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Kinetics, Thermodynamics and Mechanisms of Reduction of Au(III) Complex Ion by Methanol in Acidic Medium

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ABSTRACT

Kinetics, thermodynamics and mechanisms of the reduction of gold(III) complex ion, $[AuCl_3(OH)]^-$, by methanol (MeOH) was studied spectrophotometrically in perchloric acid medium at ionic strength (μ) = 0.05 mol dm^{-3} ($NaClO_4$) and T = 30.0 ± 1 °C. Stoichiometry of the reaction showed that one mole of $[AuCl_3(OH)]^-$ was reduced by one mole of methanol. The rate of reaction was first order in oxidant concentration as well as in $[CH_3OH]$ with a second order overall. Addition of acid within the range 5.0×10^{-4} to 1.2×10^{-2} mol dm^{-3} decreased the rate of the reaction. Increasing μ from 2.0×10^{-2} to 1.2×10^{-1} mol dm^{-3} ($NaClO_4$) had no effect on the rate of the reaction. The same trend was observed on varying dielectric constant from 78.40 to 73.59. Michaelis – Menten – type plot was linear and with negligible intercept. Entropy of activation was found to be -196.82 $JK^{-1}mol^{-1}$ while activation enthalpy was also found to be 6.101 kJ mol^{-1}. Au^I was found to be the product of $[AuCl_3(OH)]^-$ reduction while aldehyde was obtained for MeOH oxidation. FTIR spectral showed band for aldehyde formation (C=O) at 1764 cm^{-1}. Based on negligible intercept from Michaelis – Menten – type plot and the absence of spectroscopically determinable intermediate complex, the reaction was proposed to have proceeded through the outer – sphere pathway.

Keywords: Au(III) complex ion, Kinetics, Mechanism, Reduction, Thermodynamics

INTRODUCTION

Electron transfer reactions of metal ions and their complexes especially those of transition metals is a vital chemical process in nature and it plays a key role in bioinorganic chemistry and molecular biology where they investigate the functions of metal complexes as metalloproteins. They are also employed in the chemistry of industries for harnessing complexes of these metals as homogeneous catalysts and in medicinal and environmental chemistry for chelate therapy (Sodhi and Paul, 2019). Among the many targets of current research and interest of bioinorganic and medicinal chemists is the use of metal-based drugs for therapeutic purposes and to develop new metal based anti-tumor agents having pharmacological activities that are significantly not the same with platinum-based anti-tumor agents (Casini and Messori, 2011). Included in these recent antitumor drugs of non-platinum base, complexes of gold(III) are considered as a group of anti-tumor agents with pharmacodynamic and pharmacokinetic features different from platinum-based drugs, but have powerful inhibitory properties on cell growth (Nobili *et al.*, 2010). The biomedical applications of gold compounds and nanoparticles especially in cancer therapy, diagnostics and bioimaging require biocompatible preparation routes with mild reaction conditions (Ungor *et al.*, 2019). Paclawski and Fitzner (2005) reported only the cationic effect of groups I and II cations on the reduction of gold(III) ion by $[HSO_3]^-$. Studies on the reactions of $[AuCl_4]^-$ with different nucleophiles in aqueous solution was undertaken (Mirjana *et al.*, 2014). The study centered on the substitution and redox reaction of gold(III) with the nucleophiles and emphasized on the stability of the metal center in the nucleophiles. Since gold(III) complexes hold much promise as anti-tumor agents, a lot of them have been synthesized and applied in cancer therapy and targeted drug delivery as nano rods. In addition, gold(I) drugs may be activated *in vivo* to gold(III) metabolites under physiological conditions. However, the intrinsic mechanisms driving these physiological processes have not been fully unraveled. This paucity of kinetic and mechanistic data have limited applications of gold(III) derived drugs.

Experimental

The chemicals used are of analytical grade and used without further purification. Hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4.3H_2O$) [Sigma–Aldrich, 99 %] was used as the oxidizing agent, methanol [BDH, 99.5 %] was the reducing agent, hydrogen tetraoxochlorate(VII) ($HClO_4$) [Sigma –Aldrich, 70 %] was used to maintain $[H^+]$, $NaClO_4$ [Sigma–Aldrich, 98 %] was used to maintain ionic strength. Prop-2-enamide (C_3H_5NO) was used to check for the presence of free radical in the reaction. Solutions were prepared in deionised water by dissolving 0.1969 g of $HAuCl_4.3H_2O$ to prepare 1.0 x 10^{-3} mol dm^{-3}, 0.41 cm^3 of MeOH was used to prepare 0.1 mol dm^{-3}, 2.03 cm^3 of $HClO_4$ was used to make 0.5 mol dm^{-3} and 7.025 g of $NaClO_4$ was used to 0.2 mol dm^{-3}.

