



## KINETICS AND MECHANISM OF OXIDATION OF L-SERINE BY TETRACHLOROAUROATE (III) IN SODIUM ACETATE-ACETIC ACID BUFFER

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### ABSTRACT

The kinetics of oxidation of L-serine by gold(III) was studied spectrophotometrically at 313 nm in sodium acetate – acetic acid buffer. The reaction is first order in tetrachloroaurate(III) and fractional order with respect to L-serine. A mechanism consistent with the kinetic data has been proposed where  $[AuCl_3(OH)]^-$  was presumed to be the reactive species of gold(III). The reaction product 2-hydroxy acetaldehyde was identified by  $^1H$  NMR spectroscopy and  $^{13}C$  NMR spectroscopy. The mechanism proposed leads to the rate equation:

$$\text{rate} = \frac{kK_1K_2K_3[Ser]_t[Au^{III}]_t}{\{1 + K[H^+]\} \{ [H^+][Cl^-] + K_1[H^+] + K_1K_2 \} + K_1K_2K_3[Ser]_t}$$

The activation parameters have been determined to be  $E_a = 28.35 \pm 1.68 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = -194.43 \pm 4.21 \text{ JK}^{-1} \text{ mol}^{-1}$  respectively.

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## INTRODUCTION

L-serine(ser) is an aliphatic, non-essential amino acid and is required for the metabolism of fat, tissue growth and immune system as it assists in the production of immunoglobins and antibodies. It participates in the biosynthesis of purines and pyrimidines and it is a precursor of several amino acids.

Gold (III) compounds are biologically active substances and were reported to be potential anticancer agents (Parish 1996 and Calamai 1998) and also anti HIV(Che 2004) activities. The hydrolysis of tetrachloroaurate(III) has been studied by several investigators and the existence of different gold(III) species has been reported(Biswajit Pal 2001, Vimal Soni 2005, Pratik 2008, Kalyan kali 1984). Many investigators have studied the reduction of tetrachloroaurate(III) and in most of these studies  $Au^I$  is the reduction product while in the oxidation of oxalic acid,  $Au^{III}$  was reduced to metallic gold as has been proven (Soni 2007). There is no literature data to date on the oxidation of L-serine by gold(III). Therefore kinetic study has been carried out to study its mechanism of oxidation in sodium acetate-acetic acid medium.

## MATERIALS AND METHODS

Stock solution of gold(III) was prepared by dissolving  $HAuCl_4 \cdot 3H_2O$  in water.

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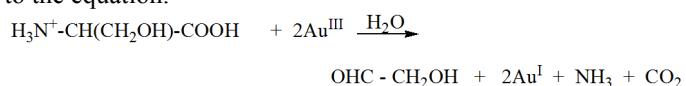
Its concentration was determined from the optical density measured at 313 nm on a Milton roySpectronic 1201 UV-Visible Spectrophotometer using molar extinction coefficient  $\epsilon = 4.86 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . All other reactants used were of analytical reagent grade.

The kinetic studies were carried out at a constant temperature of 303K using sodium acetate-acetic acid buffer medium under the conditions of  $[serine] \gg [tetrachloroaurate(III)]$ . The progress of the reaction is followed by measuring the absorbance of tetrachloroaurate(III) at 313 nm(Fig.1). The plots of  $\log(\text{absorbance})$  versus time are found to be linear even beyond 80% completion of the reaction indicating that the reaction is first order with respect to  $[gold(III)]$ . The pseudo-first order rate constants  $k'$  were calculated from the plots of  $\log(\text{absorbance})$  versus time and the rate constants were found to be reproducible within  $\pm 5\%$ .

## RESULTS

### Stoichiometry of the reaction

To determine the stoichiometry of the reaction, a known amount of serine is mixed with a known excess of  $[gold(III)]$  at 303K and at pH 4.2. After 24 hours the residual  $[gold(III)]$  in each case is determined spectrophotometrically at 313 nm. The stoichiometry of the reaction was found to correspond to the equation:



**Product analysis**

The product analysis was carried out by adopting the following procedure and confirmed the product as 2 – hydroxy acetaldehyde.

