Kinetics and Mechanism of the Oxidation of Some α-Hydroxy Acids by Tetrachloroaurate(III) in Acetic Acid-Sodium Acetate Buffer Medium

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> ABSTRACT: The kinetics of oxidation of some neutralized α -hydroxy compounds such as glycolic (GA), lactic (LA), α -hydroxyisobutyric(IB), mandelic (MA), atrolactic (AL), and benzilic (BA) acids by tetrachloroaurate(III) have been studied. The substrates are oxidized to give formaldehyde, acetaldehyde, acetone, benzaldehyde, acetophenone, and benzophenone for the respective reactions. The rate of the reaction increases with increasing [substrate] and pH but decreases with increase in [Cl⁻]. Temperature influence is quite marked in all these reactions. A mechanism involving the formation of an unstable complex, which decomposes to give the respective reaction products, is proposed. The reactivity of the α -hydroxy acids towards gold(III) are as follows: AL > MA > BA > IB > LA > GA. © 1999 John Wiley & Sons, Inc. Int J Chem Kinet 31: 873–882, 1999

INTRODUCTION

The kinetics of oxidation of some α -hydroxy acids by some oxidants have been published [1–12]. There are no literature data involving the oxidation of α -hydroxy carboxylates by gold(III) although the oxidations of a number of inorganic reductants by gold(III) [13–15] have been studied. Since halide of gold(III) are partially hydrolysed [16] at lower acidities (1.1–12.6)×10⁻⁷mol dm⁻³ and the reactions are too slow to be monitored in a high acid medium (>10⁻³ mol dm⁻³), the reactions have been carried out in the presence of a sodium acetate-acetic acid buffer medium. Au(III) as an oxidant is of interest since it may behave as a one equivalent or a two equivalent oxidant in the reaction with α -hydroxy acids. The present report deals with the kinetics and mechanism of oxidation of some α -hydroxy carboxylates by tetrachloroaurate(III) under different experimental conditions.

EXPERIMENTAL

Reagents

Mandelic (BDH), benzilic (E. Merck, AG), α -hydroxy isobutyric (Fluka, AG), lactic (E. Merck), glycolic

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(E. Merck), and atrolactic (Aldrich Chem) acids were used without further purification and their neutral salts were prepared by the addition of the requisite amount of NaOH. α -Deutero mandelic acid was prepared following the procedure of Jones, Waters and Littler [17] by equilibrating three times of sodium mandelate in a sealed tube at 150°C for 7 days with sodium hydroxide (5%) in deuterium oxide (99.8%). Labile hydrogen was then removed by recrystallizing the free acid twice from water. (m.p. 121°C). Analysis showed that 98.5% deuteration had been achieved. A stock of gold(III) was prepared dissolving HAuCl₄ (Johnson Matthey) in 0.1 mol dm⁻³ HCl. The strength of the solution was estimated gravimetrically [18]. To a known volume (5 ml) of the standard gold solution in a 150 ml beaker, was added dropwise with stirring, a 1N solution of KOH(A.R.) until the yellow color was just discharged. A further amount of 2 ml KOH solution was added, followed by dilution to about 75 ml with distilled water. 5-6 ml of 1N oxalic acid solution was then added dropwise with stirring and the contents were kept on a boiling water bath. The solution turned purple with a violet tinge when gold separated out. The beaker was kept on the water bath for about an hour with occasional stirring. The solution was filtered through a Whatman No. 42 (7 cm) filter paper. The precipitate was washed with about 75 ml of distilled water, dried, ignited in a silica crucible and weighed as metal. The gold(III) solution after estimation was stored in the dark and used under subdued lighting condition and was diluted to desired concentrations before kinetic experiments.

Inorganic materials were of the highest available purity. All solutions were made in doubly distilled water. The oxidation studies were carried out in a NaOAc-HOAc buffer. Buffer solutions were prepared [19] from standard solution of sodium acetate and acetic acid. The pH of the solution was checked against standard buffer solution with a pH meter (Elico India LI 120).