Stoichiometry

The stoichiometry was determined by spectrophotometric titrations using mole ratio method (Ukoha *et al.*, 2018) under the conditions of $[H^+]$ = 1.0 x 10^{-3} mol dm^{-3}, μ = 0.02 mol dm^{-3} ($NaClO_4$), $[AuCl_3(OH)]^-$ = 1 x 10^{-4} mol dm^{-3}, $[CH_3OH]$ = (2.5 x 10^{-5} to 2.5 x 10^{-4}) mol dm^{-3}, Temperature (T) = 30.0 ± 1.0 °C and λmax = 310 nm. A plot of absorbance versus mole ratio of the reactants was made from which the stoichiometry was determined.

Kinetic Measurements

All kinetic measurements were performed under pseudo-first-order conditions, where $[CH_3OH]$ was present in at least 20 folds excess over that of $[AuCl_3(OH)]^-$ at T= 30.0 ± 1.0 °C, $[H^+]$ = 1.0 x 10^{-3} mol dm^{-3} and 0.05 mol dm^{-3}($NaClO_4$) ionic strength, using a JENWAY 6405 UV-Vis spectrophotometer. The course of reaction was followed by measuring change in absorbance of $[AuCl_3(OH)]^-$ at 310 nm as a function of time where it was ascertained that there was no interference from other reagents at that wavelength. Under these conditions, the kinetic curves were exponential and rate constants were obtained from plot of log (A_t - A_∞) versus time, from the relationship; $In(At - A_\infty) = In(A_o - A_\infty) - k_{obs}\,t$ where A_t = absorbance at time t, A_∞= absorbance at infinity, A_o = initial absorbance, k_{obs} = pseudo – first order rate constant. Second order rate constants, k_2 , were determined as the ratio of k_{obs} : $[CH_3OH]$ (Ukoha and Ibrahim, 2004).

The influence of $[H^+]$ and ionic strength ($NaClO_4$) on the rate of the reaction were investigated within the ranges 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} respectively while maintaining other reaction conditions constant.

Effect of Dielectric Constant on Rate of Reaction

The dielectric constant of the medium was estimated (Equation 1) by varying the ratio of acetone to water using the relation;

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

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

Test for free radical

Exactly 2 g of acrylamide was added to the partially reduced reaction mixture containing various concentrations of oxidant, methanol and hydrogen ion for the system and allowed to stand for about 2 minutes, this was followed by adding a large excess of methanol. 2 g of acrylamide followed by an excess of methanol were also added to solutions of CH_3OH and $[AuCl_3(OH)]^-$ separately to serve as control. The absence of gel formation suggests that free radical was not produced in the course of the reaction (Ukoha and Ibrahim, 2004; Abiti *et al*., 2018).

Temperature dependence study

At constant $[AuCl_3(OH)]^-$, $[CH_3OH]$, $[H^+]$ and μ, the temperature was varied between 308 to 318 K using a thermostatic water bath to adjust the reaction temperature. The reagents were quickly mixed after attaining the desired temperature and the reaction was monitored. The temperature of the reaction product was measured at the completion of the reaction to ensure there is no significant loss in initial temperature. Plot of ln (k/T) against 1/T was made from the linear form of Eyring – Polanyi equation expressed as Equation 2, from where the activation entropy and enthalpy were determined.

$$\ln\frac{k}{T} = 23.759 + \frac{\Delta S^{\mp}}{R} - \frac{\Delta H^{\mp}}{R}.\frac{1}{T} \qquad (2)$$

Product Analysis

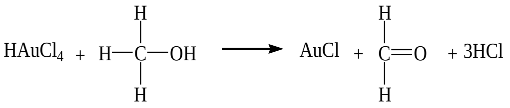
The presence or absence of aldehyde was tested by combining 2 cm^3 of the reaction mixture with 3 cm^3 of 2, 4-dinitrophenylhydrazine solution. The appearance of yellowish precipitate indicated the presence of aldehyde. A confirmatory test was also done with Fehling's solutions; to 1 cm^3 of Fehling's solution A, equal volume of Fehling's solution B was added until precipitation occurred. 3 cm^3 of the Fehling's Solution B was added in drops until the precipitate disappeared. 3 cm^3 of the liquid product was added and boiled. A brick-red colour indicated the presence of aldehyde as the oxidation product of methanol. The absence of Au(III) ion was checked to ensure its reduction using the qualitative test as described by (Vogel, 1979) with slight modifications. Excess of MeOH was reacted with the gold(III) complex ion and the reaction allowed to go to completion. A 2 cm^3 portion of the reaction mixture was afterwards reacted with alkaline solution of hydrogen peroxide as expressed in Equation 3. Lack of precipitate confirmed the absence of Au(III).

