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Oxidation of Phenylalanine using Rhodium (iii)-catalyst by bromate in acidic medium

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Abstract: The kinetics of the rhodium(III)-catalyzed oxidation of **phenylalanine** in an acidified $KBrO_3$ solution, utilizing $Hg(OAc)_2$ as a scavenger, were systematically investigated across a temperature range of 30–45 °C. The reaction demonstrated **first-order dependence** on Rh(III) concentration, confirming its pivotal catalytic role, while exhibiting first-**order kinetics** with respect to bromate, implying that bromate does directly influence the rate-determining step. The order of reaction with respect to each reactant was determined by varying the concentration of oxidant, substrate and Rh(III) .The reaction shows negligible effect of [Hg(OAc)2],[H+] and ionic strength of the medium. Chloride ion positively influenced the rate of reaction and mercuric acetate one by one in different sets keeping the concentration of all other reaction constant temperature 35^0C. A plausible **multi-step mechanism** was proposed, involving (i) the formation of a Rh(III)-phenylalanine coordination complex, (ii) its rate-limiting oxidation to generate reactive intermediates, and (iii) subsequent fast steps yielding final products. The derived **rate law**, consistent with experimental data, emphasized the dominance of the Rh(III)-phenylalanine interaction in controlling the reaction kinetics. **Thermodynamic parameters** (activation energy *Ea*, enthalpy Δ*H*, entropy Δ*S*) were calculated from Arrhenius and Eyring plots using rate constants at 30–45 °C, revealing insights into the energy barrier and transition state structure. The negative Δ*S* values suggested a **structured associative mechanism**, while Δ*H* highlighted the energy demands of bond reorganization. These findings collectively elucidate the intricate interplay of catalyst-substrate coordination, acid-base equilibria, and intermediate stability in governing the oxidation dynamics of phenylalanine under acidic conditions.

Keywords: bromate, catalysis, oxidation, rhodium (III), acidified potassium bromate.

Aims and Background:

Potassium bromate ($KBrO_3$) is a well-established oxidant in synthetic chemistry, extensively employed for the oxidation of diverse organic and inorganic substrates, including alcohols, amines, and amino acids (refs. 1–4). Despite its widespread use, studies probing its reactivity in **catalytic systems** remain sparse, with only limited reports on metal-catalyzed $KBrO_3$-mediated oxidations (refs. 5,6). Notably, the catalytic potential of **rhodium(III) chloride** [$RhCl_3$] in conjunction with $KBrO_3$ under acidic conditions has not been systematically explored, leaving a critical gap in understanding transition metal-catalyzed bromate redox chemistry. This knowledge deficit motivated the present investigation, which

focuses on the **oxidation of Phenylalanine** by acidified $KBrO_3$ using $RhCl_3$ as a catalyst and mercuric acetate [$Hg(OAc)_2$] as a bromide ion (Br^-) scavenger. The acidic medium was selected to stabilize Rh(III) species and enhance bromate's oxidative capacity, while $Hg(OAc)_2$ ensures the removal of Br^- a potential inhibitor—via precipitation as $HgBr_2$, preventing side reactions. By employing kinetic and mechanistic analyses, this study elucidates the interplay between Rh(III) catalysis, bromate activation, and substrate specificity in acidic environments. Furthermore, the choice of Phenylalanine, a biologically relevant α-amino acid, underscores the broader implications of this work in modeling redox processes in biochemical and industrial contexts. These aspects collectively address the unexplored synergies between Rh(III) and $KBrO_3$, offering insights into catalytic design for selective oxidation reactions.

Experimental:

Materials: Aqueous solutions of **Phenylalanine** (E. Merck, ≥99%, HPLC grade), **potassium bromate**(BDH, Analytical Reagent grade), **sodium perchlorate** ($NaClO_4$), and **mercuric acetate** [$Hg(OAc)_2$;] E. Merck, 98%] were prepared by dissolving precisely weighed quantities in **triply distilled water** to eliminate trace metal interference and ensure solution homogeneity. **$HClO_4$** (S.D. Fine Chemicals, 70%) was employed to adjust the acidity, providing a stable source of H^+ ions for maintaining the reaction's acidic medium. A **rhodium(III) chloride** [$RhCl_3$; Sigma Chemical Company, 99.9%] stock solution was prepared in **0.5 M HCl** to stabilize the Rh(III) ions as chlorido complexes and prevent hydrolysis. All reagents, unless specified, were of analytical grade and used without further purification. To suppress photochemical side reactions, particularly those involving light-sensitive bromate intermediates, all reaction vessels were **coated with black epoxy paint** and stored in dark conditions prior to use. Additionally, solutions were thermally equilibrated at the desired temperature (±0.1°C) using a calibrated thermostatic water bath to ensure kinetic consistency. The exclusion of ambient light, coupled with rigorous control of ionic strength and acidity, minimized experimental artifacts and enhanced reproducibility. This meticulous protocol highlights the precision required to investigate the catalytic role of Rh(III) in bromate-driven oxidations under controlled acidic conditions.