The reaction mixture containing  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup> L-serine,  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup> tetrachloroaurate(III) was allowed to stand at 303 K at pH 4.2 using sodium acetate-acetic acid buffer. After completion of the reaction, the reaction mixture was extracted with ether. The product obtained from the ethereal layer was analysed by <sup>1</sup>H NMR and <sup>13</sup>C NMR data (Fig.2.1 & 2.2).

In the <sup>1</sup>H NMR spectrum (Fig. 2.1) the doublet at  $\delta$  7.724 ppm correspond to aldehydic proton, multiplet at  $\delta$  4.668 ppm corresponds to C-H proton, doublet at  $\delta$  3.391 ppm corresponds to alcoholic proton (O-H) respectively.

The product was further confirmed by <sup>13</sup>C NMR spectrum (Fig. 2.2) showing the C-H carbon at  $\delta$  66.66 and aldehydic carbon at  $\delta$  162.66 ppm respectively.

**Test for free radicals**

A freshly prepared acrylamide solution was added to the L-serine – tetrachloroaurate(III) reaction mixture in sodium acetate-acetic buffer at pH 4.2 to initiate polymerization by free radicals. The reaction mixture was kept aside and even after 24 hours no precipitate was observed indicating the absence of free radical formation in the reaction mixture.

**Effect of ionic strength**

The effect of ionic strength on the rate of the reaction was studied by varying ionic strength from 0.1–0.6 mol dm<sup>-3</sup> using sodium perchlorate. It was observed that the ionic strength has negligible effect on the rate of the reaction (Table-1).

**Table 1** Effect of ionic strength, ' $\mu$ ' on the pseudo-first order rate constant,  $k'$  [serine] =  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>; [Au<sup>III</sup>] =  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>; pH = 4.2 ; T = 303 K

$\mu$ mol dm <sup>-3</sup>	$k' \times 10^4$ sec <sup>-1</sup>
0.1	6.65
0.2	6.60
0.3	6.68
0.4	6.71
0.5	6.62
0.6	6.68

**Effect of [gold(III)]**

In order to study the effect of [gold(III)] kinetic runs are carried out at 303 K varying the initial concentration of gold(III) from 0.5- 3.0 x 10<sup>-4</sup> mol dm<sup>-3</sup>, keeping [ser], pH and temperature constant. Further the pseudo-first order constants at different gold(III) were found to remain constant indicating first order dependence on [Au<sup>III</sup>]. The plots of log(absorbance) versus time were found to be linear upto 80% completion of the reaction indicating the reaction is first order with respect to gold(III) (Table-2).

**Effect of serine**

The order with respect to serine was determined by carrying out at pH 4.2 keeping the concentration of [Au<sup>III</sup>] constant but varying that of [serine] from 0.5-5.0 x 10<sup>-2</sup> mol dm<sup>-3</sup>, at four different temperatures 298, 303, 308 and 313 K. The pseudo-first order rate constants thus obtained were recorded (Table-3). It was observed from the data presented in the table that

pseudo first order rate constants,  $k'$  increase with increase in [serine]. When log  $k'$  values are plotted against the logarithms of corresponding [serine] at 303 K, a straight line with a slope of 0.45 is obtained indicating the order with respect to serine is fractional. Further, the plots of  $1/k'$  versus  $1/[ser]$  at four different temperatures, were found to be straight lines with positive intercepts on ordinate, indicating the formation of a 1:1 complex between serine and gold(III).