$$2[AuCl_4]^- + 3H_2O_2 + 6OH^- \rightarrow 2Au_{(S)} + 3O_{2(g)} + 8Cl^- + 6H_2O \quad (3)$$

RESULTS AND DISCUSSION

Stoichiometry

Spectrophotometric estimation of the reaction using the mole ratio method showed that one mole of $[AuCl_3(OH)]^-$ was reduced by one mole of methanol as seen in Figure 1. This result suggests that the stoichiometric ratio of the reaction conforms to the stoichiometry as in Equation 4



$$HAuCl_4 + CH_3OH \longrightarrow AuCl + HCHO + 3HCl$$

(4)

Stoichiometric ratios for the reduction of Au(III) ion are 1:1 $AuCl_4^-$ using NH_3OH^- (Soni and Mehrotra, 2003), 1:1 $AuCl_4^-$ by HSO_3^-, 2:3 $AuCl_4^-$ with H_2O_2 (Paclawski and Fitzner, 2005, 2006), 1:1 $AuCl_3SR$ by thioether (Kostin *et al.*, 2006), 1:14 $AuBr_4$ with $H_2C_2O_4$ (Shen *et al.*, 2010), 1:1 $AuCl_4^-$ with L-Tyrosine (Baby Nirmala and Vani, 2013), 1:3 Au^{3+} with thiourea (Mirjana *et al.*, 2014) 1:1 $AuCl_4^-$ by formic acid (Paclawski and Sak, 2015), 1:1 Au^{3+} with sodium malonate (Sen *et al.*, 2016).

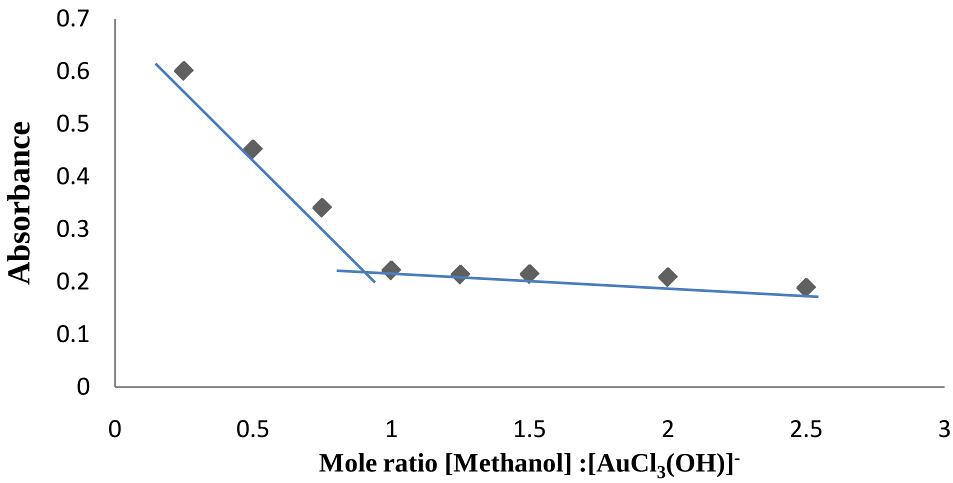


Figure 1: Mole ratio plot for the reduction of $[AuCl_3(OH)]^-$ by methanol

Kinetics

Pseudo-first order plot of log ($A_t - A_\infty$) versus time was linear for over 80 % extent of reaction. A typical plot is depicted in Fig. 2. Linearity of the plot suggests a first order dependence on the gold(III) complex ion, $[AuCl_3(OH)]^-$. Also a plot of log k_{obs} versus log $[CH_3OH]$ was linear with a slope 1.007 (Fig. 3), suggesting a first order with respect to $[CH_3OH]$ and a second order overall. The rate equation for this system can be written as in Equation 5;

$$-\frac{d[AuCl_3(OH)^-]}{dt} = k_2[AuCl_3(OH)^-][CH_3OH] \quad (5)$$

where mean value of k_2 ($dm^3\ mol^{-1}\ s^{-1}$) = 0.912±0.016. Similar second order kinetics has been reported for the reduction of Au(III) ions with hydroxylamine (Soni and Mehrotra, 2003) and oxalic acid (Shen *et al.*, 2010).

