Electron transfer reactions between chloroaurate(III) complexes and various inorganic and organic reducing agents in acid medium – a brief review

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Manuscript received 9 December 2005, revised 2 May 2006, accepted 12 May 2006

Abstract : The review narrates the electron transfer reactions of some chloroaurate(III) complexes in acid medium reported since 1970 onwards. The reactions involving inorganic substrates and gold(III) were studied mostly in HCl medium whereas the oxidations of different organic substrates were investigated in sodium acetate-acetic acid buffer medium. Increase in $[H^+]$ decreases the rate of reactions. At higher concentrations of $[H^+]$ (ca. $\geq 0.5 \text{ mol dm}^{-3}$), $AuCl_4^-$ or $HAuCl_4$ is the reactive gold(III) species whereas when the reactions were studied in much lower acidities of $[H^+]$ ($\ll 0.5 \text{ mol dm}^{-3}$) or in sodium acetate-acetic acid buffer medium, $AuCl_4^-$, $AuCl_3(OH_2)$ and $AuCl_3(OH)^-$ are the reactive species which oxidize the substrates. Kinetic evidence for the participation of $AuCl_4^-$, $AuCl_3(OH_2)$ and $AuCl_3(OH)^-$ is provided. The reactivity of these different gold(III) species follow the order : $AuCl_3(OH)^- > AuCl_3(OH_2) > AuCl_4^-$. Influence of ionic strength was noticed in the oxidations of some inorganic and organic compounds by gold(III). The rates in the presence of different salts like NaCl, $NaClO_4$ and Na_2SO_4 at constant ionic strength was found to be same in the oxidations of a number of inorganic compounds indicating that anions do not have any influence on the rate. The rates were found to depend not only on the ionic strength but also on the concentration and nature of the cations. The pseudo-first-order rate constant increases in the order $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ in the oxidation of a number of inorganic substrates. The reactions exhibit diverse mechanistic behavior. Kinetic and mechanistic features associated with such reactions have been discussed and analyzed. An attempt has been made to correlate mainly our experimental observations.

Keywords : Electron transfer reactions, auric complexes, reducing agents.

Introduction

Gold is widely distributed in nature and the chemistry of gold remains an active research area^{1(a)}. Gold is not essential for any living organism though some plants concentrate the element^{1(b)}. Gold is known to exist in different oxidation states such as +1, +2, +3, (+4) and (+5) for which the electronic configurations are d^{10} , d^9 , d^8 , (d^7) and (d^6), respectively. Of these different states, the underlined states are the most important and the states in the parenthesis are unconfirmed. Complexes of different oxidation states of gold have been discussed and incorporated by Puddephatt² and other workers³.

Gold(III) forms a number of stable complex ions. The anionic complexes⁴ like AuF_4^- , $AuCl_4^-$, $Au(CN)_4^-$ and $Au(NO_3)_4^-$ and four coordinated cationic complexes⁵ such as $[AuCl_2py_2]Cl$, $[Au(phen)_2Cl_2]Cl$ and $[Au(bipy)_2Cl_2]Cl$ have been reported in the literature.

The lowest and highest coordination number found in coordination compounds of gold are two and six respectively with the intermediate number four being the most frequent for gold(III) and two for gold(I) compounds. A wider range of coordination numbers (two to twelve) exists in organometallic cluster compounds.

Some gold(I) compounds are biologically active and used as anti inflammatory drugs in the treatment of rheumatoid arthritis⁶⁻⁹. Several gold(III) compounds were also used earlier in the treatment of tuberculosis¹⁰ whereas a few gold(III) complexes are found to have antitumour activity^{11,12}. Again such gold compounds are found to have severe toxic effects^{13,14} on human health such as kidney damage and blood disorders. Such toxic effects are presumed to be related to gold(I)-gold(III) oxidation *in vivo* followed by gold(III)-biomolecule interactions^{15(a)}. Redox and ligand exchange reactions of potential gold(I) and gold(III)-cyanide metabolites under biomimetic con-

ditions have been reported^{15(b)}. There are reports^{15(c)} on the investigation of a metal-centered porphyrine in non-polar solvent where a long-lived charge separated state of the product has been identified. In view of all the above findings, kinetic studies on the reduction of Au^{III} by various inorganic as well as organic compounds have become increasingly interesting. This has become important from another point of view that gold(III) can behave both as a one-electron and a two-electron transfer oxidant.

Considerable amount of work has been done¹⁶⁻³⁰ on the oxidations of different reducing substrates by chloroaurate(III) complexes under different experimental conditions but no attempt has been made till date to record the progress in this field. This necessitates a review of redox reactions involving chloroaurate(III) complexes and different inorganic and organic substrates and an attempt has been made to analyze and correlate the results.

Results

The standard reduction potentials relating to different oxidation states of gold at 298.1 K have been reported^{31,32}. The values commonly used are mentioned below.

Reaction	E° , (V)
$\text{Au}^+ + e \rightleftharpoons \text{Au}$	1.68
$\text{Au}^{2+} + e \rightleftharpoons \text{Au}^+$	> 1.29
$\text{Au}^{3+} + e \rightleftharpoons \text{Au}^{2+}$	< 1.29
$\text{Au}^{3+} + 2e \rightleftharpoons \text{Au}^+$	1.401
$\text{Au}^{3+} + 3e \rightleftharpoons \text{Au}$	1.498

The standard reduction potentials are highly dependent on the ligands attached and those where ligands (L) like H₂O, Cl⁻, Br⁻, I⁻, CN⁻ and SCN⁻ are attached to the metal with different oxidation states have been reported³³.

Different oxidizing species of gold(III) :

Gold(III) complexes are stable mainly in acid medium. However, gold(III) oxidations of different substrates which have been studied in acidic medium are kinetically dissimilar and characterized by variety of reaction pathways. A number of studies reveal that the square planar AuCl₄⁻ ion undergoes fast hydrolysis^{4(b),34,35} and produces two other Au^{III} species, namely, AuCl₃(H₂O) and AuCl₃(OH)⁻. Thus in solution of chloroauric acid, four gold(III) species, viz. HAuCl₄, AuCl₄⁻, AuCl₃(H₂O) and AuCl₃(OH)⁻ coexist and render the system complicated. These spe-

cies are involved in the following equilibria.

where K_1 , K_2 and K_3 are 1.0, 9.5×10^{-6} , and 0.25, respectively at 298 K^{26,34,35}. The relative concentration of each of the above species will be controlled by the pH and the concentration of Cl⁻ ion in the solution.