**Table 2** Effect of [gold(III)] on the pseudo-first order rate constant,  $k'$  [serine] =  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>; pH = 4.2 ; T = 303 K

[Au <sup>III</sup> ] x 10 <sup>4</sup> , mol dm <sup>-3</sup>	$k' \times 10^4$ , sec <sup>-1</sup>
0.5	6.77
1.0	6.57
1.5	6.71
2.0	6.67
2.5	6.65
3.0	6.73

**Table 3** Effect of [serine] on the pseudo-first order rate constant,  $k'$  at different temperatures [Au<sup>III</sup>] =  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup>; pH = 4.2

[serine] x 10 <sup>2</sup> , mol dm <sup>-3</sup>	$k' \times 10^4$ , sec <sup>-1</sup>			
	298 K	303 K	308 K	313 K
0.5	2.58	3.23	3.91	4.92
1.0	4.11	4.61	5.74	6.66
2.0	5.14	6.70	7.66	8.51
3.0	7.13	7.93	8.90	9.53
4.0	7.44	8.58	9.23	10.0
5.0	7.98	8.91	9.62	10.46

**Effect of pH**

The effect of pH on the rate of the reaction was studied by changing the pH from 4.0 -5.2 with sodium acetate-acetic acid, keeping the concentrations of reductant, oxidant and temperature constant. The rate constants were found to increase with increase in pH (Table-4).

**Table 4** Effect of pH on the pseudo-first order rate constant,  $k'$  [Serine] =  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>; [Au<sup>III</sup>] =  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>; T = 303 K

pH	$k' \times 10^4$ , sec <sup>-1</sup>
4.0	4.51
4.2	6.57
4.4	8.00
4.6	9.03
4.8	9.85
4.9	11.12

**Effect of [Cl<sup>-</sup>]**

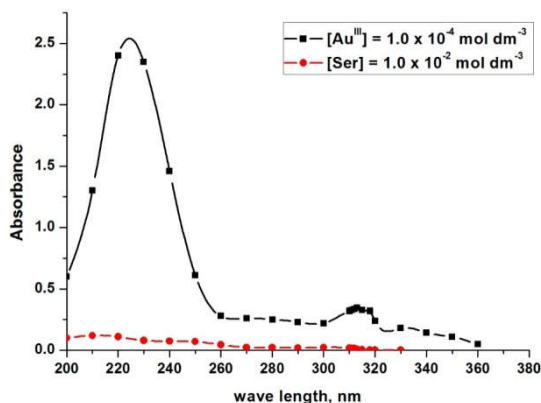
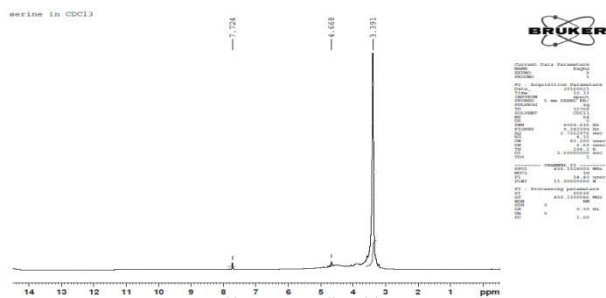
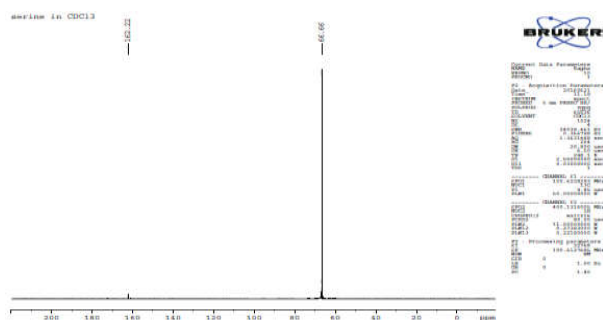
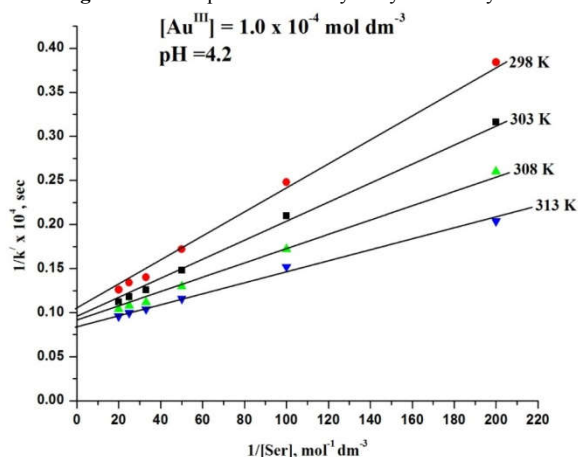
The effect of [Cl<sup>-</sup>] on the reaction rate was studied in the range 0.2 -10.0 x 10<sup>-4</sup> mol dm<sup>-3</sup> keeping [serine], [gold(III)] and pH constant at 303K. It was observed that the rate of the reaction decreases with increase in [Cl<sup>-</sup>] (Table-5).