Kinetics: The requisite volumes of all reagents, including the phenylalanine substrate, were pre-equilibrated in a **calibrated thermostatic water bath** at 35 ± 0.1 °C for 15 minutes to ensure thermal equilibrium. A measured volume of preheated $KBrO_3$ solution, maintained at identical conditions, was rapidly transferred into the reaction vessel under **constant mechanical stirring** to ensure instantaneous mixing and minimize temperature fluctuations. The reaction progress was monitored by withdrawing **1.0 mL aliquots** at predetermined time intervals, which were immediately quenched in an ice-cold solution of excess KI (0.1 M) to arrest further oxidation. The liberated iodine (I_2) from unreacted bromate was titrated **iodometrically** against standardized sodium thiosulfate ($Na_2S_2O_3$, 0.01 M) using starch as a sharp endpoint indicator (blue → colourless). To ensure accuracy, each aliquot was analyzed in triplicate, and the residual bromate concentration was calculated from the mean titre values. This approach allowed precise tracking of bromate consumption over time, enabling the determination of reaction rates under controlled kinetic conditions.

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Results and Discussion: The stoichiometry of the reaction was determined by equilibrating reaction mixtures containing a **large excess of $KBrO_3$** over phenylalanine (in varying molar ratios) at 50 °C for 48 h under inert conditions to prevent aerial oxidation. Residual bromate analysis via iodometric titration revealed a **1:1 molar consumption ratio,** where 1 mole of phenylalanine quantitatively reduced 1 mole of bromate, consistent with a two-electron transfer process. Product isolation and characterization by **FTIR and 2,4-dinitrophenylhydrazine (DNPH) derivatization** confirmed the formation of **phenyl acetaldehyde** as the primary oxidation product, aligning with oxidative deamination of the α-amino group. Control experiments with omitted substrate or catalyst showed no significant bromate depletion, validating the role of phenylalanine as the reactive species. The overall reaction (Eq. 1) summarizes the stoichiometric conversion, highlighting the cleavage of the C–N bond in phenylalanine to yield the aldehyde, CO_2, and NH_4^+ as byproducts. This stoichiometric consistency, coupled with product identification, provides critical insight into the redox pathway and mechanistic intermediates involved in the Rh(III)-catalyzed system.

Kinetics of Rh(III) catalyzed oxidation of L-Phenylalanine and Bromate in acidic medium was investigated at 35ºC. The kinetic results were collected at several initial concentrations (Table 1 and 2). The order of reaction with respect to each reactant was determined by varying the concentration of oxidant, substrate, Rh(III) chloride, H+ ions, [Cl^-] and mercuric acetate one by one in different sets keeping concentration of all other reactants constant at constant temperature 35ºC. In each kinetic runs, the initial rate (i.e.,–dc/dt) of the reaction was determined from the slope of the tangent drawn at a fixed concentration of Bromate except for the Bromate variation in which the slope of the tangent was drawn at fixed time. The first order reaction rate constant (k1) for the variation of all the reagents were calculated:

$$k_1 = \frac{-dc/dt}{[BrO_3^-]^*}$$

Where, $[BrO_3^-]^*$ denotes the $[BrO_3^-]$ at which (-dc/dt) was determined.

Phenylalnine + BrO_3^- + H^+ → **phenyl acetaldehyde** + NH_3 ↑ + CO_2 ↑ + $2BrO_2^-$ **phenyl acetaldehyde** (1)

