



REDUCTION OF THE GOLD(III) COMPLEX ION, $[\text{AuCl}_3(\text{OH})]^-$, BY ETHANOL IN AQUEOUS ACID: KINETIC, THERMODYNAMIC AND MECHANISTIC STUDIES



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Abstract: Kinetic, thermodynamic and mechanistic studies of the reduction of gold(III) complex ion, $[\text{AuCl}_3(\text{OH})]^-$, by ethanol (EtOH) was studied spectrophotometrically in perchloric acid medium at ionic strength (μ) = 0.05 mol dm⁻³ (NaClO₄) and T = 30.0 ± 1 °C. Stoichiometric result of the reaction revealed that one mole of the oxidant, $[\text{AuCl}_3(\text{OH})]^-$, was reduced by one mole of the reductant, ethanol. The rate of reaction was first order in $[\text{AuCl}_3(\text{OH})]^-$ as well as in $[\text{C}_2\text{H}_5\text{OH}]$ with a second order overall. Varying concentration of acid within the range 5.0 x 10⁻⁴ to 1.4 x 10⁻² mol dm⁻³ decreased the rate of the reaction. Increasing μ from 2.0 x 10⁻² to 1.2 x 10⁻¹ mol dm⁻³ (NaClO₄) had no noticeable effect on the rate of the reaction. The same trend was observed on varying dielectric constant from 78.40 to 73.59. Michaelis – Menten's type plot of k_{obs}^{-1} against $[\text{C}_2\text{H}_5\text{OH}]^{-1}$ was linear with negligible intercept. Entropy of activation was found to be -175.74 JK⁻¹mol⁻¹ while activation enthalpy was found to be 13.010 kJ mol⁻¹. Au^I was the product of $[\text{AuCl}_3(\text{OH})]^-$ reduction while aldehyde was obtained for EtOH oxidation. FTIR spectrum showed band for $\nu(\text{C}=\text{O})$ at 1762 cm⁻¹ for aldehyde formation. Based on negligible intercept from Michaelis – Menten's type plot and the absence of spectroscopically determinable intermediate complex, the reaction was proposed to have proceeded through the outer-sphere mechanistic pathway.

Key words: Ethanol, Gold(III) complex ion, Mechanism, Kinetics, Thermodynamics

Introduction

In bioinorganic chemistry and molecular biology where researchers examine the roles of metal complexes as metalloproteins, electron transfer reactions of metal ions and their complexes, particularly those of transition metals, are essential chemical processes (Ayalew and Jeevan, 2022). In industries, these metal complexes are utilised as homogeneous catalysts and in chemistry for chelate therapy (Sodhi and Paul, 2019). The use of metal-based pharmaceuticals for therapeutic purposes and the development of novel metal-based anti-tumor agents with pharmacological activities that differ markedly from those of platinum-based anti-tumor agents are among the many areas of current research and interest for bioinorganic and medicinal chemists (Zouet *et al.*, 2015). Gold complexes have been identified as an important class of non-platinum compounds which restrains cell growth. Oftentimes, the anti-mitochondrial properties of the gold complexes make them intriguing medications since they impede cell proliferation. The most impressive use of gold complexes is in chemotherapy for tumours (Mjos and Orvig, 2014). Allocrysin, myocrysin, solganol and auranofin all include significant amounts of gold(I) thiolates, such as aurothiomalate, aurothioglucose, and aurothiopropionatesulphonate, these are all gold(I) drugs currently used in medicine. Apart from its antiarthritic properties, aurothiomalate has been shown to have anti-leishmanial activity in hamsters (Sabine and Sadler, 1996). Organometallic complexes of gold(III) have also been applied in catalysis, medicinal inorganic, chemistry material science and in the development of probes (Messina *et al.*, 2018). A dimethyl Au(III) complex was reported in early 1980s which displayed modest *in vivo* anti-cancer activities on mice bearing P388 leukemia (Dasari and Tchounwou, 2014). This report subsequently triggered the

anti-cancer studies of various Au(III) complexes containing monodentate or bidentate ligand(s). For these purposes, numerous Au(III) complexes with profoundly different molecular structures, have been designed, synthesised and tested as antiproliferative agents (Muggia *et al.*, 2015). Furthermore, under physiological conditions, gold(I) medications may be converted *in vivo* into gold(III) metabolites. However, the fundamental mechanisms driving these physiological changes are still not fully understood. The usage of gold(III)-based pharmaceuticals has been limited due to lack of kinetic and mechanistic data.