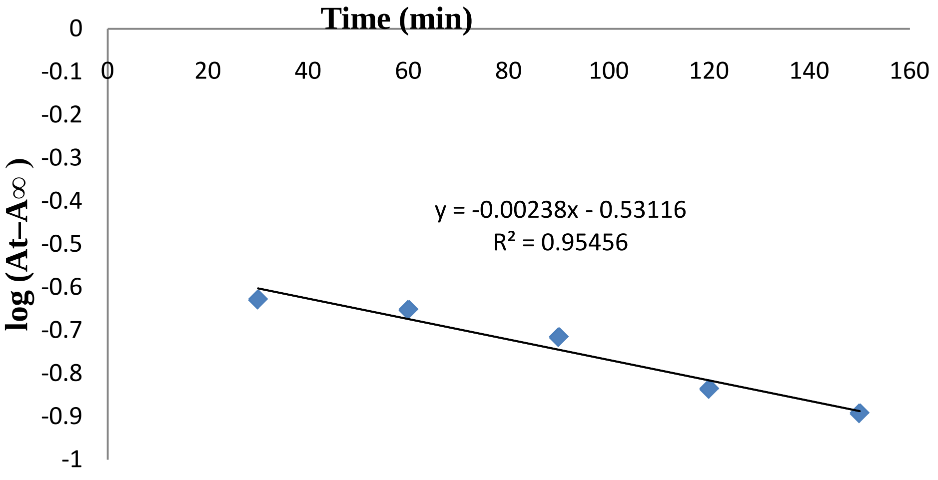


Figure 2: Typical pseudo-first order plot for the reduction of $[AuCl_3(OH)]^-$ by CH_3OH

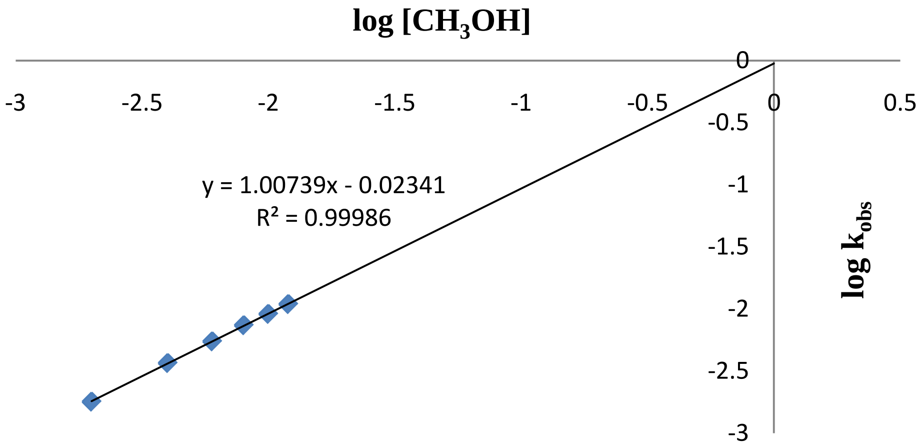


Figure 3: Plot of log k_{obs} against log $[CH_3OH]$

Table 1:Pseudo-first order and second order rate constants for the reaction of $[AuCl_3(OH)]^-$ and CH_3OH

$10^3[CH_3OH]$, mol dm^{-3}	$10^3[H^+]$, 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	3.67	0.918
6.0	1.0	5.0	5.48	0.913
8.0	1.0	5.0	7.39	0.924
10.0	1.0	5.0	9.11	0.911
12.0	1.0	5.0	10.93	0.911

$[AuCl_3(OH)^-] = 1.0 \times 10^{-4}$ mol dm^{-3}, $\mu = 0.05$ mol dm^{-3} ($NaClO_4$), T = 30 ± 1°C and λmax = 310 nm

Table 2: Effect of $[H^+]$ on the rate of reaction

$10^3[H^+]$, mol dm^{-3}	0.5	2.0	4.0	6.0	8.0	10.0	12.0
10^3k_{obs}, s^{-1}	5.73	4.40	3.92	3.30	2.14	1.93	1.61
k_2, dm^3 mol^{-1} s^{-1}	0.956	0.733	0.653	0.551	0.357	0.322	0.269

$[AuCl_3(OH)]^- = 1.0 \times 10^{-4}$ mol dm^{-3} and $[CH_3OH] = 6.0 \times 10^{-3}$ mol dm^{-3}

Within the acid range of 5.0×10^{-4} to 1.20×10^{-2} mol dm^{-3}, the reaction rate decreased as $[H^+]$ increased as seen in Table 2. Onu et al. (2010) suggested that in this form of dependence, the rate has a limiting value at low $[H^+]$ tending to a zero value at large $[H^+]$. In this case, a plot of $(\text{rate})^{-1}$ versus $[H^+]$ would yield a straight line with a non-zero intercept. This type of rate dependence on acid concentration occurs when a particular reactant exists in two or more 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 proceeded by two parallel pathways where one is inverse acid dependent and the other is acid independent as in Figure 4 and fits into Equation 6.

