
Mandelic Acid	57.16	54.60	105.45	87.08

Reaction Mechanism

In view of these observations, a probable mechanism for the oxidation can be given as shown in scheme -1



Scheme-1

From the above mechanism, the following rate equation is derived.

$$k_{\text{obs}} = \frac{k_1 k_2 k_3 [\text{H}^+] [\text{Substrate}]}{[\text{Anisamide}][k_2^{-1} + k_3]}$$

Above rate equation is in good agreement with the experimental result.

Conclusion

Kinetic studies demonstrate that the complex between substrate and oxidant decompose to give product. The experimental stoichiometry is in good agreement first order to oxidant and fractional order to substrate at higher concentration is supported by derived rate equation.

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