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REDUCTION OF THE GOLD(III) COMPLEX ION, $[AUCl_3OH]^-$, BY *N*-METHYLTHIOUREA, *N, N*'–DIMETHYLTHIOUREA AND *N, N'*- DIETHYLTHIOUREA IN AQUEOUS ACID: KINETIC, THERMODYNAMIC AND MECHANISTIC STUDIES

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ABSTRACT

The kinetic, thermodynamic and mechanistic studies of the reduction of the gold(III) complex ion, $[AuCl_3OH]^-$ by *N*-methylthiourea (MTU), *N, N*'- dimethylthiourea (DMTU) and *N, N*'– diethylthiourea (DETU) were studied spectrophotometrically in aqueous acid. Stoichiometry revealed that two moles of *N*-methylthiourea, *N,N*'–dimethylthiourea and *N,N'*- diethylthiourea each were oxidised by one mole of gold(III) ion. The rate showed a first order dependence on $[AuCl_3OH]^-$ and half-order on [reductants] with one and half order overall. The reactions were biphasic revealing an initial substitution step and a final electron transfer phase. Addition of acid within the range 5.0 x10^{-4} - 1.0 x 10^{-2} mol dm^{-3} led to decrease in the reaction rate. The rate equation at constant $[H^+]$ and ionic strength is $\frac{-d[AuCl_3(OH)^-]}{dt} = k_{1\frac{1}{2}}[H^+]^{-1}[[AuCl_3(OH)^-][reduc\tan ts]^{\frac{1}{2}}$ where $k_{1\frac{1}{2}}$ (dm$^{\frac{3}{2}}$ mol$^{-\frac{1}{2}}$s^{-1}) = 0.335±0.09 ((MTU), 0.389±0.09 (DMTU and 0.408±0.11 (DETU) for the substitution process, 0.044±0.003 (MTU), 0.058±0.001 (DMTU) and 0.059±0.002 (DETU) for the electron transfer reaction, Varying ionic strength from 1.0 x 10^{-2} - 1.0 x10^{-1} mol dm^{-3} had no significant effect on the rate of the reaction. Added anion and cation as well as change in the dielectric constant of the reactions media had no effect on the reactions rates. Presence of free radical was detected in the course of the reactions. Entropies of activation (JK^{-1} mol^{-1}) were -189.65, -215.82 and -214.74 for MTU, DMTU and DETU respectively while activation enthalpies (kJ mol^{-1}) were 7.329, 8.424 and 3.837 for MTU, DMTU and DETU. For all the reactions, Au(I) was found to be the product of $[AuCl_3(OH)]^-$ reduction while disulphide was obtained for reductants oxidation. Michaelis-Menten's type plot showed appreciable positive intercepts for these reactions. Mechanisms consistent with experimental data have been proposed.

Keywords: Reduction, Gold(III) complex ion, *N*-methylthiourea, *N, N*'- dimethyl thiourea, *N, N*'– diethyl thiourea

INTRODUCTION

The interest in the chemistry of thiourea and its derivatives stem from the fact that they possess two donor atoms (nitrogen and sulphur) which are susceptible to coordination or binding relevant to those in living organisms [1]. Derivatives of thiourea have a broad range of importance in synthetic reactions as intermediates which makes them versatile compounds [2]. These compounds are utilized in many commercial products such as dyes, elastomers, photographic films, plastics and textiles [3]. The most significant and effective usage of thioureas is in the biological functions they exhibit as antioxidant, antibacterial, anti-inflammatory, anticancer, anti-Alzheimer, antimalarial and antitubercular agents as a result of their tautomeric forms by electron movement [4-6].

The electron transfer reaction of these thioureas with metal ions especially those of transition metals is an important chemical process in nature. It plays a key role in biochemical phenomenon and investigates the functions of metal complexes such as metalloproteins and haemoglobin. These reactions are also employed in industrial chemistry for exploiting metal complexes as homogeneous catalysts and in medicinal and environmental chemistry for chelate therapy [7]. Electron transfer reactions involved in biological processes are collagen synthesis, steroid metabolism, the immune response, drug activation, neurotransmitter metabolism, nitrogen fixation, respiration and photosynthesis.

The electron transfer reactions of transition metal complexes including those of gold have been linked to their numerous biological functions. Gold complexes have been used in chrysotherapy for the treatment of rheumatoid arthritis and as anti- tumor agents. Due to these functions, several gold compounds have been synthesized and applied in drug delivery systems as complexes and nano rods [8]. At physiological conditions, gold(I) drugs may be activated *in vivo* to gold(III) metabolites but the intrinsic mechanisms driving these physiological processes have not been fully unraveled. This paucity of kinetic and mechanistic data have limited the applications of gold(III) derived drugs. The paper presents the kinetic, thermodynamic and mechanistic insights of the reduction of gold(III) ions with biomolecules derived from thiourea. It is hoped that our results will unravel the mechanisms driving the speciation of gold compounds under physiological conditions.

MATERIALS AND METHODS

The following analytical grade chemicals available commercially were used without further purification. Hydrogen tetrachloroaurate(III) trihydrate (Sigma–Aldrich, 99 %) was used as the oxidizing agent, *N*-methylthiourea, *N, N*'-dimethylthiourea and *N, N*'– diethylthiourea (Sigma –Aldrich, 99 %) were the reducing agents, hydrogen tetraoxochlorate (VII) (70 %, Sigma –Aldrich) was used to maintain [H^+], $NaClO_4$ (Sigma–Aldrich, 98 %) was used to maintain ionic strength while sodium acetate (ThermoFisher Scientific, 99.9 %) and potassium tetraoxochlorate (VII) (ThermoFisher Scientific, ≥95 %) were used as catalysts. Acrylamide with methanol were used to check for the presence of free radicals in the reaction. UV-Vis spectra were obtained using Jenway 6405 UV-Vis spectrophotometer, FTIR spectra were recorded on ThermoFisher Scientific Nicolet^{TM} iS50 spectrophotometer, OHAUS PX224/E digital weighing balance was used to weigh all solid chemicals, HH-4 PEC medical USA thermostat water bath was used to heat the reaction mixtures during the temperature dependent study while a digital stop watch was used to monitor the reactions rate.

Kinetic measurements

The stoichiometry was determined by spectrophotometric titrations using mole ratio method [9] under the conditions of $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, $\mu = 0.02$ mol dm^{-3} ($NaClO_4$), $[AuCl_3(OH)]^- = 1 \times 10^{-4}$ mol dm^{-3}, [reductants] = ($2.0 \times 10^{-5} – 4.0 \times 10^{-4}$) mol dm^{-3}, T = 30.0 ± 1.0 ºC and λ_{max} = 310 nm. Stoichiometries of the reactants were determined from points of inflexion on the curves of absorbance at infinity versus mole ratio of reactants.