Kinetics and Measurements

The reaction rate was determined spectrophotometrically using a sodium acetate-acetic acid buffer solution under the condition where [Na-salt of α -hydroxy acids] \gg [Au^{III}]. Gold(III) absorbs maximum at $\lambda =$ 313 nm. However, according to a number of authors, there is a possibility of formation of colloidal gold [20] when aqueous solutions of AuCl₃ or HAuCl₄ are exposed to UV light. The formation of colloidal gold upon exposure to UV light may be enhanced in the presence of reducing species. Consequently, the kinetics were followed in the visible region at $\lambda = 400$ nm using higher gold(III) concentration, in order to eliminate the possibility of the formation of colloidal gold. All of the kinetic investigations were carried out in a Systronics (India) UV-visible spectrophotometer using a thermostatted cell of 1 cm path length. The water was circulated from the bath maintained at the required temperature ($\pm 0.1^{\circ}$ C). At least 8–10 experimental readings were taken depending upon the temperature of the experiment. The pseudo-first-order rate constant (k_{obs}) was determined from the linear plots of log A (A = absorbance) against time and the linearity was observed up to two half-lives. The k_{obs} values were reproducible to within $\pm 4\%$.

Product Analysis

The product analysis of the oxidations of α -hydroxy carboxylate by tetrachloroaurate(III) were carried with the reaction mixture: $\left[\alpha-hydroxy\right]$ out carboxylate] = 3×10^{-1} mol dm⁻³, [Au^{III}] = $2.2 \times$ 10^{-3} mol dm⁻³ and pH = 4.05. The reaction mixture (30 ml) for each substrate was kept at 30°C for 120 min in a stoppered bottle since the b.p.s. of formaldehyde and acetaldehyde are low. It was then filtered to remove suspended particles, if any. In one part of the filtrate the oxidation products were tested by the formation of colors with different reagents in Table I [21-23]. The other part of the filtrate was acidified with dilute H₂SO₄ and added to 2,4-dinitrophenyl hydrazine hydrochloride solution, heated on a steam bath for 15 mins and left at room temperature for an hour when the yellow crystals of 2,4-dinitrophenyl hydrazone derivative of the product was obtained. The crystals were filtered, washed with water and dried. The crude derivative was chromatographed over neutral alumina (Brockman) and eluted with dry benzene. The purified 2,4-DNP derivative thus obtained, was crystallized from ethanol, filtered and dried to record the yield and m.p. of the sample. The melting points were checked against the literature values [24]. The results are furnished in Table I. The oxidation occurs according to the equation.

$$R \xrightarrow{OH} + AuCl_4^{-} \longrightarrow$$

$$R \xrightarrow{C=O + CO_2 + AuCl_2^{-} + 2H^{+} + 2Cl^{-} \quad (1)$$

Substrate	Product	Test	Color	% yield (2,4-DNP derivative)	mp(°C) of 2,4-DNP derivative	Lit. mp.(°C)[24] of 2,4-DNP derivative
Glycolic acid	CH ₂ O	Chromotropic acid and conc.H ₂ SO ₄	Pinkish violet [21]	88	163-165	166–167
Lactic acid	МеСНО	Equal volumes of 20% piperidine and 5% sodium nitroprus- side	Blue [22]	89	147-148	148
α-Hydroxyisobutyric acid	Me ₂ CO	Equal volumes of 5% sodium nitroprus- side and 30% NaOH	Red [23]	80	127-128	126–128
Mandelic acid	PhCHO	_	_	94	233-235	235-237
Atrolactic acid	PhCOCH ₃	_	_	85	239-240	238-240
Benzilic acid	Ph ₂ CO	_	—	91	237-239	238-239

Table I Identification of Products of Reactions

where,

R = R' = -H for glycolic acid

 $R = -CH_3$, R' = -H for lactic acid

 $R = R' = -CH_3$ for α -hydroxyisobutyric acid

 $R = -C_6H_5$, R' = -H for mandelic acid

 $R = -C_6H_5$, $R' = -CH_3$ for atrolactic acid

 $R = R' = -C_6H_5$ for benzilic acid

Test for Free Radicals

Acrylonitrile [50% (v/v)] was added to the reaction mixture during the course of the reactions. No precipitation of white polyacrylonitrile in the absence or presence of methanol was formed (during the oxidation of α -hydroxy carboxylate by gold(III)). The result is in conformity with a one-step two-electron transfer process with no free radical intermediate.