Materials and Methods

Analytical grade compounds were utilised as purchased without additional purification. The oxidising agent was hydrogen tetrachloroaurate(III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) [Sigma–Aldrich, 99 %], the reducing agent was ethanol [BDH, 99.5%], hydrogen tetraoxochlorate(VII) (HClO_4) [Sigma–Aldrich, 70 %] was used to maintain $[\text{H}^+]$, and the ionic strength was maintained by NaClO₄ [Sigma–Aldrich, 98%]. The use of prop-2-enamide ($\text{C}_3\text{H}_5\text{NO}$) allowed for the detection of free radicals in the course of the reaction. In doubly distilled deionised water, solutions were made by dissolving 0.1969 g of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ to make 1.0 x 10⁻³ mol dm⁻³, 0.1 mol dm⁻³ was made with 0.58 cm³ of EtOH, 0.5 mol dm⁻³ of HClO_4 was made with 2.03 cm³ while 0.2 mol dm⁻³ of NaClO₄ was prepared with 7.025 g of the salt.

Stoichiometry

Utilising the mole ratio method (Ukoha *et al.*, 2018), spectrophotometric titrations were used to determine the stoichiometry under the following conditions: $[\text{H}^+] = 1.0 \times 10^{-3}$ mol dm⁻³, $\mu = 0.02$ mol dm⁻³ (NaClO₄), $[\text{AuCl}_3(\text{OH})]^- = 1 \times 10^{-4}$ mol dm⁻³, $[\text{C}_2\text{H}_5\text{OH}] = (2.5 \times 10^{-5} \text{ to } 2.5 \times 10^{-4})$ mol dm⁻³, temperature (T) = 30.0 ± 1.0 °C, and $\lambda_{\text{max}} = 310$

nm. The stoichiometry was ascertained by plotting absorbance against the mole ratio of the reactants where point of inflexion gave stoichiometry of the reaction.

Kinetic study

JENWAY 6405 UV-Vis spectrophotometer was used to perform all kinetic experiments under pseudo-first-order conditions, with [C₂H₅OH] present in at least 20 folds excess over that of [AuCl₃(OH)]⁻ at T= 30.0 ± 1.0 °C, [H⁺] = 1.0 × 10⁻³ mol dm⁻³, and 0.05 mol dm⁻³ (NaClO₄) ionic strength. After the reaction was completed, the absorbance of [AuCl₃(OH)]⁻ was measured at 310 nm as a function of time to ensure that no other reagents were interfering. Under these conditions, the kinetic curves were exponential, and the rate constants were determined by plotting log (A_t - A_∞) versus time and using the equation: ln(A_t-A_∞)=ln(A₀-A_∞)-k_{obs} t, where A_t is the absorbance at time t, A_∞ is the absorbance at infinity, A₀ is the initial absorbance, and k_{obs} is the pseudo-first order rate constant. The ratio of k_{obs}: [C₂H₅OH] was used to determine second order rate constants, k₂ (Ukoha *et al.*, 2023). Under the same reaction conditions, the effects of [H⁺] = (5.0 × 10⁻⁴ to 1.2 × 10⁻²) mol dm⁻³ and μ = (2.0 × 10⁻² to 1.2 × 10⁻¹) mol dm⁻³ on the reaction's rate were determined.

Effect of dielectric constant on rate of reaction

By adjusting the acetone to water ratio (Equation 1) the dielectric constant of the medium was determined

$$D_{\text{reaction medium}} = \frac{(D_{\text{water}} \times V_{\text{water}}) + (D_{\text{acetone}} \times V_{\text{acetone}})}{V_{\text{total}}} \quad (1)$$

where: D_{water}, D_{acetone} are dielectric constants of water and acetone respectively, V_{water} and V_{acetone} are volumes of water and acetone respectively, V_{total} is the total volume of water when V_{acetone} = zero

Effect of added anions on the rate of reaction

The effect of added anions on the rate of the reaction was investigated by adding various amounts of CH₃COONa and NaNO₃ within the range 2.0 × 10⁻³- 1.4 × 10⁻² mol dm⁻³ with constant concentrations of the oxidant, reductant, ionic strength as well as temperature constant (Ukoha *et al.*, 2018). Dependence of rate on the ions is evaluated as plots of second order rate constant, k₂, against the concentrations of the added ions.

Test for free radical

The partially reduced reaction mixture containing different amounts of oxidant, ethanol, and hydrogen ions for the system was mixed with exactly 2 g of acrylamide and allowed to stand for approximately 2 minutes. Afterwards, a significant excess of methanol was added. To act as control, two grams of acrylamide and an excess of methanol were added to solutions of C₂H₅OH and [AuCl₃(OH)]⁻ separately. According to Ukoha *et*

al. (2015) and Abiti *et al.* (2018), the lack of gel formation was an indication that no free radical was generated during the reaction.