All kinetic measurements were performed under pseudo-first-order conditions with [reductants] present in at least 20 folds excess over $[AuCl_3(OH)^-]$ at T= 30.0 ± 1.0 ºC, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3} and 0.50 mol dm^{-3} ($NaClO_4$) ionic strength. The rate data were obtained 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 plots of $\log(A_t - A_\infty)$ versus time as in equation 1

$$In(At - A_\infty) = In(A_o - A_\infty) - k_{obs}t \tag{1}$$

Where A_t is absorbance at time t, A_∞ is absorbance at infinity, A_o is initial absorbance, k_{obs} is pseudo – first order rate constant. The one and half order rate constants, $k_{1\frac{1}{2}}$, were determined as the ratio of k_{obs} : [reductants] [9]. The influence of acid concentration from $5.0 \times 10^{-4} – 1.2 \times 10^{-1}$ mol dm^{-3} and ionic strength $1.0 \times 10^{-2} – 1.2 \times 10^{-1}$ mol dm^{-3} on the rates of the reactions were investigated while maintaining other reaction conditions constant. The dielectric constants of the media were estimated by varying the ratio of acetone to water using equation 2

$$D_{reaction\ medium} = \frac{(D_{water} \times V_{water}) + (D_{acetone} \times V_{acetone})}{V_{total}} \tag{2}$$

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

Keeping other parameters constant, $1.0 \times 10^{-3} – 1.4 \times 10^{-2}$ mol dm^{-3} of sodium acetate, sodium nitrate and potassium perchlorate were added to determine their catalytic or inhibitory role on the rates of the reactions.

Presence of free radical intermediate was determined by adding acrylamide to the partially reduced reaction mixtures in excess methanol as reported elsewhere [10]. Gel formation indicated the presence of free radical. The presence of stable and detectable intermediates formed during the course of the reaction was monitored by reacting 1 .0 x 10^{-4} moldm^{-3} of oxidant and 6.0

x 10^{-3} $moldm^{-3}$ of each reductant at constant condition of other parameters.

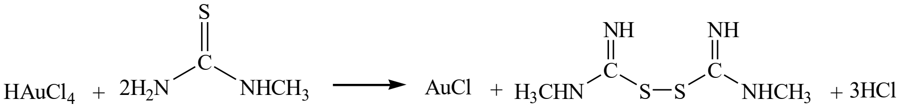
Temperature of the reactions was varied from 303-318 K and its effect on the rates of the reactions was investigated. Using equation 3, plots of ln(k/T) versus 1/T were made from where the activated enthalpy and entropy were determined.

$$\ln\frac{k}{T} = 23.759 + \frac{\Delta S^{\mp}}{R} - \frac{\Delta H^{\mp}}{R}.\frac{1}{T} \qquad (3)$$

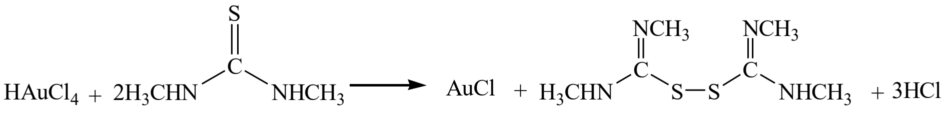
RESULTS AND DISCUSSION

Stoichiometry

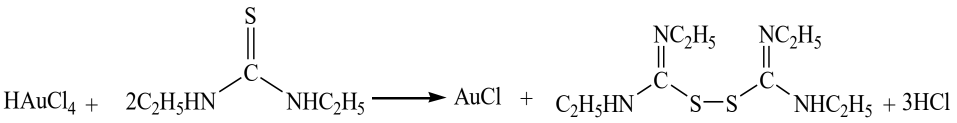
Spectrophotometric estimation of the reaction showed that one mole of $AuCl_3(OH)^-$ was consumed for two moles each of reductants oxidised. The results agree with equations (4 - 6)



$$HAuCl_4 + 2H_2N{-}C(=S){-}NHCH_3 \longrightarrow AuCl + H_3CHN{-}C(=NH){-}S{-}S{-}C(=NH){-}NHCH_3 + 3HCl \qquad (4)$$



$$HAuCl_4 + 2H_3CHN{-}C(=S){-}NHCH_3 \longrightarrow AuCl + H_3CHN{-}C(=NCH_3){-}S{-}S{-}C(=NCH_3){-}NHCH_3 + 3HCl \qquad (5)$$

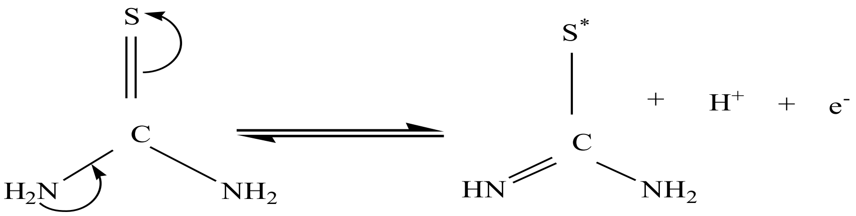


$$HAuCl_4 + 2C_2H_5HN{-}C(=S){-}NHC_2H_5 \longrightarrow AuCl + C_2H_5HN{-}C(=NC_2H_5){-}S{-}S{-}C(=NC_2H_5){-}NHC_2H_5 + 3HCl \qquad (6)$$

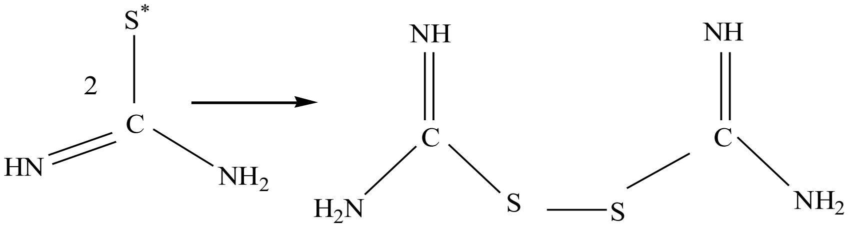
The absence of Au(III) ion was checked to ensure its reduction using the qualitative test as described by [11] with slight modifications. Excess of each of the reductants was reacted with $AuCl_3OH^-$ and allowed to go to completion. About 2 cm^3 portion of the reaction mixture was reacted with alkaline solution of H_2O_2 (Equation 7). Lack of precipitate showed the absence of Au(III).

$$2[AuCl_4]^- + 3H_2O_2 + 6OH^- \rightarrow 2Au_{(s)} + 3O_{2(g)} + 8Cl^-_{(aq)} + 6H_2O \qquad (7)$$