The kinetics of phenylalanine oxidation by acidified $KBrO_3$ catalyzed by Rh(III) were systematically investigated under varying initial concentrations of reactants (Table 1). The rate of reaction (–dc/dt) exhibited a **first-order dependence** on phenylalanine concentration, with (–dc/dt) increasing linearly as [substrate] increased, The Experimental results show first order Kinetics with respect to oxidant (Bromate) and cata rhodium is also first order while positive effect with respect to substrate that is i.e. L-Phenylalanine was observed. The reaction rate, however, displayed a **linear correlation** with [Rh(III)] underscoring the catalytic function of Rh^{3+} ions, which likely coordinate with phenylalanine to form an active intermediate. Temperature-dependent studies (30–45°C) revealed a linear Arrhenius relationship between lg(–dc/dt) and 1/T (Fig. 2), enabling calculation of activation parameters (E_a, ΔH‡, ΔS‡). The reactive Rh(III) species in acidic media was identified as **Rh^{3+} aqua-chloro complexes,** stabilized by Cl^- ligands from $RhCl_3$, which facilitate substrate binding

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and electron transfer. Mechanistically, the reaction is proposed to proceed via (i) rapid pre-equilibrium formation of a Rh(III)-phenylalanine coordination complex, (ii) rate-limiting intramolecular electron transfer from the amino acid to Rh(III), generating a radical intermediate, and (iii) subsequent fast oxidation steps involving bromate to yield phenyl acetaldehyde as the final product. The insensitivity to ionic strength aligns with an inner-sphere electron transfer mechanism, where charge stabilization occurs within the coordination sphere of Rh(III). These findings collectively establish a robust kinetic framework for Rh(III)-catalyzed bromate oxidations, emphasizing the interplay of substrate coordination, acid-base equilibria, and catalyst speciation in governing reaction dynamics.

Table 1: Effect of variation of HClO4, [Hg $(OAc)_2$], KCl at 35 ^{0}C

$HClO_4$ x 10^3M	**KCl x 10^3M**	**[Hg $(OAc)_2$] x 10^3M**	**(dc/dt) x 10^7 [$ML^{-1}S^{-1}$]**
0.83	1.00	1.25	1.62
1.00	1.00	1.25	1.85
1.33	1.00	1.25	1.61
1.66	1.00	1.25	1.83
4.00	1.00	1.25	1.72
8.00	1.00	1.25	1.91
1.00	0.83	1.25	2.31
1.00	1.00	1.25	2.63
1.00	1.25	1.25	3.41
1.00	1.66	1.25	3.68
1.00	2.50	1.25	3.90
1.00	5.00	1.25	4.33
1.00	1.00	1.00	1.73
1.00	1.00	1.33	2.15
1.00	1.00	1.66	2.41
1.00	1.00	2.5	1.88
1.00	1.00	4.00	1.73
1.00	1.00	5.00	1.65

Table 2: Effect of variation of oxidant, Phenylalanine, Rh (III) at 35 ^{0}C

[Oxidant] x 10^3M	**[Substrate] x 10^3M**	**Rh (III) x (11.25 x 10^{-5}M**	**(dc/dt) x 10^7 [$ML^{-1}S^{-1}$]**	
0.83	1.00	11.25	1.72	
1.00	1.00	11.25	2.35	
1.35	1.00	11.25	3.15	
1.66	1.00	11.25	3.55	
2.5	1.00	11.25	6.10	
5.00	1.00	11.25	11.82	
1.00	0.83	11.25	1.63	
1.00	1.25	11.25	2.54	
1.00	2.50	11.25	2.81	
1.00	4.00	11.25	3.20	

1.00	5.00	11.25	3.63	
1.00	8.00	11.25	3.98	
1.00	1.00	5.62	1.42	
1.00	1.00	11.25	1.84	
1.00	1.00	16.87	2.33	
1.00	1.00	22.50	3.20	
1.00	1.00	28.12	3.64	
1.00	1.00	33.74	4.35	

Table 3: activation parameter for the oxidation of Phenylalanine

Parameter	Temperature	Phenylalanine
$K1x10^{4}s^{-1}$	30	2.30
$K1x10^{4}s^{-1}$	35	3.21
$K1x10^{4}s^{-1}$	40	4.25
$K1x10^{4}s^{-1}$	45	6.67
log*A* ($KJmol^{-1}$)	-	11.12 $KJmol^{-1}$
ΔE^{*} ($KJmol^{-1}$)	35	63.13 $KJmol^{-1}$
ΔG^{*} ($KJmol^{-1}$)	35	72.45 $KJmol^{-1}$
ΔH^{*} ($KJmol^{-1}$)	35	57.31 $KJmol^{-1}$
ΔS^{*} ($KJmol^{-1}$)	35	-41.12 $KJmol^{-1}$