Temperature dependence study

A thermostatic water bath was used to regulate the temperature between 308 and 318 K while keeping [AuCl₃(OH)]⁻, [C₂H₅OH], [H⁺] and μ constant. After reaching the correct temperature, the reagents were rapidly combined while the reaction was being monitored. At the end of the reaction, the temperature of the reaction product was measured to make sure there had been no appreciable drop in the starting temperature. The linear form of the Eyring-Polanyi equation, (Equation 2) was used to plot ln(k/T) against 1/T from where activation entropy and enthalpy were determined.

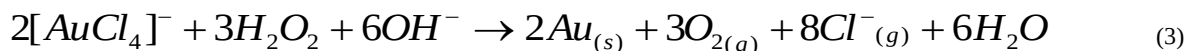
$$\ln \frac{k}{T} = 23.759 + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{R} \cdot \frac{1}{T} \quad (2)$$

Test for the formation of intermediate complex

Test for the presence of stable, detectable intermediate complex formed in the course of the reaction was carried out by recording the electronic spectrum of partially reacted reaction mixture at various time intervals depending on the speed of the reaction to determine whether there is significant shift in λ_{max} and/ or enhancement of peak. The identification or non-identification of intercept in the Michaelis-Menten's type plot of k_{obs}⁻¹ versus [reductant]⁻¹ would give an idea of the presence or absence of intermediate complex formation (Ukoha *et al.*, 2018).

Product analysis

By mixing 2 cm³ of the reaction mixture with 3 cm³ of 2, 4-dinitrophenylhydrazine solution, the presence of aldehyde was determined. The presence of aldehyde was revealed by the formation of a yellowish precipitate. Fehling's solutions were also used in a confirmatory test; about 1.0 cm³ of Fehling's solution A was mixed with an equal volume of Fehling's solution B until precipitation occurred. Drop by drop, exactly 3.0 cm³ of Fehling's solution B was added until the precipitate disappeared. After adding and boiling 3.0 cm³ of the liquid product, the presence of aldehyde as the oxidation product of ethanol was indicated by a brick-red color. With slight modifications, Vogel's (1979) qualitative test was used to confirm that Au(III) ion was absent and that its reduction had occurred. The gold(III) complex ion was reacted with excess EtOH, and the reaction allowed to go to completion. A 2.0 cm³ portion of the reaction mixture was thereafter reacted with alkaline solution of hydrogen peroxide (Equation 3). Lack of precipitate confirmed the absence of Au(III) ion.



Results and Discussion

Stoichiometry

Spectrophotometric titration of the reaction using the mole ratio method revealed that one mole of the oxidant, $[\text{AuCl}_3(\text{OH})]^-$, was reduced by one mole of the reductant, ethanol (Fig. 1). This result agrees with the stoichiometry in (Equation 4). The gold(III) complex ion was reduced to gold(I) while ethanol was oxidised to ethanal. Ukoha and Iorungwa (2023) reported earlier, the oxidation of methanol to methanal. The organic product in the reaction was extracted with diethylether and the FTIR spectrum obtained. Fig. 2 show $\nu(\text{C}=\text{O})$ band at 1762 cm^{-1} , suggesting strongly the formation of ethanal.

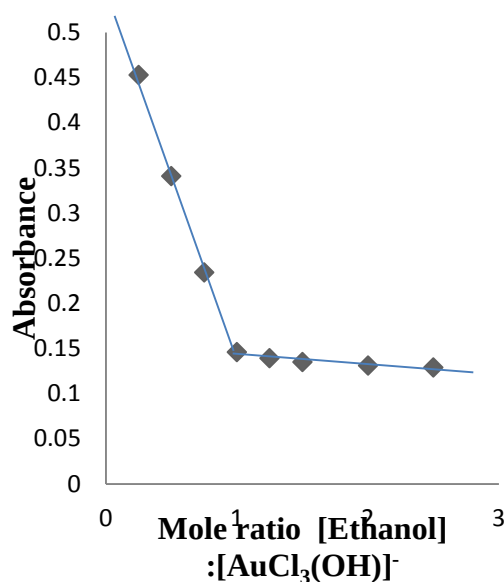


Fig. 1: Mole ratio plot for the reduction $[\text{AuCl}_3(\text{OH})]^-$ by $\text{C}_2\text{H}_5\text{OH}$