Reduction of Au(III) with thioureas has been documented to give Au(I) at low concentration of the reductants with the formation of disulphide. Formation of Au(0) is possible at higher concentration and large excess of thiourea as the Au(I) formed in solution is further reduced to Au(0) [12]. The oxidation of thioureas led to the formation of formamidine disulphide. The organic products were extracted severally with diethyl ether, washed, dried and their FTIR spectra obtained. FTIR bands for disulphide linkage formation (Figures 1a – c) showing weak bands from 574 - 414 cm^{-1}. The oxidation of thioureas in acidic and neutral media have been reported to follow a two-step mechanistic route where the tautomeric form of thiourea [HSC(=NH)NH_2], is firstly oxidized to a thiourea free radical [*SC(=NH)NH_2], which is then followed by the combination of two free radicals to form formamidine disulphide (Equations 8 and 9). It is greatly improbable that the reduction of the disulphide redox couple under these pH will proceed through its breakdown into two thiourea free radicals which are subsequently reduced to thiourea as most disulphides do not undergo thermal homolytic dissociation to generate thiyl radicals even at 100 °C [13].



(8)



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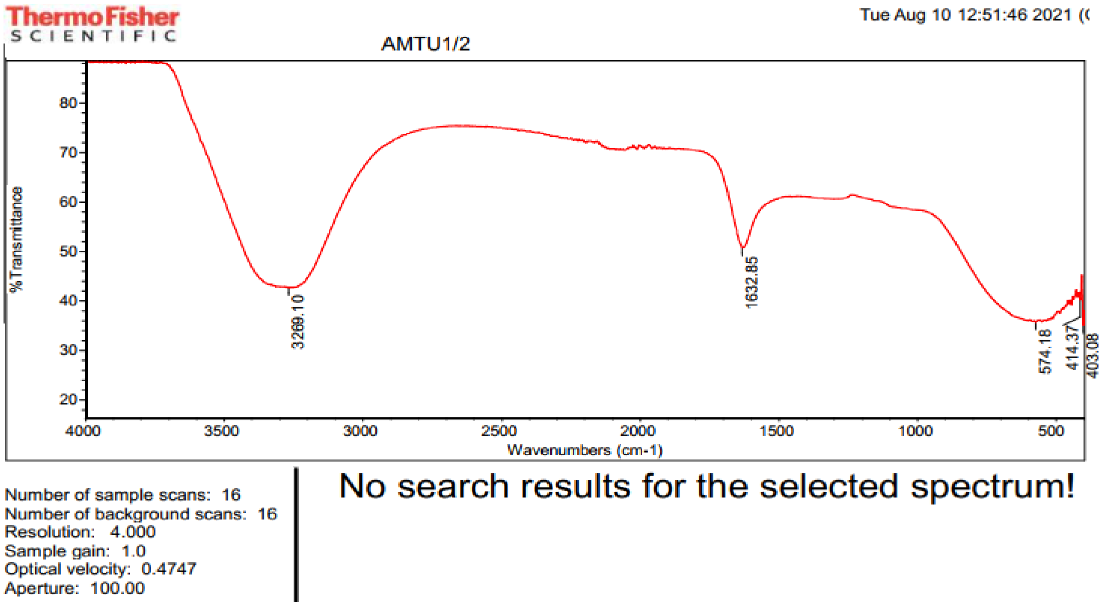

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Number of background scans: 16
Resolution: 4.000
Sample gain: 1.0
Optical velocity: 0.4747
Aperture: 100.00

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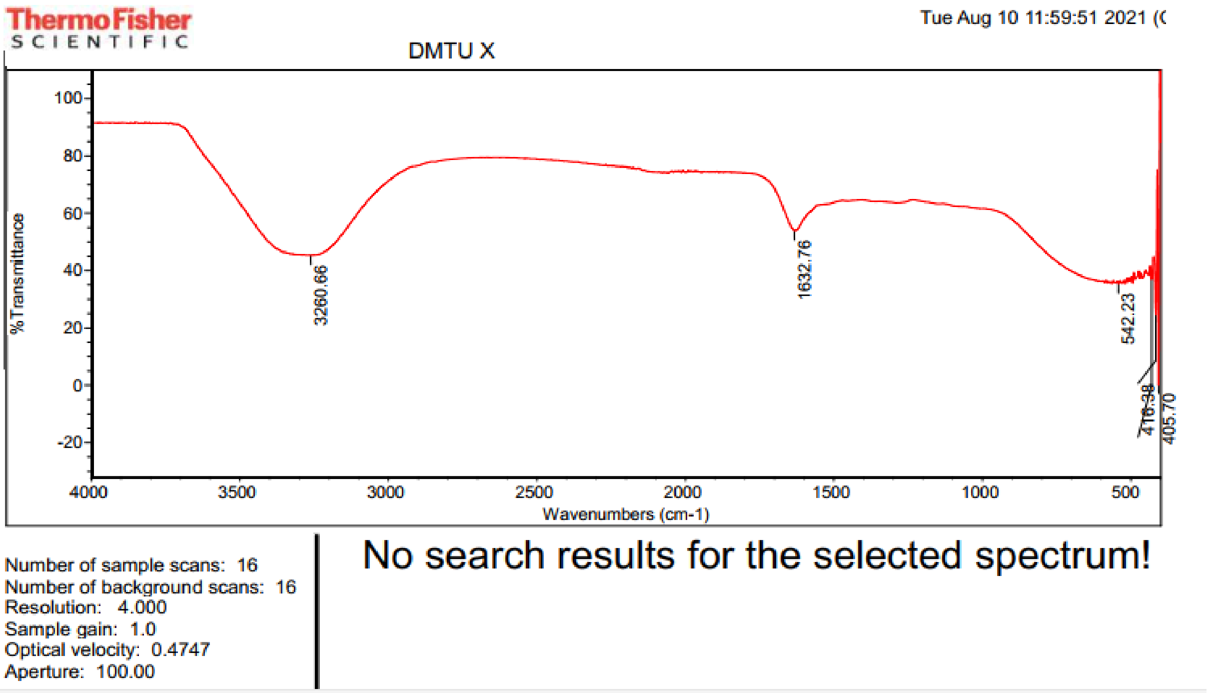
1(a)



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Resolution: 4.000
Sample gain: 1.0
Optical velocity: 0.4747
Aperture: 100.00