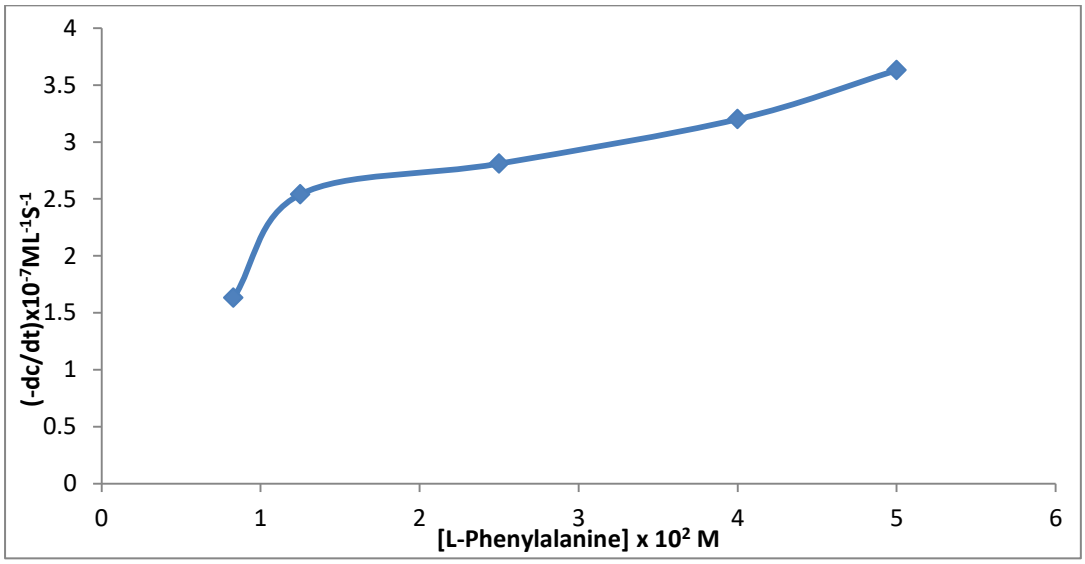

Fig.1 Plot between (-dc/dt) and Phenylalanine for the oxidation of Phenylalanine at 35 ^{o}C [Phenylalanine]= $2x10^{3}$M, [Rhodium]= $11.25x10^{-5}$M $[HClO_4]$ = $1.00x10^{3}$M [Hg(OAc)2]$1.25x10^{3}$M.

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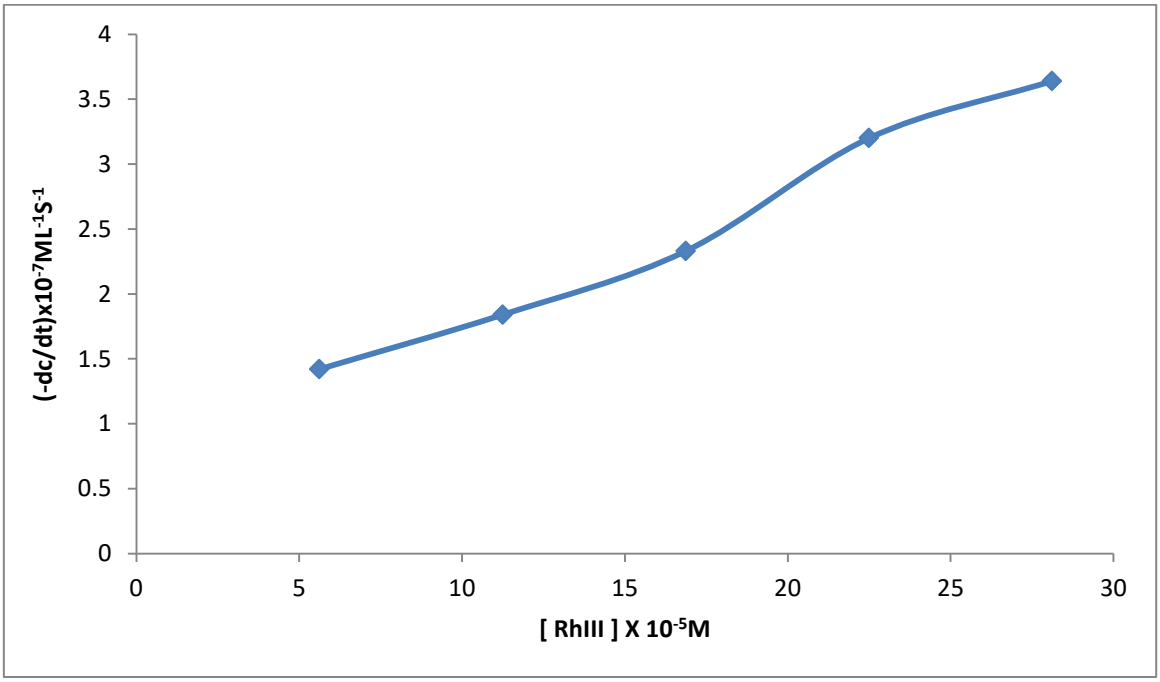

Fig.2 Plot between (-dc/dt) and Rhodium for the oxidation of Phenylalanine at 35 ^{o}C [Phenylalanine]= 2x10^{3}M, [Rhodium]= 11.25x10^{-5}M [$HClO_4$] = 1.00x10^{3}M.