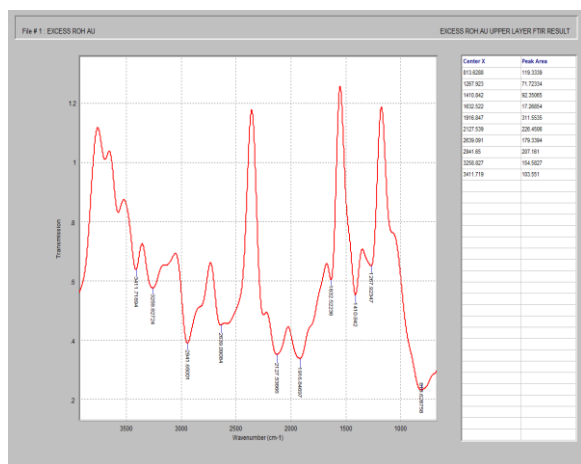
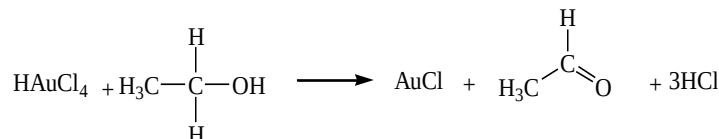


Fig. 2: FTIR spectrum of ethanal from ethanol oxidation



Kinetic study

Under pseudo-first order conditions, plot of $\log (A_t - A_\infty)$ versus time was linear for over 85 % extent of reaction. Linearity of the plot suggests a first order dependence of rate on the $[\text{AuCl}_3(\text{OH})]^-$. Pseudo-first order rate constants, k_{obs} are in (Table 1) which increased upon variation in $[\text{C}_2\text{H}_5\text{OH}]$. Plot of $\log k_{\text{obs}}$ versus $\log [\text{C}_2\text{H}_5\text{OH}]$ was linear with a slope 1.002 (Fig.3), suggesting a first order with respect to $[\text{C}_2\text{H}_5\text{OH}]$ and a second order overall. Second order kinetics had been documented for the reduction of gold(III) ions with hydroxylamine (Soni and Mehrotra, 2003), oxalic acid (Shen *et al.*, 2010) and methanol (Ukoha and Iorungwa, 2023).

From the ratio of k_{obs} : $[\text{C}_2\text{H}_5\text{OH}]$, second order rate constants, k_2 were obtained (Table 1). The rate equation for this system can be written (Equation 5).

$$\frac{-d[\text{AuCl}_3(\text{OH})^-]}{dt} = k_2 [\text{AuCl}_3(\text{OH})^-] [\text{C}_2\text{H}_5\text{OH}] \quad (5)$$

k_2 were fairly constant with mean value of $0.893 \pm 0.024\text{ dm}^3\text{ mol}^{-1}\text{ s}^{-1}$.

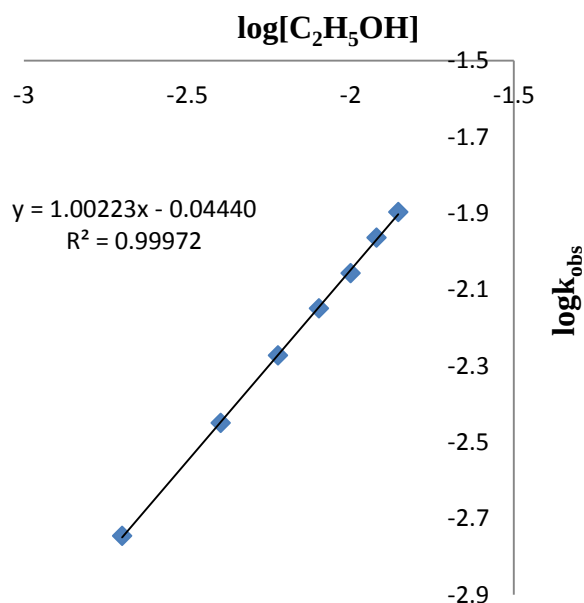


Fig.3: Plot of $\log k_{\text{obs}}$ against $\log [\text{C}_2\text{H}_5\text{OH}]$

Table 1: Pseudo-first order and second order rate constants for the reaction of $[\text{AuCl}_3(\text{OH})]^-$ and $\text{C}_2\text{H}_5\text{OH}$

$10^3[\text{C}_2\text{H}_5\text{OH}]$, mol dm ⁻³	$10^3[\text{H}^+]$, mol dm ⁻³	$10^2\mu$, mol dm ⁻³	10^3k_{obs} , s ⁻¹	k_2 , dm ³ mol ⁻¹ s ⁻¹
2.0	1.0	5.0	1.80	0.898
4.0	1.0	5.0	3.55	0.888
6.0	1.0	5.0	5.34	0.890
8.0	1.0	5.0	7.10	0.887
10.0	1.0	5.0	8.77	0.877
12.0	1.0	5.0	10.86	0.905
14.0	1.0	5.0	12.68	0.906