**Table 5** Effect of [Cl<sup>-</sup>] on the pseudo-first order rate constant,  $k'$  [Serine] =  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>; [Au<sup>III</sup>] =  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>; pH = 4.2 ; T = 303 K

[Cl <sup>-</sup> ] x 10 <sup>4</sup> , mol dm <sup>-3</sup>	$k' \times 10^4$ , sec <sup>-1</sup>
0.0	6.57
0.2	5.13
0.5	4.92
1.0	4.21
2.0	3.91
5.0	2.81
10.0	1.83

**Table 6** Calculated values of  $k$  and  $K_3$  at 298, 303, 308 and 313K  $[Au^{III}] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ;  $\text{pH} = 4.2$ 

Temperature, K	$k \times 10^3, \text{Sec}^{-1}$	$K_3 \times 10^{-3}, \text{mol}^{-1} \text{dm}^3$
298	0.85	0.94
303	1.05	1.86
308	1.56	2.05
313	2.17	2.29

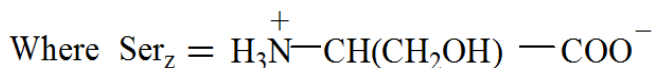
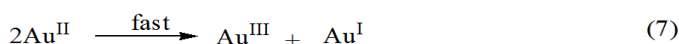
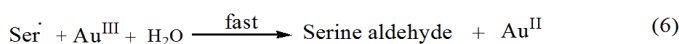
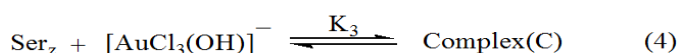
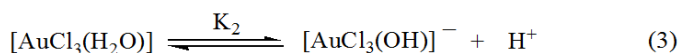
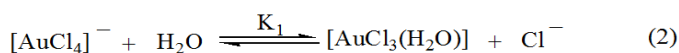

**Fig 1** Spectra of gold(III) in sodium acetate-acetic acid buffer at pH 4.2 and a 303K

**Fig 2**  $^1\text{H}$  NMR spectrum of 2- hydroxy acetaldehyde

**Fig 2**  $^{13}\text{C}$  NMR spectrum of 2- hydroxy acetaldehyde

**Fig 3** Plots of  $1/k'$  versus  $1/[\text{ser}]$  at four different temperatures

## DISCUSSION

L-serine possesses two  $\text{pK}_a$  values (Murray 2000), one corresponding to the carboxylic acid group ( $\text{pK}_1 = 2.2$ ) and the second one to amino group ( $\text{pK}_2 = 9.2$ ).

Under the present experimental conditions ( $\text{pH} = 4.2$ ) serine exists in the form of zwitterionic species,  $\text{Ser}_z$  to an extent of 94% and the remaining 6% is in its protonated form. In view of the decrease in rate with increase in  $[\text{H}^+]$ , Zwitterionic species of serine,  $\text{Ser}_z$  is presumed to be the reactive species of the substrate.

Chloroauric acid,  $\text{HAuCl}_4$  undergoes ionization in dilute mineral acids to  $\text{AuCl}_3(\text{H}_2\text{O})$  and  $\text{AuCl}_3(\text{OH})^-$  as shown in equilibria (2) and (3). Since the rate of the reaction decreases with increase in  $[\text{H}^+]$  and  $[\text{Cl}^-]$ , the retardation effect of  $[\text{Cl}^-]$ , equilibrium (2) is shifted towards right and similarly the retardation of rate by an increase in  $[\text{H}^+]$ , may be ascribed to shifting of the equilibrium(3) to the right. Basing on these observations,  $\text{AuCl}_3(\text{OH})^-$  is presumed to be the reactive species of tetrachloroaurate(III) and the following mechanism is proposed.