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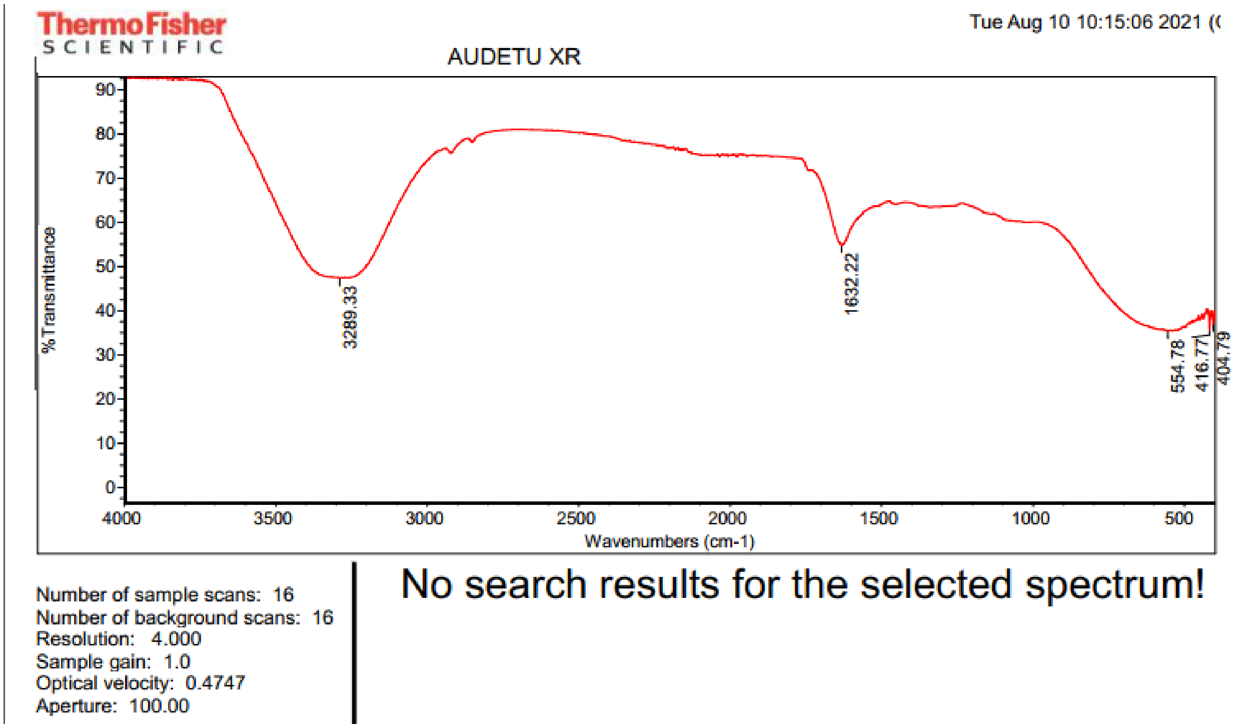
1(b)



Number of sample scans: 16
Number of background scans: 16
Resolution: 4.000
Sample gain: 1.0
Optical velocity: 0.4747
Aperture: 100.00

No search results for the selected spectrum!

1(c)

Figures 1a-c: FTIR spectra of formamidine disulphide from MTU, DMTU and DETU oxidation

Kinetic study

Under pseudo - first order kinetics at constant oxidant concentration, reactions of these thioureas with $[AuCl_3(OH)]^-$ were biphasic which revealed an initial substitution step characterized by increase in absorbance and a final electron transfer phase. Typical kinetic data obtained as absorbance against reaction time fitted into a double exponential function plot (Figure 2) showing the substitution as well as the subsequent electron transfer step. However, for ease of results analyses, they have been separated to show each phase of the reaction. Plots of $\ln(A_t-A_\infty)$ versus time were made and linear to more than 85 % extent of reaction. This indicates first order dependence of rate on concentration of the oxidant. Pseudo-first order rate constants, k_{obs} are in Tables 1- 3. Upon increasing [reductants] from 2.0×10^{-3} to 1.2×10^{-2} $moldm^{-3}$ at $[AuCl_3(OH)^-]$ of 1.0×10^{-4} $moldm^{-3}$, k_{obs} also increased.

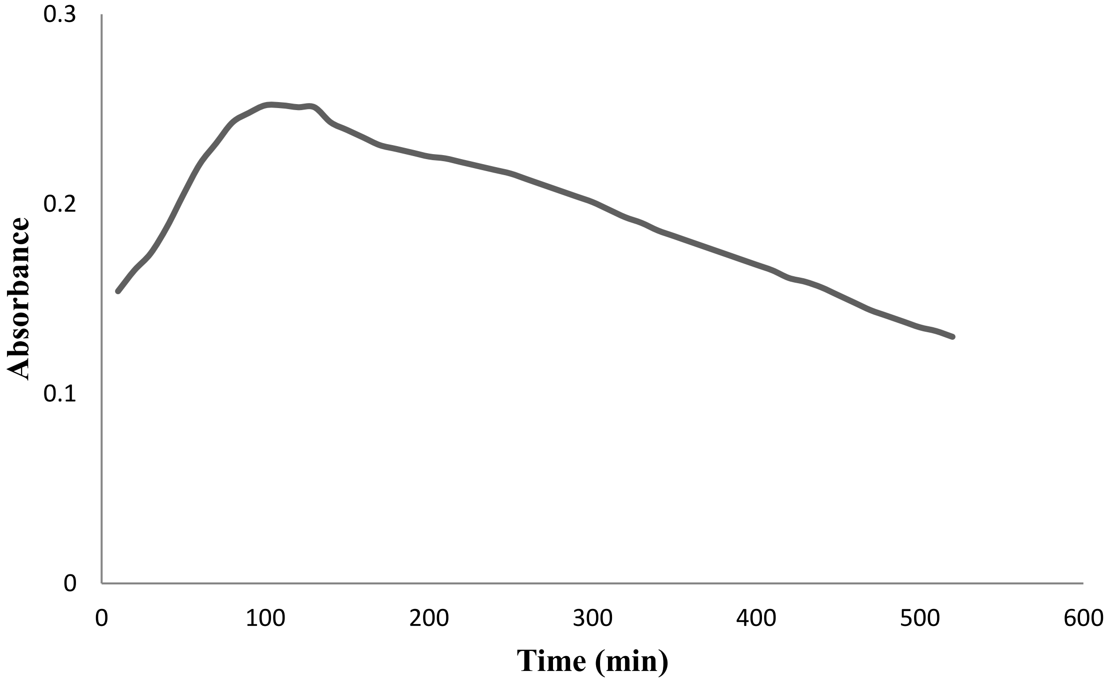


Figure 2: Typical biphasic kinetic plot obtained for the reaction of 1.0×10^{-4} mol dm^{-3} $[AuCl_3(OH)]^-$ with a forty- fold excess of MTU

From the k_{obs} obtained, one and half order rate constants, $k_{1\frac{1}{2}}$, were evaluated and presented (Tables 1 - 3). Orders of reaction in [reductants] obtained from slopes of the plots of log k_{obs} versus log[reductants] at constant $[H^+]$ and ionic strength for $[AuCl_3(OH)]^-$: *N*-methylthiourea system are 0.519 (substitution) and 0.508 (electron transfer), $[AuCl_3(OH)]^-$: *N,N'*-

dimethylthiourea system are 0.530 (substitution) and 0.506 (electron transfer) and $[AuCl_3(OH)]^-$: *N,N'*-diethylthiourea system are 0.498 (substitution) and 0.493 (electron transfer). This indicates half-order dependence of rate on [reductants] and one and half order overall. Most half order kinetics favour reactions occurring through an inner-sphere mechanism and they are rationalised on the basis of molecular dissociation [14] or monomer-polymer equilibrium where the monomer is the active specie [15].