$[\text{AuCl}_3(\text{OH})]^- = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 0.05 \text{ mol dm}^{-3}$ (NaClO_4), $T = 30 \pm 1^\circ\text{C}$ and $\lambda_{\text{max}} = 310 \text{ nm}$

Table 2: Effect of $[\text{H}^+]$ on the rate of reaction

$10^3[\text{H}^+]$, mol dm ⁻³	0.5	1.0	2.0	4.0	6.0	8.0	10.0	12.0	14.0
10^3k_{obs} , s ⁻¹		5.645	3.4	4.713	4.32	6.1	2.0184	1.50	1.29
k_2 , dm ³ mol ⁻¹ s ⁻¹	0.940	0.890	0.785	0.572	0.435	3.340	3.070	2.50	0.215

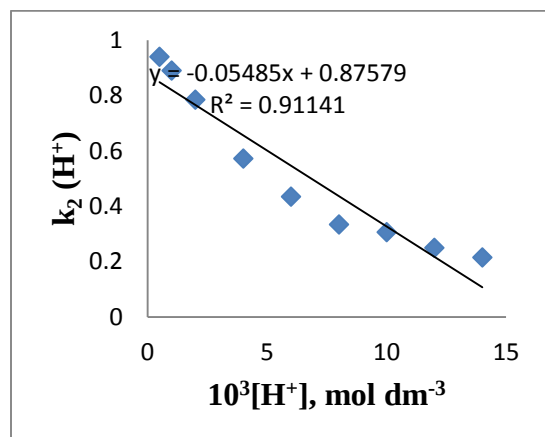
$[\text{AuCl}_3(\text{OH})]^- = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$ and $[\text{C}_2\text{H}_5\text{OH}] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$

Between the acid concentration $5.0 \times 10^{-4} \leq [\text{H}^+] \leq 1.40 \times 10^{-2} \text{ mol dm}^{-3}$, the reaction rate decreased as $[\text{H}^+]$ increased (Table 2). Inverse acid dependence is linked to deprotonation of specie before electron transfer (Ukoha *et al.*, 2023). This form of rate dependence happens when a given reacting specie exists in forms which are in equilibrium involving hydrogen ion such as hydrolytic equilibrium, complex formation with proton liberation with the deprotonated form as the reactive specie. This suggests that the reaction occurred by two parallel pathways where one is inverse acid dependent and the other is acid independent (Fig. 4) and fits into Equation 6

$$k_2(\text{H}^+) = a + b[\text{H}^+]^{-1} \quad (6)$$

where a (intercept) = $0.87579 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and b (slope) = $-0.05485 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$

In this type of acid dependence, the rate has a limiting value at low $[\text{H}^+]$, which tends to a zero value at large $[\text{H}^+]$. Here, plotting $(\text{rate})^{-1}$ against $[\text{H}^+]$ yields a straight line with intercept (Onu *et al.*, 2016).

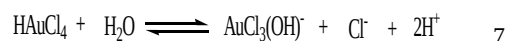
**Fig. 4: Plot of $k_2(\text{H}^+)$ against $[\text{H}^+]$** **Table 3: Effect of medium ionic strength on the rate of reaction**

$10^2\mu$, mol dm ⁻³	2.0	4.0	5.0	6.0	8.0	10.0	12.0	
10^3k_{obs} , s ⁻¹		5.39	5.18	5.32	5.27	5.48	5.30	5.37
k_2 , dm ³ mol ⁻¹ s ⁻¹	0.898	0.864	0.887	0.879	0.914	0.883	0.894	

$[\text{AuCl}_3(\text{OH})]^- = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$ and $[\text{C}_2\text{H}_5\text{OH}] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$

Acid catalysis has been documented for the oxidation of benzyl alcohols (Dharmaraja *et al.*, 2008; Bijudas, 2014). Acid catalysis in these reactions was explained based on the protonation of the poor reactive specie of these alcohols prior to electron transfer. Ethanol has a pKa of 15.9 due to its carbon length; extension of the carbon chain as well as branching raises the pKa of aliphatic alcohols which influences the electron donating ability of their alkyl group. The OH in alcohols is strongly basic and this makes them a very poor leaving group and therefore hard to replace. Consequently, alcohols are less reactive towards substitution and elimination reactions and have to be activated by protonation which converts the OH⁻ to a weaker base by forming positively charged conjugate acids for them to undergo substitution or elimination reaction at elevated temperature (Mansoor and Shafi, 2014).