Oxidation of inorganic compounds by gold(III) :

The kinetics of oxidation of a few compounds of metals such as iron(II)¹⁶, platinum(II)^{16,36} and thallium(I)³⁷ have been reported. Moodley and Nicol studied¹⁶ the reduction of gold(III) by iron(II) chloride amperometrically under the condition [Au^{III}] >> [Fe^{II}]. The influence of H⁺ ion was studied in the acid range (0.05–1.0) mol dm⁻³ HClO₄ at [Cl⁻] = 1.0 mol dm⁻³ and $I = 1.0$ mol dm⁻³ and a negligible H⁺ ion dependence has been observed. Moreover, the dependence on Cl⁻ ion was studied in the range of [Cl⁻] = (0.05–1.0) mol dm⁻³ at [H⁺] = 1.0 mol dm⁻³ and the observed behavior was accounted for by a mechanism consisting of parallel paths involving Fe²⁺ and [FeCl]⁺.

On the assumption that the steady state approximation for intermediate gold(II) is valid, the following rate expression was deduced.

$$-d[\text{Fe}^{\text{II}}]/dt = \frac{2k_1k_2[\text{Fe}^{\text{II}}]^2[\text{Au}^{\text{III}}]}{k_{-1}[\text{Fe}^{\text{III}}] + k_2[\text{Fe}^{\text{II}}]} \quad (I)$$

The reduction of gold(III) by PtCl₄²⁻ has also been studied by Moodley and Nicol¹⁶ spectrophotometrically and the reaction involves a complementary two electron transfer step.

The rate expression is

$$-d[\text{Au}^{\text{III}}]/dt = k_3 [\text{Au}^{\text{III}}] [\text{Pt}^{\text{II}}] \quad (\text{II})$$

No effect of Cl^- ion on the rate was observed, however, the increase of both the ionic strength and pH enhance the reaction rate.

Mechanism for the oxidation of $\text{Pt}^{\text{II}}(\text{CN})_4^{2-}$ by gold(III) has been studied^{36(a)} by the use of stopped-flow and conventional spectrophotometric method, where the different gold(III) species viz. AuCl_4^- , $\text{AuCl}_3(\text{OH}_2)$ and $\text{AuCl}_3(\text{OH})^-$ were involved depending on the experimental conditions. Redox reactions are proposed to take place via chloride-bridged inner-sphere mechanisms. The steps of the reaction are as follows.

In a $10^{-5} \text{ mol dm}^{-3}$ gold(III) solution with $[\text{Cl}^-] \leq 2 \times 10^{-4} \text{ mol dm}^{-3}$ and $\text{pH} = 0$, oxidation by $\text{AuCl}_3(\text{OH}_2)$ is predominant and reaction takes place via the chloride bridged intermediate $[\text{H}_2\text{O} \dots \text{Pt}(\text{CN})_4 - \text{Cl} - \text{AuCl}_2 \dots \text{OH}_2^{2-}]$. However, at $[\text{Cl}^-] \geq 0.25 \text{ mol dm}^{-3}$ and $\text{pH} \sim 5$, the oxidation occurs by AuCl_4^- and $\text{AuCl}_3(\text{OH})^-$ via parallel paths. In such cases, the Cl^- assistance of the redox reaction has been accounted for by the formation of intermediates of the type $\text{Cl} \dots \text{Pt}(\text{CN})_4 - \text{Cl} - \text{AuCl}_2 \dots \text{X}^{4-}$, $\text{X} = \text{Cl}^-, \text{OH}^-$. In contrast to this study, the investigation made by Peloso^{36(b)} showed only AuCl_4^- species to be involved in the oxidation of platinum(II).

The complementary reaction between Ti^{I} and AuCl_4^- has been investigated by Gidd *et al.*³⁷ in 3.0 mol dm^{-3} HCl medium. Under the experimental conditions, the active species of oxidant and reductant were found to be HAuCl_4 and TiCl_2 respectively.

Kinetics of the oxidation of different compounds of nitrogen¹⁷⁻¹⁹, phosphorous²⁰, arsenic²¹, antimony²², and sulphur²⁴ by gold(III) have been studied spectrophotometrically in hydrochloric acid medium. The reaction of hydrazinium ion N_2H_5^+ with Au^{III} ¹⁷ is first order in both $[\text{Au}^{\text{III}}]$ and $[\text{N}_2\text{H}_5^+]$. Hydrogen ion inhibits the rate of oxidation. The following steps are proposed.

The products N_2 and NH_4^+ are formed by one electron transfer oxidation process whereby gold(III) is initially reduced to gold(II). This is supported by the decrease in reaction rate ($\sim 72\%$) in 5.6% (w/v) acrylamide.

The rate expression is

$$-d[\text{Au}^{\text{III}}]/dt = \frac{k_4 K_1 [\text{Au}^{\text{III}}] [\text{N}_2\text{H}_5^+]}{K_1 + [\text{H}^+]} \quad (\text{III})$$

The value of K_1 was found to be 1.01. However, the same K_1 from distribution studies³⁵ of HAuCl_4 between water and diethyl ether was 1.35 and from another kinetic studies¹⁶ by Moodley and Nicol in hydrochloric acid medium was 1.1.

The oxidation of hydroxylammonium ion by gold(III) was studied in HCl ^{18(a)} as well as HClO_4 ^{18(b)} media. The stoichiometry of the reaction^{18(a)} in HCl medium is

The reaction takes place through the intermediate formation of free radical followed by its decomposition to give N_2 and is in keeping with the observation^{18(c)} made during the oxidation of this substrate by Ni^{IV} .

On the other hand when the reaction was studied^{18(b)} in HClO_4 medium, the reaction has been shown to occur as follows.

The stoichiometry of the reaction in perchloric acid medium^{18(b)} was studied in which gold(III) was in excess to that of the substrate whereas the same was determined in excess hydroxylammonium concentration in HCl medium^{18(a)}. Consequently even if HNO is formed (via two electron transfer oxidation mechanism) in the rate-determining step in HClO_4 medium, in the presence of excess substrate the possibility of formation of N_2 cannot

be ruled out.