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

where a = 0.90051 dm^3 mol^{-1} s^{-1} and b = -0.05797 dm^6 mol^{-2} s^{-1}

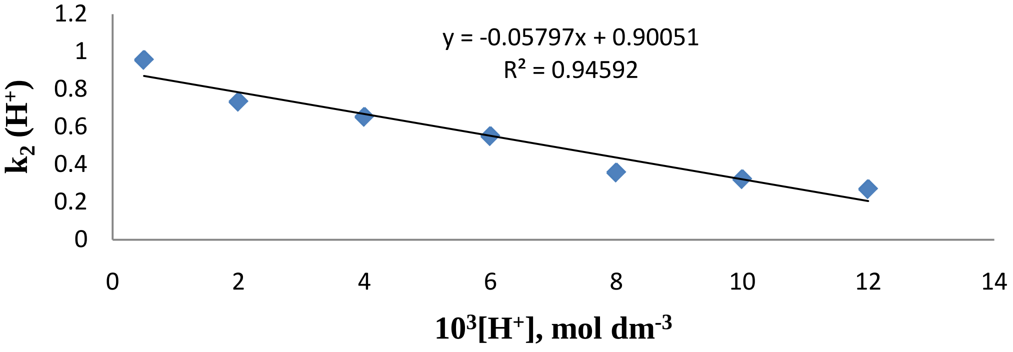


Figure 4: Plot of $k_2(H^+)$ against $[H^+]$

Similar inverse acid dependence has been documented for the reduction of gold(III) ions by L-tyrosine (Baby-Nirmala and Vani, 2013) and oxalic acid (Shen *et al*., 2010), while redox reaction of alcohols has been stated to occur through acid catalysis; reduction of quinolinium bromochromate by aliphatic alcohols (Saraswat *et al*., 2003) and sodium N-chloroethylcarbamate (Mittal *et al*., 2004). Acid catalysis has also been reported for the oxidation of benzyl alcohols by benzimidazolium fluorochromate (Dharmaraja *et al*., 2008) and in the reduction of acidified dichromate by benzyl alcohol (Bijudas, 2014). Acid catalysis in these reactions was explained based on the protonation of the poor reactive species of these alcohols before the transfer of electron. Methanol has a pKa of 15.1 which is lowest for aliphatic alcohols due to its carbon length as extension of the alkyl chain as well as branching raises the pKa of these aliphatic alcohols. The electron donating ability of their alkyl group is influenced by the length of the carbon chain. The leaving group of alcohols (OH^-) is a strong base, and this makes it a very poor leaving group and therefore hard to replace. As a consequence, alcohols are less reactive to substitution and elimination reactions. There has to be activation by protonating the reaction mixture which converts the OH^- to a weaker base for them to undergo substitution or elimination reaction at elevated temperature (Mansoor and Shafi, 2014). Protonation of alcohols form positively charged conjugate acids. This should ordinarily have catalysed this reaction since the reactive form of the gold(III) complex ion, $[AuCl_3(OH)]^-$, carries a negative charge but the reverse was observed. $HAuCl_4$ is a strong acid salt which deprotonates in aqueous solution as established by various equilibra as seen in Equations 7 to 9. Increase in hydrogen ion concentration will lead to common ion effect which will retard the rate of the forward reaction.

$$HAuCl_4 \rightleftharpoons AuCl_4^- + H^+ \qquad 7$$

$$AuCl_4^- + H_2O \rightleftharpoons AuCl_3(H_2O) + Cl^- \qquad 8$$

$$AuCl_3(H_2O) \rightleftharpoons AuCl_3(OH)^- + H^+ \qquad 9$$

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}	5.85	5.71	5.92	5.83	5.80	5.55	5.92
k_2, dm^3 mol^{-1} s^{-1}	0.956	0.952	0.986	0.971	0.967	0.925	0.980

$[AuCl_3(OH)]^- = 1.0 \times 10^{-4}$ mol dm^{-3} and $[CH_3OH] = 6.0 \times 10^{-3}$ mol dm^{-3}

Investigating the effect of ionic strength on the rate of the reaction showed that the rate was independent of ionic strength concentration, as varying ionic strength concentration had no effect on the rate of the reaction as seen in Table 3. Rate independence on ionic strength means either one or both redox partners is/are neutral (Asperger, 2003) or that the reaction occurred between species that formed an ion-pair or adduct (Mohammed, 2015), and this is characteristic of most reactions occurring through the outer- sphere mechanism. The non-dependence of rate on ionic strength observed in this reaction is an implication that one of the reactants is not charged at the rate determining step. The lack of primary salt effect observed for this reaction is therefore, not unexpected. Similar non-dependence of rate on variation in ionic strength has been reported for the reduction of $HAuCl_4$ (Baby-Nirmala and Vani, 2013) and $AuBr_4$ (Shen *et al*., 2010). Singh *et al* (2013) also reported that variation in ionic strength had negligible impact on the rate of methylglycol oxidation by N- bromosuccinimide in alkaline medium catalysed by Os(VII).