Similar fractional order with respect to [reductants] has been reported for the reduction of Au(III) ions with L-tyrosine[16] and formic acid [17]. Half order with respect to formic acid concentration was rationalised on the basis of the complexity in the electron transfer reaction of gold(III) ion. The rate equation for the reaction between $[AuCl_3(OH)]^-$ and the reductants is represented (equation 10).

$$-d\frac{[AuCl_3(OH)]^-}{dt} = k_{1\frac{1}{2}}[AuCl_3(OH)^-][reduc\tan ts]^{1/2} \tag{10}$$

From the ratios of k_{obs}: [reductants], one and half orders rate constants $k_{1\frac{1}{2}}$ ($dm^{3/2}\ mol^{-1/2}\ s^{-1}$) were obtained and fairly constant (Tables 1- 3) with mean values of $[AuCl_3(OH)^-]$ – [MTU] = 3.35 x 10^{-1} ±0.09 (substitution) and 4.40 x 10^{-2} ±0.003 (electron transfer); $[AuCl_3(OH)^-]$ – [DMTU] = 3.89 x 10^{-1} ±0.09 (substitution) and 5.80 x 10^{-2}±0.001 (electron transfer); $[AuCl_3(OH)^-]$ – [DETU] = 4.08 x 10^{-1} ±0.11(substitution) and 5.92 x 10^{-2}±0.002 (electron transfer).

Table 1: kobs and one and half order rate constants for the reaction of $[AuCl_3(OH)]^-$ and MTU

10^3[MTU], mol dm^{-3}	$10^3[H^+]$, mol dm^{-3}	$10^2\mu$, mol dm^{-3}	k_{sub}		k_{et}	
			10^2k_{obs}, s^{-1}	$k_{3/2}$, dm$^{3/2}$ mol$^{-1/2}$ s^{-1}	10^3k_{obs}, s^{-1}	$10^2k_{3/2}$, dm$^{3/2}$ mol$^{-1/2}$ s^{-1}
2.0	1.0	5.0	1.49	0.332	2.00	4.48
4.0	1.0	5.0	2.06	0.326	2.74	4.33
6.0	1.0	5.0	2.65	0.343	3.22	4.14
8.0	1.0	5.0	2.92	0.326	3.87	4.32
10.0	1.0	5.0	3.42	0.342	4.54	4.54
12.0	1.0	5.0	3.76	0.344	4.97	4.54
6.0	0.5	5.0	2.76	0.356	3.75	4.84
6.0	2.0	5.0	2.26	0.292	2.93	3.78
6.0	4.0	5.0	1.98	0.255	2.65	3.42
6.0	6.0	5.0	1.77	0.228	2.44	3.15
6.0	8.0	5.0	1.61	0.208	2.23	2.88
6.0	1.0	1.0	2.64	0.341	3.25	4.19
6.0	1.0	2.0	2.65	0.342	3.16	4.07

6.0	1.0	4.0	2.65	0.342	3.20	4.13
6.0	1.0	5.0	2.65	0.342	3.22	4.16
6.0	1.0	6.0	2.65	0.342	3.39	4.37
6.0	1.0	8.0	2.63	0.340	3.34	4.31
6.0	1.0	10.0	2.69	0.347	3.25	4.19

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

Table 2: kobs and one and half order rate constants for the reaction of $[AuCl_3(OH)]^-$ and DMTU

10^3[DMTU], mol dm^{-3}	**$10^3[H^+]$, mol dm^{-3}**	**$10^2\mu$, mol dm^{-3}**	**k_{sub}**		**k_{et}**	
			10^2k_{obs}, s^{-1}	**$k_{3/2}$, dm$^{3/2}$ mol$^{-1/2}$ s^{-1}**	**10^3k_{obs} s^{-1}**	**$10^2k_{3/2}$, dm$^{3/2}$ mol$^{-1/2}$ s^{-1}**
2.0	1.0	5.0	1.69	0.377	2.57	5.75
4.0	1.0	5.0	2.40	0.379	3.69	5.83
6.0	1.0	5.0	3.05	0.394	4.42	5.71
8.0	1.0	5.0	3.54	0.396	5.23	5.85
10.0	1.0	5.0	3.94	0.394	5.87	5.87
12.0	1.0	5.0	4.32	0.394	6.32	5.77
6.0	0.5	5.0	3.52	0.454	4.74	6.12
6.0	2.0	5.0	2.73	0.353	4.01	5.17
6.0	4.0	5.0	2.54	0.328	3.71	4.79
6.0	6.0	5.0	2.27	0.293	3.46	4.46
6.0	8.0	5.0	2.07	0.267	3.06	3.95
6.0	10.0	5.0	1.84	0.238	2.93	3.78
6.0	1.0	1.0	3.08	0.397	4.40	5.68
6.0	1.0	2.0	3.04	0.392	4.40	5.68
6.0	1.0	4.0	3.03	0.391	4.38	5.65
6.0	1.0	5.0	3.05	0.393	4.35	5.62
6.0	1.0	6.0	3.04	0.392	4.42	5.71
6.0	1.0	8.0	3.15	0.406	4.35	5.62
6.0	1.0	10.0	3.04	0.392	4.38	5.65

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

Table 3: kobs and one and half order rate constants for the reaction of $[AuCl_3(OH)]^-$ and DETU

10^3[DETU], mol dm^{-3}	**$10^3[H^+]$, mol dm^{-3}**	**$10^2\mu$, mol dm^{-3}**	**k_{sub}**	**k_{et}**