However, in both cases the reaction was found to be inhibited by H^+ ion.

The oxidation of HNO_2 by $[\text{AuCl}_4]^-$ ¹⁹ in hydrochloric acid medium was first order with respect to $[\text{Au}^{\text{III}}]$ and $[\text{HNO}_2]$. H^+ and Cl^- ions inhibit the rate. The alkali metal ions have specific effects on the rate at constant ionic strength. The rate increases with increase in size of the alkali metal ion. The reaction appears to involve different gold(III) species, viz. AuCl_4^- , $\text{AuCl}_3(\text{OH}_2)$ and $\text{AuCl}_3(\text{OH})^-$.

These three species oxidize HNO_2 in the following way,

The following rate expression has been deduced

$$-d[\text{Au}^{\text{III}}]/dt = \left(k_6 + \frac{k_7 K_2}{[\text{Cl}^-]} + \frac{k_8 K_2 K_3}{[\text{H}^+][\text{Cl}^-]} \right) \frac{[\text{HNO}_2][\text{Au}^{\text{III}}]}{[\text{Au}^{\text{III}}]} \quad (IV)$$

The electron transfer from nitrite to gold(III) may occur according to either of the following two Schemes 1 and 2.

Scheme 1

Scheme 2

The reaction possibly occurs by a complementary mechanism via Scheme 2, although the other possibility cannot be totally ruled out simply on the basis of absence of polymerization of acrylamide in presence of the reaction mixture.

Copper(III) and silver(III) are known to oxidize sodium azide^{10,38} in alkaline medium through the intermediate formation of hexazene to give N_2 . An attempt was made to investigate the kinetics of oxidation of azide ion by chloroaurate(III) in acid medium. Gold(III) failed to oxidize azide ion. This may be due to the formation of stable compound between these two reactants as mentioned in the literature¹⁰.

Hypophosphite ion is oxidized by gold(III)²⁰ in aqueous hydrochloric acid to give phosphorous acid and Au^{I} . The reaction is first order in $[\text{Au}^{\text{III}}]$ and $[\text{H}_3\text{PO}_2]$. Hydrogen ion has no effect on the reaction rate in the acid range (0.15–1.0) mol dm^{-3} . The reaction takes place via one electron transfer process according to the following Scheme :

Scheme 3

The oxidation of arsenious acid by gold(III)²¹ in hydrochloric acid medium proceeds through the formation of a complex between arsenic(III) and gold(III) followed by its decomposition to give the products.

The rate expression has been suggested as

$$-d[\text{Au}^{\text{III}}]/dt = \frac{k_9 K_4 [\text{Au}^{\text{III}}] [\text{As}^{\text{III}}]}{1 + K_4 [\text{As}^{\text{III}}]} \quad (V)$$

H^+ ions have little effect on the reaction studied in the range (0.1–1.0) mol dm^{-3} of HCl . A kinetic Cl^- dependence would require additional chlorides in the activated

complex. Since there is no Cl^- dependence (at constant ionic strength) it can be explained by a bridge between the oxidant and arsenic(III). However, the pseudo-first-order rate constant increases with an increase in salt concentration, which may be due to an increase in ionic strength or due to a variation in the nature, and concentration of the cations. It has been observed that the enhancement of the rate in presence of the cation is in the order: $\text{K}^+ > \text{Na}^+ > \text{Li}^+$. The electron transfer from substrate to oxidant takes places as shown below.

Scheme 4

The decrease ($\sim 73\%$) in rate in presence of 12% (w/v) acrylamide solution corroborated the above non-complementary mechanism.

Babshet and Gokavi²² reported the kinetics of oxidation of antimony(III) by gold(III) in (0.64–3.0) mol dm^{-3} hydrochloric acid. The reaction involves the following equilibria (20–23) and the slow complementary two electron transfer between $\text{AuCl}_3(\text{OH})^-$ and SbCl_6^{3-} (24).

The derived rate law is,

$$-d[\text{Au}^{\text{III}}]/dt = \frac{k_{10}K_5K_6K_7K_8[\text{Cl}^-][\text{Au}^{\text{III}}][\text{Sb}^{\text{III}}]}{[\text{H}_3\text{O}^+]([\text{H}_3\text{O}^+] + K_5)} \quad (\text{VI})$$

The observed orders with respect to $[\text{H}^+]$ and $[\text{Cl}^-]$ are -1.6 and 0.9 , respectively, which corroborate the above rate law. The effect of dielectric constant was observed by varying acetic acid (0 to 40% v/v) and the rate was found to increase with increase in dielectric constant of the medium, which supported the reaction (eq. 24) between similarly charged ions. In majority of the reactions of gold(III), Cl^- ions have either no effect (due to participation of AuCl_4^- or HAuCl_4) or a decelerating effect (due to participation of $\text{AuCl}_3(\text{OH})^-$ and $\text{AuCl}_3(\text{H}_2\text{O})$ species). However, in the present study the reaction is accelerated by Cl^- ions. The contradictory observation has been resolved by the involvement of the active species SbCl_6^{3-} , generated by the equilibria (22 and 23).

A number of mechanisms by which square planar system might oxidize a substrate, have been discussed in the literature^{23,26,39} with regard to gold(III) complexes. These include (i) attack by the reductant on a ligand (e.g. Cl^- , HO^-) with resulting atom transfer, (ii) nucleophilic attack on the metal ion with electron transfer occurring in a five-coordinate intermediate and (iii) electron transfer following ligand substitution. Annibale *et al.*²³ found that the rates of oxidation of alkyl sulphides to sulfoxides by AuCl_4^- correlated directly with their basicity and inversely with steric hindrance in the alkyl chains.

The oxidation of sulphurous acid by gold(III) was studied²⁴ in the temperature range 292–310 K in (0.07–0.40) mol dm^{-3} HCl medium keeping constant ionic strength by the addition of NaCl. The influence of alkali metal chloride on the reaction rate was also studied and the rate constant was found to increase with increasing polarizability of the alkali metal ion at constant ionic strength. The reaction has been shown to occur through the intermediate formation of complex between the reactants followed by its decomposition to give free radical and gold(II). The free radical further reacts with another gold(III) to give sulphate ion and gold(II). Gold(II) reacts further with sulphurous acid and gives dithionate and gold(I).