Table 4: **Effect of medium dielectric constant on the rate of reaction of $[AuCl_3(OH)]^-$ and CH_3OH**

D	10^3k_{obs}, s^{-1}	k_2, $dm^3\ mol^{-1}\ s^{-1}$
78.40	5.48	0.913
77.59	5.25	0.875
76.79	5.14	0.856
75.99	5.37	0.894
75.19	5.46	0.909
74.39	5.27	0.879
73.59	5.34	0.890

$[AuCl_3(OH)^-] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[CH_3OH] = 6.0 \times 10^{-3}$ mol dm^{-3}

The effect of medium dielectric constant on the rate of this reaction was also investigated by using a binary solvent system of water and acetone from 78.40 to 73.59. Varying dielectric constant had no significant effect on the rate as seen in Tables 4. This is an indication that the reaction occurred between a charged molecule and neutral specie, and it agrees with the nature of ionic strength dependence observed for this reaction. The result is in conformity with those obtained for the oxidation of oxo-bridged ruthenium(IV) by alcohols (Mohammed, 2015).

Test for free radical

Addition of acrylamide to the reaction mixture followed by adding 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 Baby-Nirmala and Vani, 2013 for the oxidation of L-tyrosine by gold(III) ion.

Effect of temperature

Effect of temperature on the reaction rate was monitored by altering temperature from 308 to 318 K. Plot of ln(k/T) against T^{-1} was made as seen in Figure 4. The activation enthalpy and entropy evaluated from this plot are 6.101 kJmol^{-1} and -196.82 JK^{-1} mol^{-1}. The negative value $\Delta S^‡$ obtained is unexpected as it suggests a highly ordered situation considering that other variables point towards outer-sphere mechanisms. Solvent reorganization can result in negative values of $\Delta S^‡$ even for a reaction occurring via an outer-sphere mechanism, hence the assertion that $\Delta S^‡$ should be large and negative to indicate an inner-sphere pathway is not completely true (Housecroft and Sharpe, 2008).

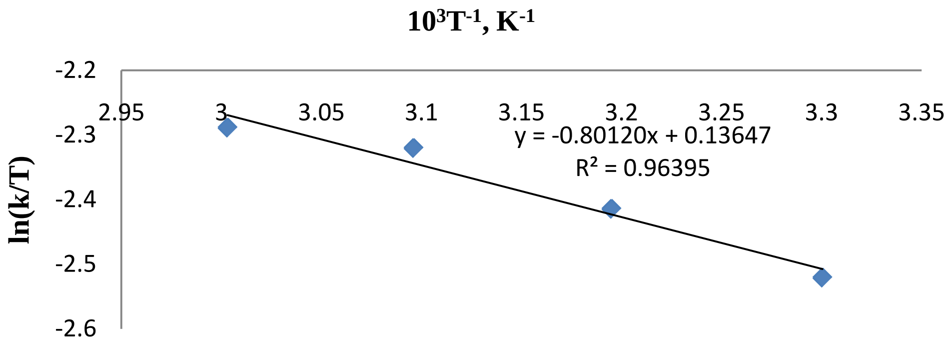


Figure 5: Plot of ln(k/T) vs. T^{-1} for the reduction of $[AuCl_3OH]^-$ by CH_3OH

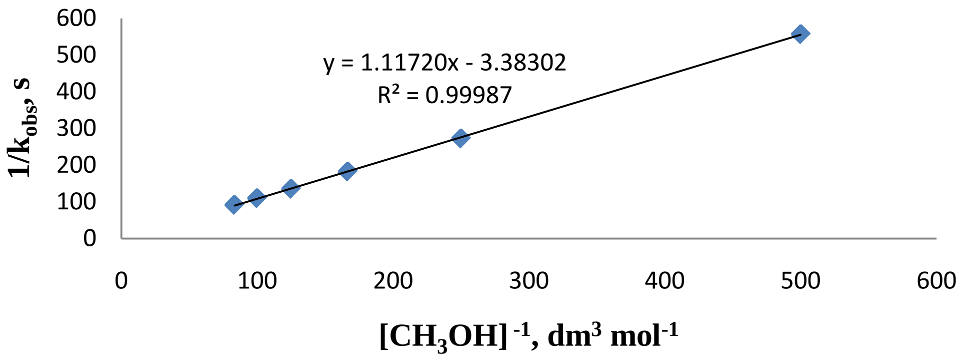


Figure 6: Michaelis-Menten-Type plot for the reaction of $[AuCl_3(OH)]^-$ and CH_3OH