			10^2k_{obs}, s^{-1}	**$k_{3/2}$, $dm^{3/2}\ mol^{-1/2}\ s^{-1}$**	**10^3k_{obs}, s^{-1}**	**$10^2k_{3/2}$, $dm^{3/2}\ mol^{-1/2}\ s^{-1}$**
2.0	1.0	5.0	1.86	0.416	2.69	6.03
4.0	1.0	5.0	2.44	0.386	3.73	5.90
6.0	1.0	5.0	3.24	0.418	4.49	5.80
8.0	1.0	5.0	3.74	0.418	5.37	6.00
10.0	1.0	5.0	4.07	0.407	5.85	5.85
12.0	1.0	5.0	4.40	0.401	6.54	5.97
6.0	0.5	5.0	3.67	0.473	4.63	5.98
6.0	2.0	5.0	3.16	0.407	3.66	4.73
6.0	4.0	5.0	2.84	0.367	2.67	3.45
6.0	6.0	5.0	2.45	0.317	2.46	3.18
6.0	8.0	5.0	2.25	0.290	2.07	2.68
6.0	10.0	5.0	2.15	0.278	1.91	2.47
6.0	1.0	1.0	3.39	0.437	4.42	5.71
6.0	1.0	2.0	3.32	0.429	4.15	5.35
6.0	1.0	4.0	3.43	0.443	4.28	5.53
6.0	1.0	5.0	2.93	0.378	4.28	5.53
6.0	1.0	6.0	3.43	0.443	4.31	5.56
6.0	1.0	8.0	3.43	0.443	4.31	5.56
6.0	1.0	10.0	3.39	0.437	4.37	5.64

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

The order of reactivity followed the trend DETU > DMTU > MTU. The alkyl substituents attached to the thioureas had inductive effect on these thioureas. The trend of rate constants observed could be explained on the basis of more positive inductive effect from the di-alkyl substituted thioureas than on the mono-alkyl substituted thiourea. For this reason, the rate for dimethylthiourea and diethylthiourea are of comparable magnitude and higher than the rate for methylthiourea. It is also noted that rate for the substitution phase, k_{sub}, was about seven times greater than rate of the electron transfer process, k_{et}, indicating substitution-controlled reactions which points to inner - sphere mechanistic pathway.

Within the acid concentration range, 5.0×10^{-4}- 1.0×10^{-2} mol dm^{-3}, the reaction rate decreased as $[H^+]$ increased for all the reductants. Inverse acid dependence is generally linked with reactions involving a deprotonation step before the electron transfer step or for situations when a particular reactant exists in two or more forms which are in equilibrium involving hydrogen ion with the deprotonated form as the reactive species. The oxidant, $HAuCl_4$ is a strong acid which deprotonates in aqueous solution (equation 11)

$$HAuCl_4 + H_2O \rightleftharpoons AuCl_3(OH)^- + Cl^- + 2H^+ \qquad (11)$$

The inverse acid dependence observed for these reactions can be attributed to the equilibrium established by the ionisation of $HAuCl_4$. Increasing hydrogen ion concentration led to common ion effect thereby decreasing the rate of the forward reaction. Similar inverse acid dependence has been documented for the reduction of gold(III) ion by L-tyrosine [16] and oxalic acid [18]. This study explained the inverse acid dependence on the basis of the deprotonation of the gold(III) compound. At constant [H+], ionic strength and temperature, rate equation is expressed (Equation 12).

$$Rate = a + \frac{b}{[H^+]}[AuCl_3(OH)^-][reductants]^{1/2} \qquad (12)$$

This suggests that the reaction proceeded by two parallel pathways of inverse acid dependent and the other is acid independent where the inverse dependence predominated the reaction.

Variation of ionic strength within the range (1 x10^{-3} – 1.2 x10^{-2}) moldm^{-3} at constant concentrations of the other reactants showed that rate was not dependent on the ionic strength. The non-dependence of rate on ionic strength observed in these reactions was an implication of the neutrality of one or more of the reacting specie. Rate independence on ionic strength means either one or both redox partners is/are neutral [19] or the reaction involves an ion-pair or adduct [20]. Similar non-dependence of rate on variation in ionic strength has been reported for the reduction of gold(III) ions [16,18].

Table 4 Dependence of rate constant on dielectric constant and on added ions for the reaction of $[AuCl_3(OH)]^-$ and MTU

10^3 (MTU) (mole dm^{-3})	X	10^3[X] (mole dm^{-3})	Substitution		Electron transfer	
			10^2k_{obs}, s^{-1}	$k_{3/2}$, dm$^{3/2}$ mol$^{-1/2}$ s^{-1}	10^3k_{obs}, s^{-1}	$10^2k_{3/2}$, dm$^{3/2}$ mol$^{-1/2}$ s^{-1}
6.0	CH_3COO^-	2.0	2.64	0.340	3.16	4.07
6.0		4.0	2.66	0.343	3.18	4.10
6.0		6.0	2.64	0.341	3.25	4.19
6.0		8.0	2.65	0.342	3.16	4.07
6.0		10.0	2.65	0.342	3.25	4.19
6.0		12.0	2.65	0.342	3.21	4.15
6.0	K^+	2.0	2.64	0.340	3.29	4.25

6.0		4.0	2.64	0.340	3.29	4.25
6.0		6.0	2.66	0.343	3.27	4.22
6.0		8.0	2.65	0.342	3.31	4.28
6.0		10.0	2.66	0.343	3.22	4.16
6.0		12.0	2.66	0.343	3.22	4.16
	D					
6.0	78.40		2.65	0.343	3.22	4.14
6.0	77.59		2.68	0.345	3.27	4.22
6.0	76.79		2.64	0.341	3.27	4.22
6.0	75.99		2.70	0.349	3.22	4.16
6.0	75.19		2.67	0.344	3.27	4.22
6.0	74.39		2.65	0.342	3.25	4.19
6.0	73.59		2.65	0.342	3.29	4.25

Table 5 Dependence of rate constant on dielectric constant and on added ions for the reaction of $[AuCl_3(OH)]^-$ and DMTU

10^3 (DMTU) (mole dm^{-3})	X	10^3[X] (mole dm^{-3})	Substitution		Electron transfer	
			10^2k_{obs}, s^{-1}	$k_{3/2}$, $dm^{3/2}$ $mol^{-1/2}$ s^{-1}	10^3k_{obs}, s^{-1}	$10^2k_{3/2}$, $dm^{3/2}$ $mol^{-1/2}$ s^{-1}
6.0	CH_3COO^-	2.0	3.06	0.395	4.47	5.77
6.0		4.0	3.04	0.393	4.40	5.68
6.0		6.0	3.06	0.395	4.40	5.68
6.0		8.0	3.04	0.393	4.46	5.75
6.0		10.0	3.03	0.392	4.42	5.71
6.0		12.0	3.05	0.394	4.40	5.68
6.0	K^+	2.0	2.96	0.382	4.35	5.62
6.0		4.0	3.03	0.392	4.42	5.71
6.0		6.0	3.03	0.392	4.38	5.65
6.0		8.0	3.04	0.393	4.42	5.71
6.0		10.0	3.02	0.389	4.28	5.53
6.0		12.0	3.03	0.392	4.39	5.66
	D					