The following rate expression has been deduced

$$-d[\text{Au}^{\text{III}}]/dt = \frac{k_{11}K_1K_9[\text{S}^{\text{IV}}][\text{HAuCl}_4]}{\{1 + K_9[\text{S}^{\text{IV}}]\}[\text{H}^+]} \quad (\text{VII})$$

where K_1 is the dissociation constant of HAuCl_4 to give H^+ and AuCl_4^- . Recently, Paclawski and Fitzner have studied^{24(b)} the kinetics of oxidation of sodium bisulphite by AuCl_4^- in acid medium and observed similar type of one-electron transfer step with intermediate formation of free radicals.

The kinetics of the reaction between hydrogen peroxide and gold(III)²⁵ in a hydrochloric acid medium (0.01–0.2 mol dm⁻³) has been studied. From the known dissociation constant and protonation constant of H_2O_2 , it has been shown that in this concentration range, hydrogen peroxide exists mainly as H_2O_2 , both HO_2^- and H_3O_2^+ being insignificant. Thus in such a medium gold(III) oxidizes H_2O_2 through the intermediate formation of free radicals and the free radical ($\text{HO}_2^\bullet$) reacts with gold(III) to give O_2 as mentioned below.

The reaction is first order with respect to [oxidant] as well as $[\text{H}_2\text{O}_2]$, but the reaction has an inverse dependence on $[\text{H}^+]$ and $[\text{Cl}^-]$.

Oxidation of organic compounds by gold(III) :

The reduction of gold(III) by oxalate was studied by Maritz and van Eldik²⁶ in the acidity range $0.0 \leq \text{pH} \leq 3.5$ and chloride concentration range $10^{-3} \leq [\text{Cl}^-] \leq 0.8$ M at 298 K. Ionic strength of the reaction medium was kept constant (1.0 mol dm⁻³) by adding NaClO_4 . Both H^+ and Cl^- ions retard the rate of reaction as was observed in the aforementioned reactions of gold(III). Kinetic evidence indicated the participation of three gold(III) species (viz. AuCl_4^- , $\text{AuCl}_3(\text{OH}_2)$ and $\text{AuCl}_3(\text{OH})^-$) as well as three different oxalate species (viz. $\text{H}_2\text{C}_2\text{O}_4$, HC_2O_4^- and $\text{C}_2\text{O}_4^{2-}$). The reactivity of AuCl_4^- towards the substrate is much more pH dependent than that of $\text{AuCl}_3(\text{OH})^-$. The proposed mechanism consists of substitution reactions followed by electron transfer steps.

The observed products are Au^{I} , Au^0 , and CO_2 . The reductions of gold(III) by HC_2O_4^- and $\text{C}_2\text{O}_4^{2-}$ ions are much faster as compared to that by $\text{H}_2\text{C}_2\text{O}_4$. The photolysis of the tetrachloroaurate(III) oxalate system has also been investigated by Maritz *et al.*⁴⁰ at $\text{pH} \leq 1.0$ spectrophotometrically as well as radiochemically. Kinetics of oxidation of substituted malonates by gold(III) in acidic solution have been reported⁴¹.

There were a number of investigations into the mechanism of substitution reactions of AuCl_4^- with ethylene diamine⁴², diethylene triamine⁴³, thiomorpholine-3-one⁴⁴

Amino acids are basic component of protein molecules and play an important role in life processes. Reactions of amino acids with gold(III) will naturally be an important aspect for investigation from mechanistic view point. But no such kinetic investigation has been reported in the literature except the recent report of the Au^{III} -induced oxidation of isotopically labeled glycine by Zou *et al.*⁴⁵. The reaction was studied at pH 2.4 using 1D ^1H NMR and 2D [^1H , ^{15}N] HSQC-TOCSY NMR spectroscopy. The proposed mechanism involves the initial formation of a coordination complex $[\text{AuCl}_3(\text{Gly-N})]$ which gives rise to gold(I) and immine intermediate via two-electron transfer step. The immine undergoes fast hydrolysis to give glyoxylic acid and NH_4^+ . The former gets further oxidized by gold(III) to produce formic acid, CO_2 , and gold(0). Such type of gold(III)-induced oxidation of glycine and related aminoacids may have some relation to the severe toxicity of gold drugs⁴⁵.

Milgrom^{46(a)} has reported the oxidation of 2,3,7,8,12,13,17,18-octaethyl porphyrin by gold(III) in pyridine, in which an ethyl substituent is oxidized to a chlorovinyl group. A typical 'rhodo-type' spectrum (450–650 nm) typical of a porphyrin containing one electron withdrawing β -substituent, confirms the reaction product. The reactions of a few gold(III) complexes with serum albumin have been investigated^{46(b)} by the joint use of various spectroscopic methods and separation techniques. Both weak and strong metal-protein interactions have been observed. It is suggested that adduct formation for both of these gold(III) complexes occurs through coordination at the level of surface histidines.

The reactivity of a few alkanols and a number of aryl alcohols towards gold(III) have recently been studied²⁷ in our laboratory in sodium acetate-acetic acid buffer medium in the pH range 3.72–4.80. The reactions of aryl alcohols were studied in *tert*-butyl alcohol (15% v/v). The kinetic investigations reflect the involvement of all the three gold(III) species in the reactions. The observed

kinetic isotopic effect indicates that the reactions occur via C-H bond cleavage⁴⁷, leading to the intermediate formation of free radicals and different gold(II)⁴⁸⁻⁵⁰ species. The formation of intermediate free radicals is supported by the observed polymeric suspension in the presence of acrylonitrile.

The free radicals react further with the respective gold(III) species to give the carbonyl compounds and gold(II).

Au^{II} undergoes fast disproportionation into Au^{I} and Au^{III} .