Michaelis – Menten – type plot of k_{obs}^{-1} versus $[CH_3OH]^{-1}$ was made as in Figure 6. The plot was linear with negligible intercept which supports the absence of intermediate complex with an appreciable equilibrium constant. Also, comparing the electronic spectrum of $[AuCl_3(OH)]^-$ complex with that of the reaction mixture as seen in Figure 7 showed no shift in λmax of $[AuCl_3(OH)]^-$ at 310 nm, indicating the absence of spectroscopically detectable intermediate complex formation. For enzymatic action where [enzyme] is < [substrate], the rate of formation of product is given by Equation 10.

$$d\frac{[product]}{dt} = k_{obs}[E_o] \qquad (10)$$

$$k_{obs} = \frac{V\max[S]}{km + [S]} \qquad (11)$$

It is observed that taking the reciprocal of Equation 11 and rearranging it, gives Equation 12.

$$\frac{1}{k_{obs}} = \frac{1}{V\max} + \frac{km}{V\max}[S]^{-1} \qquad (12)$$

For a normal redox reaction, S stands for the reductant. A plot of k_{obs}^{-1} vs. $[S]^{-1}$ 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 (Ukoha, 1999). The negligible intercept observed for this reaction confirm that the reactions occurred through the outer-sphere mechanism.

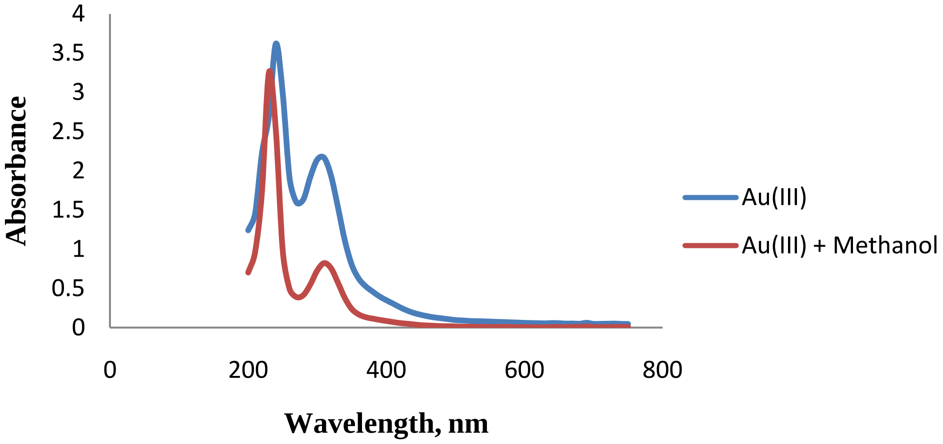
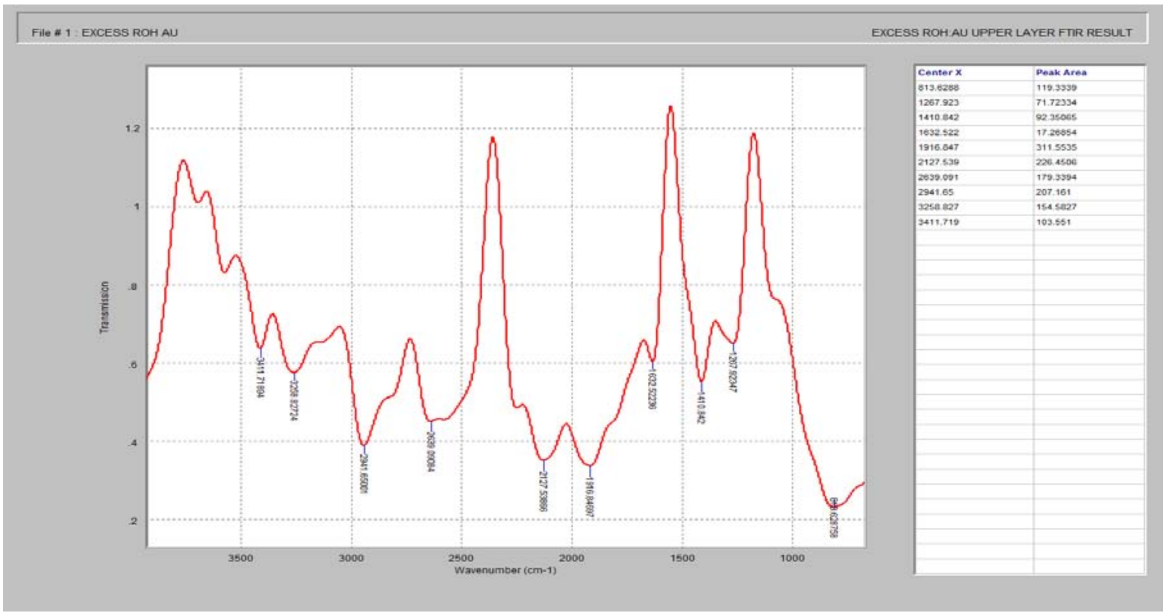