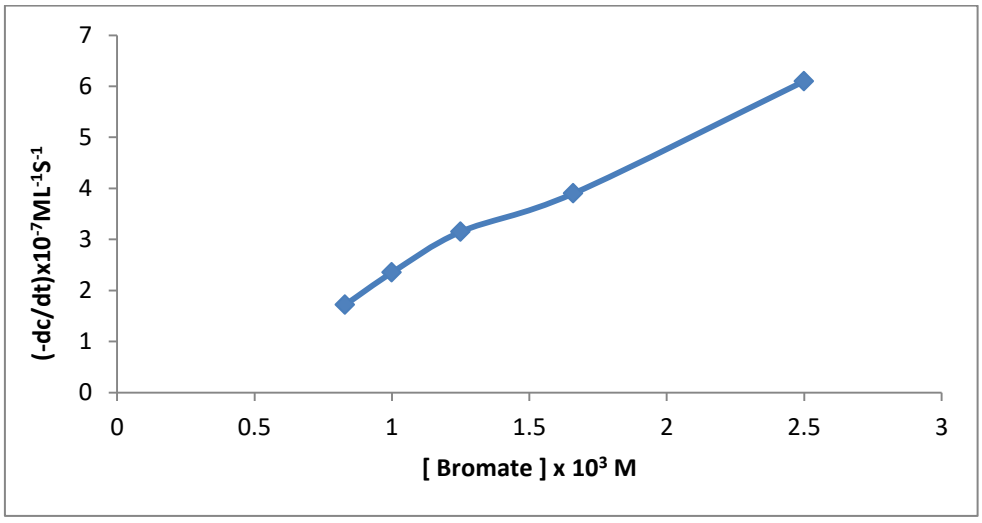

Fig.3 Plot between (-dc/dt) and Bromate for the oxidation of Phenylalanine at 35 ^{o}C [Phenylalanine]= 2x10^{3}M, [Rhodium]= 11.25x10^{-5}M [$HClO_4$] = 1.00x10^{3}M [Hg(OAc)2]1.25x10^{3}M.

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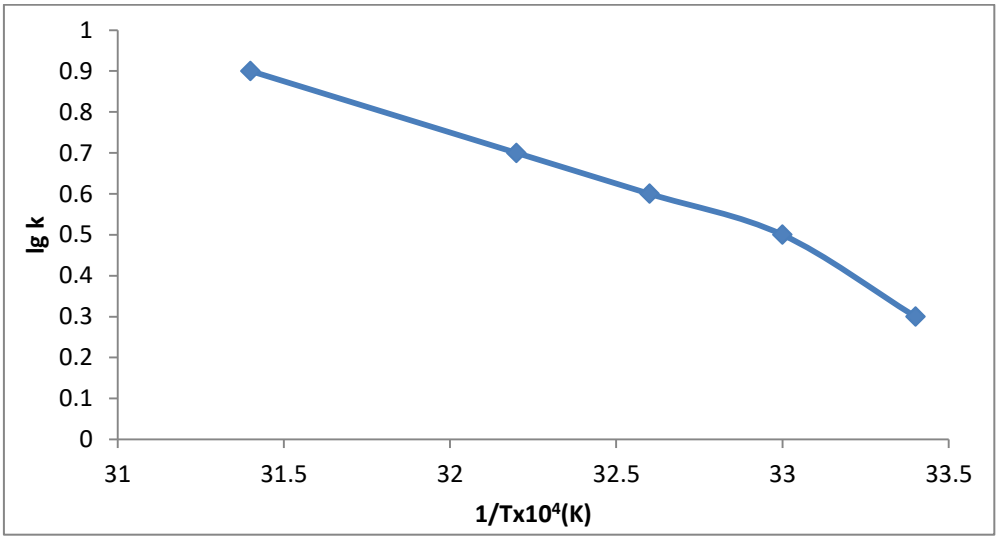

Fig.4 Plot between lg k and 1/T for the oxidation of Phenylalanine, [$KBrO_3$] = $1.00x10^3$M, [Hg(OAc)2]$1.25x10^3$M, [KCl] = $1.00x10^3$M, [Phenylalanine] = $2.00x10^3$M, [Rh(III)] = $11.25x10^{-5}$M, [$HClO_4$] = $1.00x10^3$M.