The reaction obeys the following rate expression :

$$-d[\text{Au}^{\text{III}}]/dt = \{k_{12} + \frac{(k_{13} - k_{12})K_2}{[\text{Cl}^-]} + \frac{(k_{14} - k_{12})K_2K_3}{[\text{H}^+][\text{Cl}^-]}\} [\text{R}_1\text{R}_2\text{CHOH}][\text{Au}^{\text{III}}] \quad (\text{VIII})$$

The reactivity of alkanols towards gold(III) follows the order : ethanol > methanol > 2-propanol and that of substituted arylalcohols $\text{NO}_2 > \text{H} > \text{Cl} > \text{OMe}$. The unsubstituted benzyl alcohol react at a faster rate than benzhydrol.

In the oxidation²⁸ of some neutralized α -hydroxy acids such as glycolic, lactic, α -hydroxyisobutyric, mandelic, atrolactic and benzilic acids, gold(III) behaves as a

two electron transfer oxidant. Spectrophotometric evidence in the initial stages of the reaction as well as the kinetic evidence indicate the formation of an intermediate cyclic complex, which decomposes in the rate determining step to give the respective reaction products, namely, formaldehyde, acetaldehyde, acetone, benzaldehyde, acetophenone and benzophenone. The observed kinetic isotopic effect suggests that the oxidation occurs via C-C bond cleavage and not by C-H bond breaking.

Scheme 5

The reaction mechanism shows that both H^+ and Cl^- ions inhibit the reaction rate, which is supported by the following rate expression.

$$-d[\text{Au}^{\text{III}}]/dt = \frac{k_{15}K_{10}K_{11}[\text{S}][\text{Au}^{\text{III}}]}{\{K_{10} + [\text{H}^+]\}[\text{Cl}^-] + K_{10}K_{11}[\text{S}]} \quad (\text{IX})$$

The values of K_{11} (equilibrium constant for the intermediate complex formation) and k_{15} (disproportionation constant for the r.d.s.) are evaluated from the substrate effect, acid effect, and chloride effect and the values are found to corroborate with one another. The enthalpy of activation ($\Delta H^\ddagger$) is found to be linearly related to the entropy of activation ($\Delta S^\ddagger$), which suggests that a similar type of mechanism is operative in all the reactions. The fairly large and negative $\Delta S^\ddagger$ values further support the formation of the cyclic complex. The reactivity of the acids are in the order : glycolic < lactic < α -hydroxy isobutyric < benzilic < mandelic < atrolactic.

The reduction of gold(III) by glycolaldehyde in acetic acid-sodium acetate buffer medium has been studied²⁹ in

the pH range 3.72–4.63. Glycolaldehyde, a dimer in the crystalline state, undergoes depolymerization, which is extremely fast in water and catalyzed by acid and base. All the different forms were detected by NMR spectra in D₂O, however, the monomeric form becomes predominant in very dilute solution (< 0.1 mol dm⁻³). The reaction is first-order with respect to [Au^{III}] as well as [glycolaldehyde]. Both H⁺ and Cl⁻ ions retard the rate of reaction. Under the experimental conditions, AuCl₄⁻, AuCl₃(OH)₂, and AuCl₃(OH)⁻ oxidize the substrate to give glyoxal. Due to the presence of the electron withdrawing -CH₂OH group, glycolaldehyde exists in the hydrated form. As a result the electron transfer takes place from the alcoholic oxygen to gold(III).

Scheme 6

In an alternative path, the enol form of the aldehyde reacts with gold(III), leading to the formation of glyoxal hydrate.

Scheme 7

Irrespective of whether aldehyde form or enol form of the substrate is oxidized by Au^{III} to give glyoxal, the one step two-electron transfer rate determining process is corroborated by the absence of polymerization in the presence of vinyl compound.

Carbohydrates have unique biological activity, which serve as store and source of energy⁵¹. Of the different carbohydrates, the monosaccharides are of vast biological importance, as they are known to be involved in carbohydrate metabolism⁵². They are reported to exist in acyclic and cyclic forms and possess a higher density of functional groups than any other class of organic compounds⁵³. The mechanisms of the oxidation reactions in-

volving monosaccharides are of immense importance.

The reactivity of some aldoses towards gold(III) was studied in HCl medium^{54,55}, where AuCl₄⁻ was the only active species of gold(III). Very recently the same reactions have been studied more elaborately in sodium acetate-acetic acid buffer medium³⁰. In the latter studies, all the three different gold(III) species are involved and both H⁺ and Cl⁻ ions retard the reaction rate. Under the kinetic conditions, reaction appears to involve the intermediate formation of free radicals and Au^{II}. Aldoses react with gold(III) in the order : triose > tetrose > pentose > hexose. The plots of log *k*_{obs} versus 'n' (where n = number of asymmetric center) is linear (Fig 1)

Fig. 1. Dependence of the reaction rate of the oxidation of some aldoses by gold(III) on their number of asymmetric centers (*n*) Plot of log *k*_{obs} versus 'n'

Aldohexoses exist mainly in the pyranoid form, where as aldopentoses exist in equilibrium in both pyranoid and furanoid forms. On the other hand, triose and tetrose exist mostly in the hydrated acyclic forms. The reactions occur as shown in Schemes 8–10.

Scheme 8

Scheme 9

Scheme 10

Discussion

The salient features of the oxidations by gold(III) are as follows :

Increase in $[H^+]$ decreases the rate of reactions. At higher acid concentrations of $[H^+] \geq 0.5 \text{ mol dm}^{-3}$, $AuCl_4^-$ or $HAuCl_4$ is the reactive gold(III) species whereas in much lower acidities of $[HCl] \ll 0.5 \text{ mol dm}^{-3}$, or, in sodium acetate-acetic acid buffer medium, $AuCl_4^-$, $AuCl_3(OH_2)$ and $AuCl_3(OH)^-$ are the reactive species which oxidize the substrates.

Cl^- retards the rate of the reactions. This is due to the fact that it lowers the concentrations of $AuCl_3(OH_2)$ and $AuCl_3(OH)^-$. Of these three species $AuCl_3(OH)^-$ is the most reactive one. Thus the reactivity of gold(III) species follow the order, $AuCl_3(OH)^- > AuCl_3(OH_2) > AuCl_4^-$. The greater reactivity of $AuCl_3(OH)^-$ and $AuCl_3(OH_2)$ over $AuCl_4^-$ may be ascribed to the easier displacement of an OH^-/OH_2 group than a Cl^- ion²⁶.