Figure 7: UV-Vis spectrum of reaction mixture after three minutes of reaction


File # 1 : EXCESS ROH AU

EXCESS ROH:AU UPPER LAYER FTIR RESULT

Center X	Peak Area
813.6288	119.3339
1267.923	71.72334
1410.842	92.35065
1632.522	17.26854
1916.847	311.5535
2127.539	226.4506
2639.091	179.3394
2941.65	207.161
3258.827	154.5827
3411.719	103.551

Figure 8: FTIR spectrum of aldehyde from methanol oxidation

Based on the underlisted evidence obtained from the reaction;

1. Absence of spectroscopically determinable intermediate complex
2. Negligible intercepts from Michaelis - Menten – type plot

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

$$\text{HAuCl}_4 + \text{H}_2\text{O} \overset{K_1}{\rightleftharpoons} \text{AuCl}_3(\text{OH})^- + \text{Cl}^- + 2\text{H}^+ \qquad 13$$

$$\text{AuCl}_3(\text{OH})^- + \text{MeOH} \xrightarrow[\text{slow}]{k_1} \text{MeO} + \text{H}_2\text{O} + \text{AuCl}_2 + \text{Cl}^- \qquad 14$$

$$\text{AuCl}_2 \overset{K_2}{\rightleftharpoons} \text{AuCl} + 1/2\text{Cl}_2 \qquad 15$$

$$\text{MeOH} + \text{H}^+ \overset{K_3}{\rightleftharpoons} \text{MeOH}_2^+ \qquad 16$$

$$\text{HAuCl}_4 + \text{MeOH}_2^+ \xrightarrow[\text{slow}]{k_2} \text{AuCl}_3^- + \text{MeO} + 2\text{H}^+ + \text{HCl} \qquad 17$$

$$\text{AuCl}_3^- + \text{H}^+ \xrightarrow[\text{fast}]{k_3} \text{AuCl}_2 + \text{HCl} \qquad 18$$

$$\text{AuCl}_2 \xrightarrow[\text{fast}]{k_2} \text{AuCl} + 1/2\text{Cl}_2 \qquad 19$$

$$\text{Rate} = k_1[\text{AuCl}_3(\text{OH})^-][\text{ MeOH}] + k_2[\text{MeOH}_2^+][\text{HAuCl}_4] \qquad 20$$

$$\text{Rate} = k_1[\text{AuCl}_3(\text{OH})^-][\text{ MeOH}] + \frac{k_2K_3[\text{MeOH}][\text{HAuCl}_4]}{[\text{H}^+]} \qquad 21$$

$$\text{Rate} = k_1 + \frac{k_2K_3}{[\text{H}^+]}[\text{ MeOH}][\text{HAuCl}_4] \qquad 22$$

Equation 22 is similar to Equation 6 where ‘a’= k_1 and ‘b’ = k_2K_3 with values previously stated. This is consistent with the nature of acid dependence observed for this reaction. Aldehyde formation has been reported as the oxidation product of methanol 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 (Kothari and Banerji, 2011; Mansoor and Shafi, 2014).

CONCLUSION

The kinetics, thermodynamics and mechanisms of the reduction of $[\text{AuCl}_3(\text{OH})]^-$ by methanol, was studied. The reaction had a 1:1 mole ratio with respect to oxidant and reductant, unity order with respect to both oxidant and reductant concentrations with second order overall was observed for the reaction. An inverse acid dependence was noted while changes in ionic strength and dielectric constant of the reaction media had negligible effect on the reaction rate. Enthalpy (kJ mol^{-1}) and entropy ($\text{JK}^{-1}\text{mol}^{-1}$) of activation for the reaction are 6.101 and -196.82. Polymerisation of acrylamide monomers was not observed suggesting the absence of free radicals in the reaction. Michaelis – Menten – type plot had negligible intercept. FTIR spectral 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 – type plot, outer sphere mechanism has been proposed for the reduction of $[\text{AuCl}_3(\text{OH})]^-$ by methanol.

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