Increasing acid concentration in this study should form EtOH_2^+ which would have catalysed the reaction since the reactive form of the gold(III) complex ion, $[\text{AuCl}_3(\text{OH})]^-$, carries a negative charge but the reverse was observed. The inverse acid dependence observed for this study is therefore attributed to the oxidant salt, HAuCl_4 , which deprotonates in aqueous solution as established by Equation 7. Increase in acid concentration subsequently resulted to common ion effect which retarded the rate of the forward reaction.



Similar inverse acid dependence has been reported for the redox reaction of Au(III) ions with L-tyrosine (Nirmala and Vani, 2013), oxalic acid (Shen *et al.*, 2010) and methanol (Ukoha and Iorungwa, 2023).

Varying ionic strength of the medium within the range 0.02 – 0.12 mol dm⁻³, revealed that rate was independent of ionic strength concentration (Table 3). Rate independence on ionic strength suggests that one or both reactants is/are neutral at the rate determining step (Asperger, 2003) or that the reaction occurred between specie that formed an ion-pair or adduct (Mohammed, 2015). This is typical of most reactions proceeding through outer- sphere mechanistic pathway. The non-dependence of rate on ionic strength observed for this reaction shows that one of the reactants is not charged at the rate determining step. This lack of primary salt effect is therefore expected. Similar non-dependence of rate on ionic strength has been documented

for the redox reaction of gold(III) ion (Shen *et al.*, 2010; Ukoha and Iorungwa, 2023).

For same charge bimolecular reaction, ionic strength within ≤ 0.1 mol dm⁻³ will result to a primary salt effect having a unity slope in conformity to Equation 8.

$$\log k_r = \log k_r^\infty + 1.02 Z_A Z_B \left(\frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0.30I \right) \quad (8)$$

Table 4: Effect of medium dielectric constant on the rate of reaction of [AuCl₃(OH)]⁻ and C₂H₅OH

D	78.40	77.59	76.79	75.99	75.19	74.39	73.59
10 ³ k _{obs} , s ⁻¹	5.34	5.25	5.37	5.37	5.27	5.25	5.39
k ₂ , dm ³ mol ⁻¹ s ⁻¹	0.891	0.875	0.894	0.894	0.879	0.875	0.898

[AuCl₃(OH)]⁻ = 1.0 x 10⁻⁴ moldm⁻³ and [C₂H₅OH] = 6.0 x 10⁻³ moldm⁻³

Using binary solvent system of water and acetone from 78.40 -73.59, the effect of medium dielectric constant on the rate of the reaction was investigated. Varying dielectric constant had no significant effect on the rate (Table 4). This explains that the reaction occurred between a charged molecule and neutral specie at the rate determining step and conforms to the nature of ionic strength dependence observed for this reaction. The result agrees with that reported for the oxidation of alcohols with oxo-bridged ruthenium(IV) ion (Mohammed, 2015).

2023). For this reaction, this trend could therefore be attributed to the negative dipole on the oxygen atom in ethanol or to parallel reactions by other species in the reaction medium. The result implies the absence of a bridge linked reactants at the activated complex which made the participation of added ions possible. Ion-catalysis and/or inhibition have been shown to favour outer- sphere reactions (Idris *et al.*, 2015).

Test for free radical

Adding acrylamide to the reaction mixture followed by excess methanol did not result to formation of gelatinous precipitate. This showed lack of polymerisation of the acrylamide monomers and absence of the participation of free radicals during the reaction. This agrees with findings by Nirmala and Vani, 2013 for the oxidation of L-tyrosine by gold(III) ion and the reduction of gold(III) ion by methanol (Ukoha and Iorungwa, 2023).

Temperature dependence study

Effect of temperature on the reaction rate was monitored by altering temperature from 308 to 318 K. Rate constant increased with increase in temperature. From Equation 2, plot of ln(k/T) against T⁻¹ was made (Fig. 5). The activation enthalpy and entropy evaluated from this plot were 13.01 kJmol⁻¹ and -175.74 JK⁻¹mol⁻¹. The negative entropy of activation obtained is unexpected as it suggests a highly ordered situation where bond formation predominate bond dissociation. Solvent reorganisation can result in negative entropy even for a reaction occurring by an outer-sphere mechanism, hence the assertion that entropy should be large and negative to indicate an inner-sphere pathway is not completely true (Housecroft and Sharpe, 2008).