Moderate ΔH* and ΔS* values are favourable for electron transfer reaction. The value of ΔH* was due to energy of solution changes in transition state. The high positive value of ΔG* represents highly solvated transition state. The negative value of ΔS* indicates that the intermediate complex is more ordered than the reactants so the formation of activated complex occurs with reduction in the degree of freedom. The observed modest enthalpy of activation and higher rate constant for the slow step shows that oxidation presumably occurs by means of an inner sphere mechanism.This conclusion is supported by earlier observations. The activation parameters evaluated for the catalyzed reaction explain the catalytic effect on the reaction. Kinetic observations show that the reaction under investigation is complex reaction, which usually takes place in more than one step.

Mechanism and derivation of rate law: In acidic solution Rhodium chloride exists as [RhCI6]3-. It has also been reported that [RhCI6]3- is involved in equilibrium as follows:

$$[RhCI6]^{3-} + H2O \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} [RhCI5(H2O)]^{2-} + CI^-$$

Thus either $[RhCI6]^{3-}$ or $[RhCI5(H2O)]^{2-}$ may act as catalytic species. If $[RhCI5(H2O)]^{2-}$ is taken as catalytic species the rate law would require negative effect of chloride ion contrary to the positive effect of chloride ion on the oxidation rate observed by us. Hence the only choice is $[RhCI6]^{3-}$ which when assumed as reactive species of Rhidium trichloride in acidic medium, explains the positive effect of chloride ion. The kinetic results reported in table 1, 2, 3 along with the above discussion lead us to suggest the following reaction scheme:

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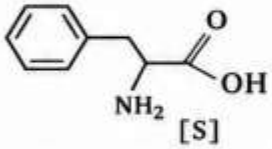
$$[RhCl_6]^{3-} + H_2O \rightleftharpoons [RhCl_5(H_2O)]^{2-} + Cl^-$$

$$\underset{C_1}{[RhCl_5(H_2O)]^{2-}} + Cl^- \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} \underset{C_2}{[RhCl_6]^{3-}} + H_2O$$

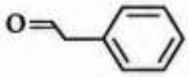


[S]

$$+ [RhCl_6]^{3-} \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} [S\text{------}RhCl_6]^{3-}$$

$$\underset{C_3}{[S\text{-----}RhCl_6]^{3-}} + BrO_3^- \xrightarrow[\text{slow step (r.d.s.)}]{K_3} [S\text{-----}RhCl_6\text{----}BrO_3]^{4-}$$

$$[S\text{-----}RhCl_6\text{----}BrO_3]^{4-} + H_2O \xrightarrow{\text{Fast}}$$



[P]

$$+ [RhCl_6]^{3-} + CO_2 + NH_3 + BrO_2^-$$

Apply S.S.A

$$\text{Rate} = \frac{-d[BrO_3^-]}{dt} = K_3[C_3][BrO_3^-] \quad \text{——} \ (1)$$

$$[Rh(III)]_T = [C_1] + [C_2] + [C_3] \quad \text{——} \ (2)$$

$$\frac{d[C_1]}{dt} = K_{-1}[C_2] - K_1[C_1][Cl^-] \quad \text{——} \ (3)$$

$$[C_1] = \frac{K_{-1}[C_2]}{K_1[Cl^-]} \quad \text{——} \ (4)$$

$$[C_3] = \frac{[C_2]}{K_1[Cl^-]} \quad \text{——} \ (5)$$

$$\text{where } K_1 = \frac{K_1}{K_{-1}}$$

In same way–

$$\frac{d[C_2]}{dt} = K_{-2}[C_3] - K_2[Cl^-][C_2]$$

$$[C_2] = \frac{K_{-2}[C_3]}{K_2[Cl^-]}$$

$$[C_3] = \frac{[C_2]}{K_1[Cl^-]} \quad \text{——} \ (6)$$

$$\text{where } K_2 = \frac{K_2}{K_{-2}}$$

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Putting the value of c_2 in equation (v), we get –

$$[c_1] = \frac{[c_3]}{K_1 K_2 [S][Cl^-]}$$

$$[Rh(III)]_T = [c_1] + [c_2] + [c_3]$$

$$[c_3] = \frac{[c_3]}{K_1 K_2 [S][Cl^-]} + \frac{[c_3]}{K_2 [S]} + c_3$$

$$[c_3] = \left[\frac{1}{K_1 K_2 [S][Cl^-]} + \frac{1}{K_2 [S]} + 1 \right] c_3$$

$$[c_3] = \left[\frac{1 + K_1 [Cl^-] + K_1 K_2 [S][Cl^-]}{K_1 K_2 [S][Cl^-]} \right] c_3$$