RESULT AND DISCUSSION

Stoichiometry

The stoichiometry of the reaction was studied under different experimental conditions. The reaction mixture containing excess [Au^{III}] as compared to [α -hydroxy acid], was kept for 24h and the unconsumed [Au^{III}] was determined by the method mentioned above [18]. The average stoichiometry for three different experiments was 1.00 ± 0.01 . The reaction stoichiometry may be expressed as [α -hydroxy acid]: [Au^{III}] = 1:1.

Effect of Reactant Concentrations

The reactions were studied at different concentrations of Au(III) of 1.0×10^{-3} , 2.0×10^{-3} , 3.0×10^{-3} , 4.0×10^{-3} , 5.0×10^{-3} , and 6.2×10^{-3} mol dm⁻³ for all the substrates but at constant [α -hydroxy acid], [H⁺], [Cl⁻], and temperature of 2×10^{-1} , 8.9×10^{-5} , 3×10^{-2} mol dm⁻³, and 313K, respectively. The pseudo-first-order rate constant was found to be independent of the initial [Au^{III}] in each case (Table II). The reactions were also studied at four different temperatures with variation of [α -hydroxy acid] from 2×10^{-1} to 7×10^{-1} mol dm⁻³ keeping [Au^{III}], [H⁺], and [Cl⁻] constant at 2.2×10^{-3} , 8.9×10^{-5} , and

Table II Effect of $[Au^{III}]$ on the Rate of Oxidation at 313K. $[Au^{III}] = (1.0-6.2) \times 10^{-3} \text{ mol } dm^{-3}$, $[Substrate] = 2 \times 10^{-1} \text{ mol } dm^{-3}$, $[H^+] = 8.9 \times 10^{-5} \text{ mol } dm^{-3}$, $[Cl^-] = 3 \times 10^{-2} \text{ mol } dm^{-3}$

Substrate	$k_{ m obs} imes 10^3 ({ m s}^{-1})$
Glycolic acid	0.58 ± 0.01
Lactic acid	0.75 ± 0.01
α -hydroxy isobutyric acid	0.89 ± 0.02
Mandelic acid	1.14 ± 0.01
Atrolactic acid	1.45 ± 0.02
Benzilic acid	1.06 ± 0.02