Table 5: Pseudo – first order and second order rate constants for the effect of added ions for the reaction of [(AuCl₃(OH)]⁻ and C₂H₅OH at [AuCl₃(OH)]⁻ = 1.0 x 10⁻⁴ moldm⁻³ and [C₂H₅OH] = 6.0 x 10⁻³ moldm⁻³, μ = 0.05 moldm⁻³ (NaClO₄), T = 30 ± 1°C and λ_{max} = 310 nm

X, mol dm ⁻³	10 ³ k _{obs} , s ⁻¹	k ₂ , dm ³ mol ⁻¹ s ⁻¹
10³[CH₃COO⁻]		
0.0	5.34	0.891
2.0	2.95	0.491
4.0	2.70	0.449
6.0	2.49	0.415
8.0	2.30	0.384
10.0	2.12	0.353
10³[NO₃⁻]		
0.0	5.34	0.891
2.0	2.53	0.422
4.0	2.30	0.384
6.0	2.21	0.369
8.0	2.12	0.353
10.0	2.10	0.350
12.0	1.91	0.319

At constant concentrations of all other reactants, varying concentrations of CH₃COO⁻ and NO₃⁻ were added to check for their catalytic or inhibitory effect on the reaction rate. It was observed that rate decreased with increase in added anions (Table 5). Rate inhibition with added anions suggests the presence of cation-anion or neutral-anion redox partners at the activated complex (Ukoha *et al.*,

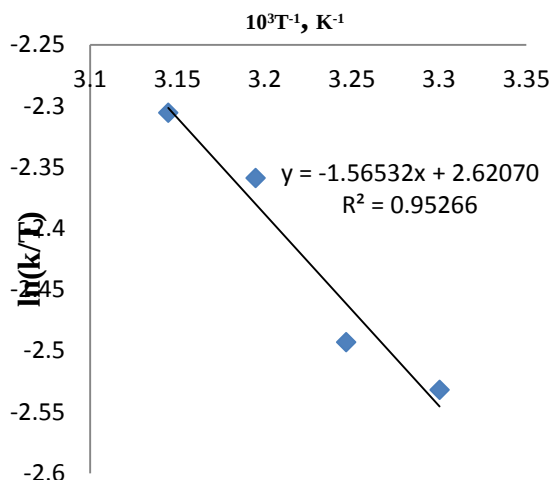


Fig. 5: Plot of $\ln(k/T)$ against T^{-1} for the reduction of $[\text{AuCl}_3(\text{OH})]^-$ by $\text{C}_2\text{H}_5\text{OH}$

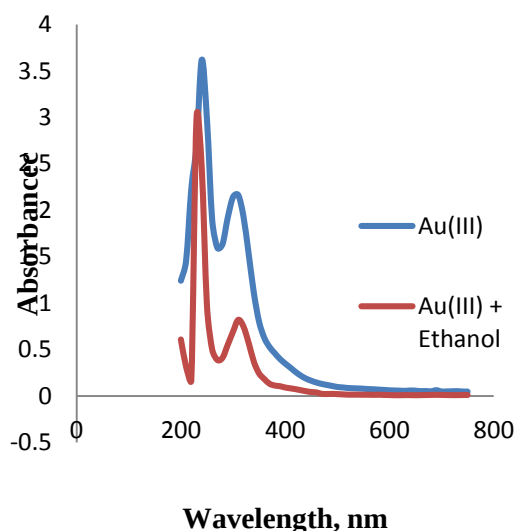


Fig. 6: UV-Vis spectrum of reaction mixture after three minutes of reaction for $[\text{AuCl}_3(\text{OH})]^-$ and ethanol reaction

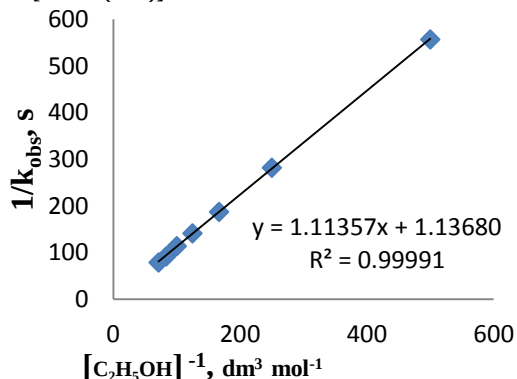


Fig. 7: Michaelis-Menten's type plot for the reduction of $[\text{AuCl}_3(\text{OH})]^-$ by ethanol