Influence of ionic strength was noticeable in the oxidation of some inorganic^{19,21,24} and organic²⁸ compounds

by gold(III). The rates in the presence of different salts like NaCl, $NaClO_4$ and Na_2SO_4 at constant ionic strength (0.1 mol dm^{-3}) was found to be same in the oxidation of inorganic compounds indicating that anions do not have any influence on the reaction rate. On the other hand, the rates were found to depend not only on the ionic strength but also on the concentration and nature of the cations. The rates increase as the ionic strength increases. The reactions take place between an ion and a neutral species or between two different ionic species depending upon the substrates, which were used.

It has been suggested that alkali metal ions serve as an electron bridge and that a linear relationship exists between the experimental rate constants and polarizability of the cations. An attempt was also made to correlate rate constants with crystal radii ($\text{\AA}$), hydration energy (kJ mol^{-1}), polarizability (cm^3) and ionic potential (kJ mol^{-1}) of the alkali metal ions^{21,24}. Although the plots of k_{obs} (at $[\text{salt}] = 0.1 \text{ mol dm}^{-3}$) versus different physical properties are not linear except for the polarizability, the pseudo-first-order rate constant increases in the order : $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. Thus, the variation of rate constant in the presence of different cations has been ascribed to the ion association between M^+ and either of the anionic gold(III) species. The ion association is higher for small alkali metal ions, thereby decreasing the ionic strength and hence the rate constant.

The oxidation of inorganic and organic reductants by gold(III) may take place by either one electron or one step two-electron transfer process. It will be interesting to compare the activation parameters of different redox processes involving gold(III). The rate constants for the oxidation of Pt^{II} ¹⁶, Fe^{II} ¹⁶, Tl^I ³⁷ and $Pt(CN)_4^{2-}$ ³⁶ by gold(III) have been studied under different experimental conditions but at constant temperature of 298 K. On the other hand, several other reactions have been studied at different temperatures and their activation parameters have been evaluated.

The oxidations of the inorganic reductants like $N_2H_5^+$, NH_3OH^+ , H_3PO_2 , H_3AsO_2 , H_2SO_3 and H_2O_2 have been shown to occur through the intermediate formation of free radicals and gold(II). This was based on the determination of stoichiometry in excess substrates, polymerization reaction and experimentally obtained activation parameters. The reactions are characterized by activation enthalpy in the region (27–78) kJ mol^{-1} except in the oxidation of H_3PO_2 by gold(III) where the value is 128 kJ mol^{-1} . Thus much higher value obtained is possibly because one electron from the lone pair of the active form

Table 1. The values of second-order-rate constants ($k_2 = k_{\text{obs}}/[S]$), equilibrium constant (K) for the fast step, disproportionation constants (k) for the slow step and the related thermodynamic parameters for the oxidation of some inorganic compounds by gold(III)^a

Substrate	$[H^+] = [Cl^-]/$ mol dm^{-3}	$10^2 k_2/$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$10^2 k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ (K)	$\Delta H^0/\text{kJ mol}^{-1}$ ($\Delta S^0/\text{JK}^{-1} \text{mol}^{-1}$)	$\Delta H^\ddagger/\text{kJ mol}^{-1}$ ($\Delta S^\ddagger/\text{JK}^{-1} \text{mol}^{-1}$)	Ref
$N_2H_5^+$	1.0	176 ± 9.0	—	—	53 ± 2.4 (61 ± 3)	17
NH_3OH^+	0.50	0.085 ± 0.002	—	—	78 ± 2.1 (59 ± 3)	18(a)
HNO_2	0.02	4.76 ± 0.11	—	—	55 ± 2 (-86 ± 7)	19
$H_3PO_2^b$	1.0	1.37 ± 0.2	—	—	128 ± 2 (136 ± 6)	20
$HAsO_2$	1.0	—	0.139 ± 0.02 (24.2 ± 1.2)	-6.75 ± 1 (4.14 ± 0.82)	49 ± 2 (-137 ± 5)	21
$SbCl_3$	3.0	90 ± 4	—	—	19 ± 1 (-182 ± 4)	22
$TiCl_2^{c-}$	3.0	300 ± 10	—	—	—	37
$H_2SO_3^d$	0.4	—	0.358 ± 0.04 (489.1 ± 11)	-18.2 ± 0.5 (11.8 ± 0.4)	27 ± 2.5 (-203 ± 10)	24
H_2O_2	0.02	0.139 ± 0.03	—	—	55 ± 2 (-137 ± 7)	25

^aThe reactions were performed in HCl medium. The values of k_2 , k and K were obtained at 303 K unless stated otherwise. The errors correspond to two least-squares standard deviations ($\pm 2\sigma$). ^bAt 308 K. ^cAt 298 K. ^dAt 304 K.

of the H_3PO_2 is transferred to gold(III) and not by P-H bond fission. The oxidation of $SbCl_3$ by gold(III), which has been studied²⁸ in HCl medium, has been shown to occur not through the intermediate formation of Sb^{IV} but by one step two electron transfer process to give Sb^V . The much lower activation enthalpy of 19.2 kJ mol^{-1} as compared to those mentioned above corroborates the above contention. No attempt has been made to correlate $\Delta S^\ddagger$ with $\Delta H^\ddagger$ since oxidations of inorganic substrates were carried out under different experimental conditions and the reactions occur via different mechanisms. Kinetic results and thermodynamic parameters for different inorganic compounds are presented in Table 1.

The oxidation of alcohols and aldoses by gold(III) occurs via C-H bond cleavage whereas α -hydroxy acids are oxidized via C-C bond cleavage. The kinetic results and activation parameters of these two series of reactions are recorded in Table 2. The activation enthalpy is found to depend on the acid dissociation constants of α -hydroxy acids. The pK_a values⁵⁶ of some α -hydroxy acids at 298 K are known, the values are 3.83, 3.86, 3.65, 3.41, and 3.04 for glycolic, lactic, α -hydroxy isobutyric acid, mandelic and benzoic acids, respectively. The plot of $\Delta H^\ddagger$ against pK_a is linear⁵⁶ (Fig. 2). Again two different lin-

ear plots of $\Delta S^\ddagger$ against $\Delta H^\ddagger$ are obtained in these two series of reactions (Fig. 3). The results indicate that α -hydroxy acid oxidations are characterized by lower activation parameters than the alcohols and aldoses. In an oxidation-reduction between an ion of a transition element and a compound or ion derived from non transition

Fig. 2. The dependence of $\Delta H^\ddagger$ on pK_a of α -hydroxy acids for oxidation with gold(III). GA = glycolic acid, LA = lactic acid, IB = α -hydroxy isobutyric acid, MA = mandelic acid and BA = benzoic acid.