This gives

$$[c_3] = \left[\frac{[Rh(III)]_T \; K_1 K_2 [S][Cl^-]}{K_1 K_2 [S][Cl^-] + 1 + K_1 [Cl^-]} \right]$$

or

$$[c_3] = \left[\frac{[Rh(III)]_T \; K_1 K_2 [S][Cl^-]}{1 + K_1 [Cl^-] + K_1 K_2 [S][Cl^-]} \right]$$

Putting the value of c_3 in eq^n ① we get –

$$Rate = \frac{K_1 K_2 K_3 [Rh(III)]_T [S][Cl^-][BrO_3^-]}{1 + K_1 [Cl^-] + K_1 K_2 [S][Cl^-]} \quad \text{——— (VI)}$$

Table 2. Activation parameters for acidic bromate oxidation of Phenylalanine

Temperature (^{0}C)	Rate constant k x 10^4 (s^{-1})
30	0.81
34	1.30
40	1.62
45	2.31
The Arrhenius parameter (at 35 ^{0}C)	valueΔ
ΔE^*	46.03
lg A	9.32
ΔS	-28.35
ΔG	71.63
ΔH	62.71

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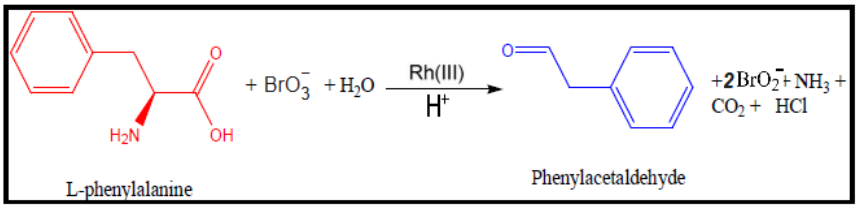
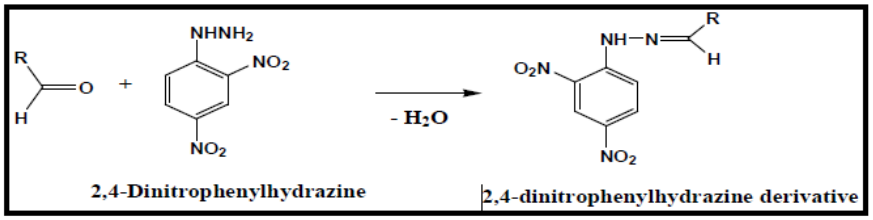
Stoichiometry and product analysis: In order to ascertain the stoichiometry of the reactions, different sets of experiments with varying [RNHCl]: [L-Phenylalanine] ratios were performed at 35ºC for 48 h and constant concentrations of all other reactants under the conditions [RNHCl] >>[LPhenylalanine]. Iodometric estimation of unconsumed [RNHCl] in different sets shows that 1 mole of RNHCl was consumed to oxidize 1 mole of L-Phenylalanine. Accordingly, the following stoichiometric equations can be formulated.



Stoichiometric equation

Phenyl acetaldehyde the main product in the oxidation of L-Phenylalanine was identified by the help of chromatography (TLC), conventional (spot test) method and also through 2,4-dinitrophenyl hydrazine (DNPH) derivative (Brady's test)(scheme 1). The functional group –CHO was also confirmed by Tollen's reagent and Schiff's base. The nature of phenyl acetaldehyde further confirmed by its IR spectrum (2920 cm^{-1} due to C-H (sp^3), 3030 cm^{-1}C-H(aromatic) stretching, 1498, 1602 cm^{-1} due to aromatic C=C stretching, 1724 cm^{-1} due to C=O stretching and 1454 cm^{-1} due to C-H bending) (Fig. 1). Similarly, ammonia was identified by Nessler's reagent and CO_2 was qualitatively detected by bubbling nitrogen gas through the acidified reaction mixture and passing the liberated gas through tube containing lime water.