Comparing the electronic spectrum of $[\text{AuCl}_3(\text{OH})]^-$ complex with that of the reaction mixture (Fig. 6) showed no shift in λ_{max} of $[\text{AuCl}_3(\text{OH})]^-$ at 310 nm, indicating the absence of spectroscopically detectable intermediate complex. Michaelis-Menten's type plot of k_{obs}^{-1} versus $[\text{C}_2\text{H}_5\text{OH}]^{-1}$ was made (Fig.7). The plot was linear with negligible intercept which supports the absence of intermediate complex with an appreciable equilibrium constant. For enzymatic action where $[\text{enzyme}]$ is $< [\text{substrate}]$, the rate of formation of product is given by Equation 9

$$d \frac{[\text{product}]}{dt} = k_{\text{obs}} [E_o] \quad (9)$$

$$k_{\text{obs}} = \frac{V_{\text{max}} [S]}{k_m + [S]} \quad (10)$$

It is observed that taking the reciprocal of Equation 10 and rearranging it, gives Equation 11

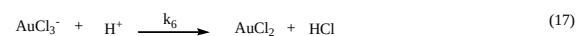
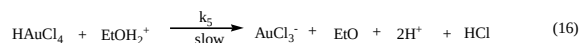
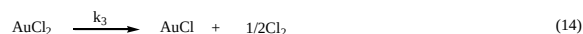
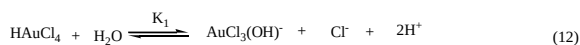
$$\frac{1}{k_{\text{obs}}} = \frac{1}{V_{\text{max}}} + \frac{k_m}{V_{\text{max}}} [S]^{-1} \quad (11)$$

For a normal redox reaction, S stands for the reductant. A plot of k_{obs}^{-1} against $[S]^{-1}$ gives V_{max}^{-1} as intercept. If a linear plot which passes through the origin is obtained, it shows that the intercept V_{max}^{-1} is zero, meaning that V_{max} or the equilibrium constant for the active intermediates is zero (Ukohaet *et al.*, 2018)). The negligible intercept observed for this reaction confirm that the reactions occurred through the outer-sphere mechanism.

Based on the underlisted evidence obtained from the reaction;

1. Rate inhibition by added anions
2. Absence of spectroscopically determinable intermediate complex
3. Negligible intercepts from Michaelis- Menten's type plot

Outer-sphere mechanism is proposed for the reaction, the plausible mechanistic steps elucidate the experimental data;



$$\text{Rate} = k_2[\text{AuCl}_3(\text{OH})^-][\text{EtOH}] + k_5[\text{EtOH}_2^+][\text{AuCl}_3(\text{OH})^-] \quad (19)$$

$$\text{But } [\text{AuCl}_3(\text{OH})^-] = K_1[\text{HAuCl}_4] \quad (20)$$

$$\text{and } [\text{EtOH}_2^+] = \frac{K_4[\text{EtOH}]}{[\text{H}^+]} \quad (21)$$

Therefore,

$$\text{Rate} = k_2K_1 + \frac{k_5K_4[\text{HAuCl}_4][\text{EtOH}]}{[\text{H}^+]} \quad (22)$$

Equation 22 is similar to Equation 6 where 'a' = k_1 and 'b' = k_2K_3 with values previously stated. This is in agreement with the nature of acid dependence observed for this reaction. Ethanal formation has been documented as the oxidation product of ethanol following hydride transfer. Hydride transfer from the alcohol to the oxidant and subsequent formation of the corresponding aldehyde has also been documented for the oxidation of alcohols (Mansoor and Shafi, 2014; Ukoha and Iorungwa, 2023).

Conclusion

The kinetic, thermodynamic and mechanistic investigations of the reduction of $[\text{AuCl}_3(\text{OH})]^-$ by ethanol was studied. Stoichiometric result gave a 1:1 molar ratio with respect to oxidant and reductant, unity order with respect to [oxidant] and [reductant], second order overall was observed for the reaction. An inverse acid dependence was noted while variation in ionic strength and dielectric constant of the reaction media had negligible impact on the reaction rate. Enthalpy (kJ mol^{-1}) and entropy ($\text{JK}^{-1}\text{mol}^{-1}$) of activation for the reaction are 13.01 and -175.74. There was no polymerisation of acrylamide monomers suggesting the absence of free radicals in the reaction. Michaelis-Menten's type plot had negligible intercept while FTIR spectrum revealed band for aldehyde formation as the oxidation product of the alcohol.

Based on the stoichiometry, order of reaction, effect of change in hydrogen ion concentration, effect of media ionic strength and dielectric constant, test for free radicals, spectrophotometric determination of intermediate complex formation, temperature dependence study, non-conformity of the results with Michaelis-Menten's type plot, outer sphere mechanism has been proposed for the reduction of $[\text{AuCl}_3(\text{OH})]^-$ by ethanol.

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Conflicts of Interest

The authors declare that there are no conflicts of interest

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