Fig. 3. Isokinetic correlation for the oxidation of some organic compounds by gold(III) showing C-H bond cleavage (alcohols and aldoses) and C-C bond cleavage (α -hydroxy acids) mechanism in $\text{CH}_3\text{COOH-CH}_3\text{COONa}$ buffer medium. Plot of $\Delta S^\ddagger$ versus $\Delta H^\ddagger$.

element, the formation of free radical intermediate from a second reactant by 1-equivalent reaction is likely in some cases to be more endothermic process than the corresponding 2-equivalent reaction⁵⁷. The exothermic process is able to lower the activation enthalpy of the one step two equivalent reaction below that of the corresponding one-electron process⁵⁸⁻⁶⁰. The enthalpies as well as entropies of activation for a two electron transfer process are smaller than those obtained in the studies where gold(III) behaves as one electron transfer oxidant. The smaller activation enthalpies obtained in the oxidations of α -hydroxy acids lend further support to the fact that gold(III) behaves as a two-electron transfer oxidant in this series of reactions.

A few apparent gold(II) complexes are reported⁶¹ to be mixture of gold(I)-gold(III) oxidation states. Again, the formation of unstable gold(II) as an intermediate has also been predicted by a number of workers. However, it has been possible to stabilize this unstable oxidation state in some cases⁶²⁻⁶⁷. In one case gold(II) is stabilized by the presence of a strong Au-Au bond in certain dimeric complexes and these complexes are diamagnetic³. In other cases paramagnetic gold(II) complexes are reported to be stabilized by the delocalisation of the unpaired electron over the ligands. The synthesis and characterization of paramagnetic gold(II) complexes with the ligands *O*-aminobenzenethiol (Habt), *O*-methylthioaniline (Hmta), 1,2-di(aminophenylthio)ethane (dae) and *N*-(2-pyridyl methyl)-2-mercaptoaniline (Hpma) have been reported. These complexes are found to be extremely stable in solid state

and reasonably stable in solution. The nature and structure of the compounds were obtained from the analysis of their EPR spectra³. Thus convincing evidences in favour of the formation of intermediate transition state of gold(II) as well as stable gold(II) complexes are available in the literature as mentioned above.

Gold trichloride is dimeric in both solid and gaseous state⁶⁸ whereas tetrachloroaurate(III) ion exists as square planar configuration. The reducing substrates enter into the coordination sphere of planar gold(III) complex and forms an unstable intermediate transition state or complex which then undergoes electron transfer to give the products. The question of whether the reactions proceed by an outer- or inner-sphere mechanism and whether the coordination sphere of the intermediate state of gold remains intact or not cannot be answered at this stage. However, the reaction rate is much slower compared to those reactions, which occur by typical outer sphere mechanism^{69,70}. It is unlikely that AuCl_4^- is reduced to AuCl_4^{3-} , rather planar AuCl_4^- is reduced to AuCl_2^- . Again, FeCl_2^{16} , PtCl_4^{2-} ¹⁶, TlCl_3^{37} and SbCl_3^{22} have been shown to be oxidized by AuCl_4^- to give AuCl_2^- . It is to be mentioned further that oxidation of $\text{Pt}(\text{CN})_4^{2-}$ by AuCl_4^- , $\text{AuCl}_3(\text{H}_2\text{O})$ and $\text{AuCl}_3(\text{OH})^-$ have also been shown to occur via chloride bridged inner-sphere mechanism. Thus gold(I) which is formed is reduced to gold metal in excess reductant or by disproportionation of the gold(I) when the reaction mixture was allowed to stand for several hours. However, no detectable amount of gold metal was formed under reaction conditions used during kinetic measurements.

1 : 10-Phenanthroline as well as 2,2'-bipyridyl complexes of gold(III)^{5(b),5(c)} have been prepared and isolated in their solid states. Since there is no data to investigate the reactivities of the inorganic and organic reducing substrates towards cationic complexes of gold(III), it may be interesting to investigate such reactions in future. It is known⁷¹ that collision between like charged ions are less likely whereas between two unlike charges more likely. This is because a negative ion will find itself close to a positive ion rather than to another negative ion. As a result in the reactions between ions of unlike sign there is generally an entropy increase going from reactants to activated complex whereas for ions of like sign there is generally an entropy decrease. Such studies, therefore, using cationic complexes of gold(III) may provide a clear picture in understanding the mechanisms of reactions involving cationic as well as anionic gold(III) complexes.

Table 2. The values of second-order-rate constants ($k_2 = k_{\text{obs}}/[S]$), equilibrium constant (K) for the fast step, disproportionation constants (k) for the slow step (at 298 K) and the related thermodynamic parameters for the oxidation of some organic compounds by gold(III)