Scheme 1: Preparation of 2, 4-dinitrophenyl hydrazine derivative.

Applications: In this study to improve the synthesis of 2-phenylacetaldehyde as an oxidized compound and furthermore applied the synthesis of Schiff base 2,4-dinitrophenyl hydrazine. This study also useful for the optimum of time, conversion of desired product, determination of yield and all operation of parameter for production of large scale synthesis of aldehyde. Schiff base is beneficial for human health, synthesis of chelating agents and organic synthesis.

Conclusions: The experimental results demonstrate a **direct proportionality** between the reaction rate and [Rh(III)], with the rate doubling when the catalyst concentration is doubled, confirming **first-order dependence** on Rh(III) and its pivotal role in the catalytic cycle. The derived rate law, aligns with all kinetic observations, including first-order dependence on

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bromate, negative acid effect, and insensitivity to ionic strength. The negligible influence of ionic strength strongly supports an **inner-sphere electron transfer mechanism,** where interactions between Rh(III) and the substrate occur within the coordination sphere, bypassing electrostatic effects typical of outer-sphere pathways. The high positive **Gibbs free energy of activation (Δ*G*)** reflects a significant energy barrier, indicative of a **highly solvated transition state** requiring extensive reorganization of solvent molecules during the rate-determining step. Concurrently, the **large negative entropy of activation (Δ*S*)** suggests a structured, associative transition state with reduced degrees of freedom, likely arising from the ordered binding of phenylalanine to Rh(III) and the formation of a rigid intermediate complex. Spectroscopic and potentiometric studies confirm that BrO_3^- and Rh^{3+} are the **reactive species** in acidic media, with $RhCl^{3-}$ (from $RhCl_3$ dissociation in HCl) acting as the catalytically active chlorido-aqua complex. The acidic medium stabilizes BrO_3^- as the dominant oxidant while suppressing Rh(III) hydrolysis, ensuring its availability for substrate coordination. Mechanistically, the reaction proceeds via (i) rapid coordination of phenylalanine's amino group to Rh^{3+}, forming a chelated intermediate, (ii) rate-limiting intramolecular electron transfer from the substrate to Rh(III), generating a Rh(II)-radical species, and (iii) fast regeneration of Rh(III) via bromate-mediated oxidation, completing the catalytic cycle. The absence of Br_2 interference, ensured by $Hg(OAc)_2$ scavenging Br^-, validates the selectivity of the Rh(III)-bromate system. These findings highlight the synergy between Rh(III)'s redox versatility and bromate's stoichiometric oxidative capacity, offering a template for designing efficient catalytic systems for amino acid oxidation. The thermodynamic and kinetic consistency of the model underscores its robustness in predicting reaction behavior under varied conditions, with implications for both synthetic chemistry and biochemical redox processes.

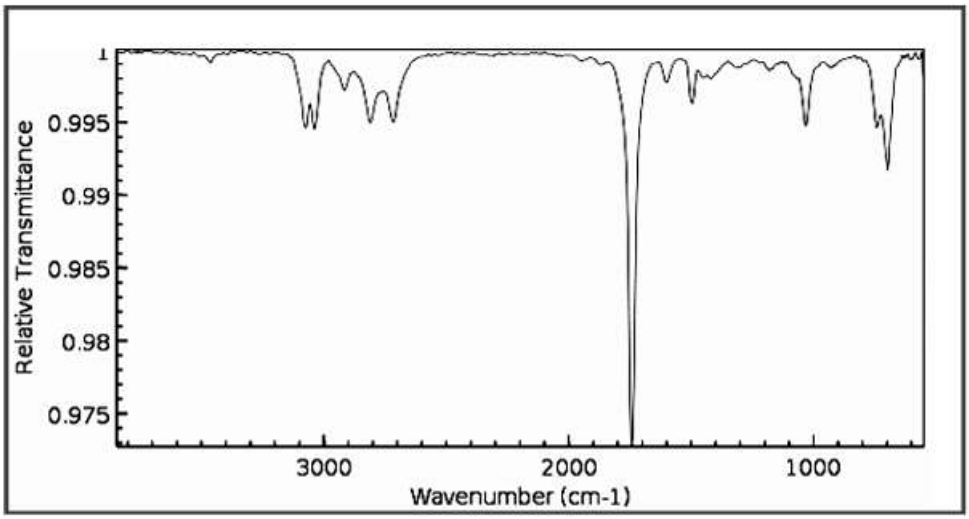

Figure 1. IR spectrum of the main product Phenyl acetaldehyde.

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