6.0	78.40		3.05	0.394	4.42	5.71
6.0	77.59		3.12	0.403	4.40	5.68
6.0	76.79		3.03	0.391	4.42	5.71
6.0	75.99		3.08	0.398	4.38	5.65
6.0	75.19		3.04	0.392	4.42	5.71
6.0	74.39		3.05	0.394	4.45	5.74
6.0	73.59		3.12	0.403	4.39	5.67

Table 6 Dependence of rate constant on dielectric constant and on added ions for the reaction of $[AuCl_3(OH)]^-$ and DETU

10^3 (DETU) (mole dm^{-3})	X	10^3[X] (mole dm^{-3})	Substitution		Electron transfer	
			10^2k_{obs}, s^{-1}	$k_{3/2}$, $dm^{3/2}$ $mol^{-1/2}$ s^{-1}	10^3k_{obs}, s^{-1}	$10^2k_{3/2}$, $dm^{3/2}$ $mol^{-1/2}$ s^{-1}
6.0	CH_3COO^-	2.0	3.32	0.428	4.58	5.92
6.0		4.0	3.34	0.432	4.51	5.83
6.0		6.0	3.14	0.405	4.35	5.62
6.0		8.0	3.38	0.436	4.51	5.83
6.0		10.0	3.43	0.443	4.47	5.77
6.0		12.0	3.49	0.451	4.49	5.80
6.0	K^+	2.0	3.19	0.411	4.45	5.74
6.0		4.0	3.30	0.427	4.28	5.53
6.0		6.0	3.39	0.438	4.35	5.62
6.0		8.0	3.31	0.429	4.49	5.80
6.0		10.0	3.14	0.406	4.31	5.56
6.0		12.0	3.32	0.430	4.44	5.73
	D					
6.0	78.40		3.24	0.418	4.49	5.80
6.0	77.59		3.44	0.444	4.49	5.80
6.0	76.79		3.22	0.416	4.35	5.62
6.0	75.99		3.34	0.431	4.33	5.59
6.0	75.19		3.13	0.404	4.35	5.62
6.0	74.39		3.39	0.439	4.35	5.62

6.0	73.59		3.26	0.421	4.40	5.68

Results for the effect of added ions are contained in Tables 4 – 6. Added anion and cation did not affect the rates of the reactions between $[AuCl_3(OH)]^-$ and TSH. Absence of ion catalysis is a common feature of inner-sphere mechanisms where there is formation of a bridged intermediate complex. Bridge formation between reactants brings them close to each other which make interaction or interference from other ions difficult.

Variation in the dielectric constant of the reaction media from 78.40-73.59 (Tables 4 – 6) using water: acetone ratios had no significant effect on the rates of these reactions. This supports the nature of salt effect observed for these systems and points towards inner-sphere mechanistic pathway.

Temperature dependence

Dependence of reaction rates on temperature were monitored from 303-318 K. Plots of ln(k/T) against T^{-1} were made (Figure 3). The activation enthalpies and entropies evaluated from these plots for the systems are contained in Table 7.

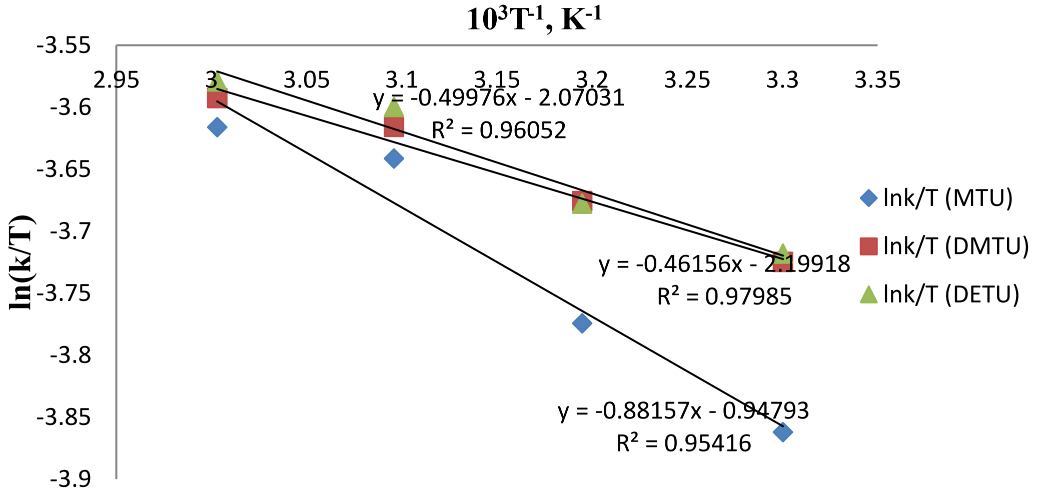


Figure 3: Plots of lnk/T against $10^3 1/T(K^{-1})$ for MTU, DMTU and DETU reactions

Table 7 Temperature dependence of rate constant and activation parameters for the reactions of $[AuCl_3(OH)]^-$ with the reductants at $[AuCl_3(OH)^-] = 1.0 \times 10^{-4}$ mol dm^{-3} and [reductant]= 6.0×10^{-3} mol dm^{-3}

Reductants	Temperature (K)	K_{sub}, dm$^{3/2}$ mol$^{-1/2}$ s^{-1} 10^2K_{et}, dm$^{3/2}$ mol$^{-1/2}$ s^{-1}	ΔS^*_{sub} ΔS^*_{et} (Jmol^{-1}K^{-1})	ΔH^*_{sub} ΔH^*_{et} (kJ mol^{-1})

MTU	303	0.343	4.14		
	308	0.540	5.26	-206.856 -205.413	6.511 7.329
	313	0.687	7.37		
	318	0.819	8.05		
DMTU	303	0.394	5.71		
	308	0.522	6.60	-205.957 -215.816	3.846 3.837
	313	0.715	7.82		
	318	0.850	8.50		
DETU	303	0.418	5.80		
	308	0.679	6.57	-206.693 -214.745	6.758 4.155
	313	0.870	8.12		
	318	0.981	8.77		

The negative entropy of activation for these reactions indicates systems where bond formation predominates bond dissociation. This could result from an ordered activation complex which is stabilized in solution [21]. The negative entropy of activation for these reactions points to an inner-sphere reaction pathway. The positive enthalpies of activation observed for these reactions can be explained in terms of enthalpy-controlled processes requiring high energy to reach transition state.

Test for free radical

Addition of acrylamide to the partially reduced reaction mixtures followed by the addition of excess methanol resulted to the formation of gelatinous precipitate. This is an indication of the polymerisation of the acrylamide monomers and confirms the participation of free radicals during the reactions. Formation of free radicals has been documented for the reduction of oxo-bridged ruthenium(IV) complex by thioureas [20].