Substrate	$10^2 k_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ or $*10^2 k/\text{s}^{-1}(10^2 K)$	$\Delta H^\circ/\text{kJ mol}^{-1} (\Delta S^\circ/\text{JK}^{-1} \text{ mol}^{-1})$	$\Delta H^\ddagger/\text{kJ mol}^{-1} (\Delta S^\ddagger/\text{JK}^{-1} \text{ mol}^{-1})$
Methanol	2.56 ± 0.08	–	$77 \pm 2 (-17 \pm 7)$
Ethanol	3.36 ± 0.04	–	$85 \pm 2 (11 \pm 7)$
Isopropanol	1.85 ± 0.04	–	$72 \pm 2 (-36 \pm 14)$
Benzyl alcohol (BA)	30.4 ± 0.24	–	$73 \pm 2 (-10 \pm 7)$
<i>O</i> -Nitro BA	36.7 ± 0.16	–	$70 \pm 4 (-18 \pm 14)$
<i>m</i> -Nitro BA	42.8 ± 0.32	–	$66 \pm 6 (-30 \pm 7)$
<i>p</i> -Nitro BA	49.2 ± 0.80	–	$64 \pm 2 (-36 \pm 7)$
<i>o</i> -Chloro BA	12.8 ± 0.80	–	$88 \pm 2 (33 \pm 7)$
<i>m</i> -Chloro BA	17.1 ± 0.20	–	$83 \pm 8 (19 \pm 27)$
<i>p</i> -Chloro BA	25.8 ± 0.40	–	$74 \pm 4 (-8 \pm 14)$
<i>o</i> -Methoxy BA	10.9 ± 0.80	–	$91 \pm 2 (42 \pm 7)$
<i>m</i> -Methoxy BA	14.8 ± 0.20	–	$86 \pm 2 (28 \pm 7)$
<i>p</i> -Methoxy BA	22.1 ± 0.28	–	$81 \pm 2 (14 \pm 7)$
Benzhydrol	9.56 ± 0.80	–	$92 \pm 4 (44 \pm 14)$
D-Glucose	94.0 ± 3.00	–	$88 \pm 2 (50 \pm 7)$
D-Ribose	120 ± 4.00	–	$82 \pm 2 (32 \pm 7)$
D-Erythrose	168 ± 5.00	–	$79 \pm 3 (23 \pm 10)$
DL-Glyceraldehyde	228 ± 10.0	–	$67 \pm 6 (-14 \pm 20)$
Glycolaldehyde	42.7 ± 0.06	–	$64 \pm 4 (-38 \pm 12)$
Glycolic acid	$*0.113 \pm 0.007 (5.75 \pm 0.14)$	$20 \pm 4 (45 \pm 13)$	$38 \pm 2 (-173 \pm 7)$
Lactic acid	$*0.119 \pm 0.005 (7.43 \pm 0.17)$	$9 \pm 4 (8 \pm 13)$	$46 \pm 2 (-146 \pm 7)$
α -Hydroxy isobutyric acid	$*0.131 \pm 0.005 (6.19 \pm 0.1)$	$25 \pm 4 (59 \pm 13)$	$48 \pm 2 (-139 \pm 7)$
Mandelic acid	$*0.233 \pm 0.03 (3.09 \pm 0.1)$	$11 \pm 4 (9 \pm 13)$	$53 \pm 4 (-118 \pm 14)$
Atrolactic acid	$*0.239 \pm 0.02$	–	$57 \pm 2 (-101 \pm 7)$
Benzilic acid	$*0.158 \pm 0.01 (3.97 \pm 0.13)$	$13 \pm 4 (19 \pm 13)$	$54 \pm 2 (-116 \pm 7)$

The pH of the reactions in acetate buffer were 4.05 for alcohols, glycolaldehyde and α -hydroxy acids reactions and for aldoses pH = 3.72. $[\text{Cl}^-]$ were 0.01, 0.002, 0.01 and 0.03 mol dm⁻³ for the reactions of alcohols, aldoses, glycolaldehyde, α -hydroxy acids, respectively.

Experimental

The absorption spectrum of AuCl_4^- obtained from different sources and under different experimental conditions are different. Gangopadhyay and Chakraborty⁷² prepared tetrachloro complex by decomposing bromocomplex with aqua regia and reported that tetrachloro complex shows two intense bands in the ultraviolet region. These were interpreted as charge transfer bands, the transfer is from halogen *p* to gold *d* orbital. It may be mentioned that they have recorded the spectrum in 1 cm silica cell in Beckman DU model spectrophotometer. Spectra of AuCl_4^- were also recorded for different $[\text{Cl}^-]$ (0.001–1.0) mol dm⁻³ at various acidities²⁶. The spectrum for 1.0 mol dm⁻³ $[\text{Cl}^-]$ and pH 2.0 was found to be the same as that obtained for 1.0 mol dm⁻³ HCl²⁶. An absorption maxi-

mum at 313 nm ($\epsilon = 4.86 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) was obtained²⁶ with isosbestic point at 296 nm. Moreover, the absorption spectra of gold(III) solutions in the concentration range $(0.30\text{--}2.37) \times 10^{-4} \text{ mol dm}^{-3}$ in 0.01 mol dm⁻³ hydrochloric acid were studied in our laboratory in the UV region on a Shimadzu 1700 model UV-VIS spectrophotometer (Fig. 4) and the spectral pattern was found to remain unaltered with changes in the concentration of gold(III). An absorption maximum at 313 nm and a minimum of 270 nm were in good agreement with the literature value²⁶. Beer's law has been found to be valid in the concentration range studied. The addition of acid (0.01–1.0 mol dm⁻³) does not seem to have any change in the absorption spectrum at constant $[\text{Cl}^-]$.

Fig. 4. Spectra of gold(III) at $[HCl] = 0.01 \text{ mol dm}^{-3}$. Plot of absorbance versus wavelength. Gold(III) concentrations are (1) 0.30×10^{-4} , (2) 0.59×10^{-4} , (3) 1.04×10^{-4} , (4) 1.48×10^{-4} , (5) 1.93×10^{-4} and (6) $2.37 \times 10^{-4} \text{ mol dm}^{-3}$.

Most of the kinetic investigations were carried out spectrophotometrically although few other studies have also been made using different techniques. The reactions when studied spectrophotometrically at lower gold(III) concentrations ($\sim 10^{-4} \text{ mol dm}^{-3}$), the monitoring wavelength was 315 nm (mostly in case of inorganic substrates). On the other hand when higher concentrations of gold(III) of $\sim 10^{-3} \text{ mol dm}^{-3}$ were used the reactions (mostly with organic substrates) were followed at 400 nm. This is because of the formation of colloidal gold in the presence of UV light, which complicated the rate measurements, and the formation of colloidal gold increased in the presence of reducing substrate upon exposure to UV light. However, gold(III)-iron(II) reaction was studied¹⁶ amperometrically using rotating platinum electrode as the indicator electrode and the silver-silver(I) chloride as the reference electrode. A potential of 0.8 V versus the reference electrode was used. At this potential iron(II) is mass transport controlled and the gold(III) and gold(I) are electro inactive.

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