From the above equations the rate law can be written as

$$\text{rate} = \frac{-d[\text{Au}^{\text{III}}]}{dt} = k[\text{C}] \quad (8)$$

$$= kK_3[\text{Ser}_z][\text{AuCl}_3(\text{OH})^-] \quad (9)$$

Where

$$[\text{Ser}_z]_e = \frac{[\text{Ser}]_t}{1 + K[\text{H}^+]}$$

and

$$[\text{AuCl}_3(\text{OH})^-]_e = \frac{K_1K_2[\text{Au}^{\text{III}}]_t}{[\text{H}^+][\text{Cl}^-] + K_1[\text{H}^+] + K_1K_2K_3[\text{Ser}_z]_e}$$

Substituting the values of  $[\text{Ser}_z]_e$  and  $[\text{AuCl}_3(\text{OH})^-]_e$  in equation (9) gives

$$\text{rate} = \frac{kK_1K_2K_3[\text{Ser}]_t [\text{Au}^{\text{III}}]_t}{\{1 + K[\text{H}^+]\} \{[\text{H}^+][\text{Cl}^-] + K_1[\text{H}^+] + K_1K_2\} + K_1K_2K_3[\text{Ser}]_t} \quad (10)$$

This rate equation explains the experimental kinetics like unit order on  $[\text{gold(III)}]$ , fractional order on  $[\text{serine}]$  and retarding effect of  $[\text{Cl}^-]$ . Equation (10) can be written as

$$\frac{\text{rate}}{[\text{Au}^{\text{III}}]_t} = k' = \frac{kK_1K_2K_3[\text{Ser}]_t}{\{1 + K[\text{H}^+]\} \{ [\text{H}^+][\text{Cl}^-] + K_1[\text{H}^+] + K_1K_2\} + K_1K_2K_3[\text{Ser}]_t} \quad (11)$$

The above equation can be transformed to

$$\frac{1}{k'} = \frac{\{1 + K[\text{H}^+]\} \{ [\text{H}^+][\text{Cl}^-] + K_1[\text{H}^+] + K_1K_2\}}{kK_1K_2K_3[\text{Ser}]_t} + \frac{1}{k} \quad (12)$$

In the absence of added  $[\text{Cl}^-]$ , equation (12) reduces to

$$\frac{1}{k'} = \frac{\{1 + K[\text{H}^+]\} \{ [\text{H}^+] + K_2\}}{kK_2K_3[\text{Ser}]_t} + \frac{1}{k} \quad (13)$$

Further the plots of  $1/k'$  versus  $1/[\text{ser}]$  were found to be straight lines with positive intercepts on Y - axis when [serine] variation studies were carried out at four different temperatures 298, 303, 308, 313 K thus supporting the proposed mechanism. This suggests a Michaelis - Menten type of behaviour with the formation of a 1 : 1 complex between serine and gold(III). The values of 'k' rate constant of slow step and 'K<sub>3</sub>' were calculated at four different temperatures (Table-6), from the intercepts of the plots of  $1/k'$  versus  $1/[\text{Ser}]$ . (Fig.3) by substituting the literature values for  $K_1 = 9.5 \times 10^{-6}$  and  $K_2 = 0.25$  (Van 1972, Moodley 1977, Hans 1960). From the values of k, the energy of activation, E<sub>a</sub> and entropy of activation,  $\Delta S^\ddagger$  were calculated using linear least squares method and were found to be  $28.35 \pm 1.68 \text{ kJ mol}^{-1}$  and  $-194.43 \pm 4.21 \text{ JK}^{-1} \text{ mol}^{-1}$  respectively.

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