Test for formation of intermediate complex

Michaelis-Menten type plot of k_{obs}^{-1} against $[reductants]^{-1}$ was made (Figure 4). Linear plots with appreciable intercepts were obtained indicating the presence of spectroscopically determinable intermediate complex with appreciable equilibrium constant. This characteristic is in favour of inner-sphere mechanism. Also, the electronic spectra of the reaction of the thioureas showed shift from the wavelength of maximum absorption of the oxidant at 310 nm indicating the presence of intermediate complex formation during the reactions (Figure 5).

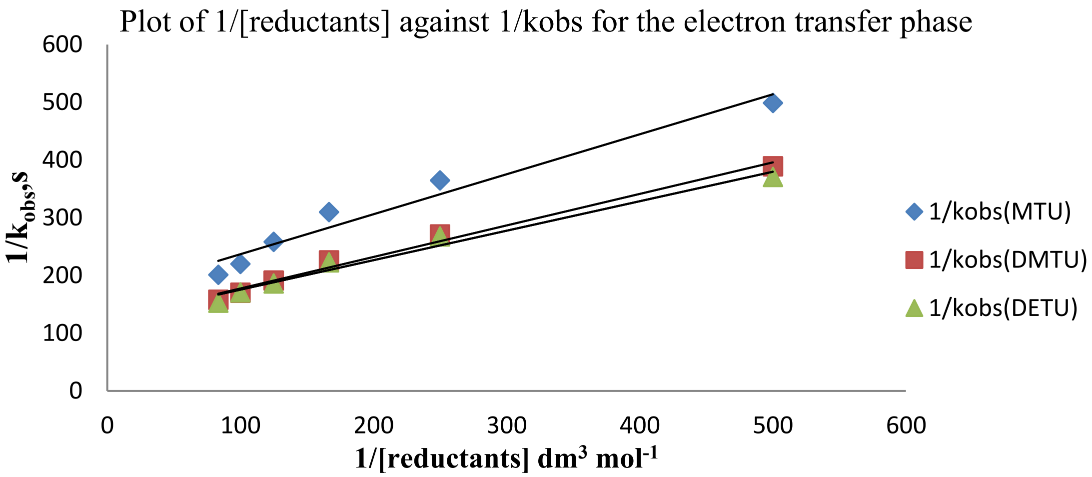


Figure 4: Michaelis-Menten type plot for the electron transfer phase of $[AuCl_3(OH)]^-$ and the reductants

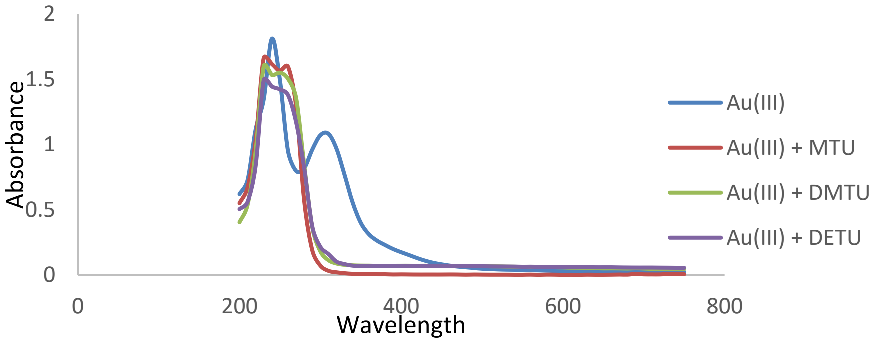


Figure 5: UV-Vis spectra of reaction mixtures after three minutes of reaction for $[AuCl_3(OH)]^-$ and the reductants

Mechanisms

Based on results of stoichiometry, acid-dependence, ionic strength, dielectric constant dependence, effect of added ions, entropy of activation and Michaelis- Menten type plots, inner-sphere mechanism has been proposed for the reaction of $[AuCl_3(OH)]^-$ with the reductants. The following plausible mechanistic steps have been outlined for the reactions (Equations 13 – 23).

$$2HAuCl_4 + H_2O \overset{K_1}{\rightleftharpoons} 2[AuCl_3OH^-] + 2H^+ + Cl^- \quad 13$$

$$TSH \overset{K_2}{\rightleftharpoons} TS^- + H^+ \quad 14$$

$$AuCl_3OH^- + TS^- \overset{k_3}{\rightleftharpoons} [AuCl_3OH^-TS]^{2-} \quad 15$$

$$[AuCl_3OH\text{-}TS]^{2-} \xrightarrow[\text{slow}]{k_4} AuCl_2 + OH^- + TS^* + Cl^- \quad 16$$

$$[AuCl_3OH]^- + TSH \xrightarrow[slow]{k_5} AuCl_2 + TS^* + Cl^- + H_2O \tag{17}$$

$$2AuCl_2 \xrightarrow[fast]{k_6} 2AuCl + Cl_2 \tag{18}$$

$$TS^* + TS^* \xrightarrow[fast]{k_7} TSST \tag{19}$$

$$2H^+ + Cl^- + OH^- \xrightarrow{K_8} HCl + H_2O \tag{20}$$

$$\text{Rate} = k_4[AuCl_3OH - TS^{2-}] + k_5[AuCl_3OH^-][TSH] \tag{21}$$

Applying steady state approximation

$$\text{Rate} = K_2K_3k_4 \frac{[AuCl_3OH^-]}{[H^+]}[TSH] + k_5[AuCl_3OH][TSH] \tag{22}$$

$$\text{Rate} = k_5 + \frac{K_2K_3k_4}{[H^+]}[AuCl_3OH^-][TSH] \tag{23}$$

Where TSH is either *N*-methylthiourea, *N, N*'–dimethylthiourea or *N, N'*- diethylthiourea and TSST is formamidine disulphide from thioureas oxidation. Equation 23 is similar to Equation 12 and agrees with the nature of acid dependence obtained where 'a' = k_5 and 'b'= $K_2K_3k_4$. Positive polymerisation in these systems are justified by Equations 15 and 16

CONCLUSION

The reaction of $AuCl_3(OH)^-$ with thioureas was monitored spectrophotometrically in aqueous acid, the results revealed biphasic reaction where the first substitution phase was noted by an increase in absorbance and followed subsequently by the electron transfer phase. Acid-dependence study showed two parallel pathways of inverse dependence and independence. Kinetic data obtained from media ionic strength, dielectric constant, catalysis and temperature study revealed highly ordered systems which occurred through inner-sphere routes. Change in absorption maxima of the oxidant was noted by running the UV- spectra of the partially reacted reaction mixtures. This change signified the formation of intermediate species of the form $[AuCl_3OH\text{-}TS]^{2-}$. Mechanistic steps consistent with experimental findings have been outlined for the reactions.

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