Temp (K)	$[S] \times 10^2$ (mol dm ⁻³)	$k_{ m obs}^{ m a} imes 10^{3} \ ({ m s}^{-1})$	$k_{ m obs}^{ m b} imes 10^{3} \ ({ m s}^{-1})$	$k^{ m c}_{ m obs} imes 10^3 onumber ({ m s}^{-1})$	$k_{ m obs}^{ m d} imes 10^3 onumber (s^{-1})$	$k_{ m obs}^{ m e} imes 10^3$ $(m s^{-1})$	$k^{\mathrm{f}}_{\mathrm{obs}} imes 10^{3}$ (s^{-1})
	20	0.219	0.275	0.298	0.337	0.416	0.306
	30	0.297	0.375	0.4	0.468	0.577	0.428
208	40	0.36	0.44	0.484	0.566	0.697	0.517
270	50	0.41	0.5	0.545	0.67	0.81	0.567
	60	0.48	0.566	0.61	0.789	0.937	0.66
	70	0.53	0.625	0.68	0.909	1.03	0.75
	20	0.31	0.38	0.429	0.538	0.6	0.455
	30	0.41	0.53	0.587	0.752	0.882	0.627
202	40	0.519	0.64	0.689	0.938	1.034	0.716
303	50	0.602	0.716	0.813	1.12	1.20	0.835
	60	0.65	0.815	0.915	1.212	1.43	0.938
	70	0.75	0.91	0.96	1.377	1.58	1.08
	20	0.44	0.547	0.59	0.735	0.857	0.733
	30	0.612	0.75	0.79	1.046	1.25	1.01
200	40	0.699	0.9	0.94	1.32	1.5	1.16
308	50	0.83	1.04	1.08	1.51	1.66	1.44
	60	0.91	1.21	1.16	1.78	2.0	1.594
	70	1.0	1.31	1.37	1.892	2.31	1.78
	20	0.59	0.77	0.88	1.16	1.428	1.08
	30	0.81	1.05	1.216	1.51	1.765	1.46
313	40	1.04	1.26	1.374	2.04	2.5	1.68
	50	1.08	1.37	1.584	2.34	2.73	1.887
	60	1.26	1.58	1.78	2.53	3.33	2.16
	70	1.31	1.68	2.02	2.75	3.75	2.34
	20	0.86	1.12	1.37	1.78	2.5	1.57
	30	1.12	1.44	1.894	2.34	3.33	2.165
a 10	40	1.38	1.887	2.34	3.02	4.285	2.52
518	50	1.51	2.02	2.517	3.37	5.2	3.036
	60	1.59	2.33	2.75	3.77	6.0	3.36
	70	1.89	2.52	3.03	4.34	7.5	3.76

Table III Variation of Pseudo-First-Order Rate Constants for the Oxidation of Substrates by Au^{III} at Different Temperatures. $[Au^{III}] = 2.2 \times 10^{-3} \text{ mol dm}^{-3}$ $[H^+] = 8.9 \times 10^{-5} \text{ mol dm}^{-3}$ $[Cl^-] = 3 \times 10^{-2} \text{ mol dm}^{-3}$

a = GA, b = LA, c = IB, d = MA, e = AL, f = BA

 3×10^{-2} mol dm⁻³, respectively. The results indicate that the rate increases with increasing [substrate] (Table III). Plots of $1/k_{obs}$ versus 1/[substrate] gave straight lines with positive intercepts on the y-axis and positive slopes at four different temperatures (Figure 1).

Effect of [H+]

The rate of the reaction was studied at 313K but at different pH values (4.05–5.89) using acetic acidacetate buffer while keeping [Au^{III}], [α -hydroxy acid], [Cl⁻] and ionic strength constant at 2.2 × 10⁻³, 2 × 10⁻¹, 3 × 10⁻², and 0.3 mol dm⁻³, respectively. The pseudo-first-order rate constant at constant concentrations of Au(III), substrate, H⁺, Cl⁻ and temperature as mentioned in Table II have been compared. The values are 0.59×10^{-3} , 0.76×10^{-3} , 0.90×10^{-3} , 1.14×10^{-3} , 1.46×10^{-3} and $1.08 \times 10^{-3} s^{-1}$ for the oxidations of GA, LA, IB, MA, AL and BA, respectively. The values of k_{obs} was found to increase with an increase in pH. The plot of $1/k_{obs}$ vs {K₁ + [H⁺]} gave a straight line with a positive slope and a positive intercept on the ordinate (Figure 2).

Effect of [Cl-]

The reaction was studied at 313K but at different [Cl⁻] $[(2-9) \times 10^{-2} \text{ mol dm}^{-3}]$ varied by the addition of NaCl but at constant [Au^{III}], [α -hydroxy acid], [H⁺] and ionic strength of 2.2 $\times 10^{-3}$, 2 $\times 10^{-1}$, 8.9 $\times 10^{-5}$, and 0.4 mol dm⁻³, respectively. The value of k_{obs} was found to decrease with an increase of [Cl⁻]. The



Figure 1 Variation of pseudo-first-order rate constant with [glycolate]. Plots of k_{obs}^{-1} versus [glycolate]⁻¹ at different temperatures. [Au^{III}] = 2.2×10^{-3} mol dm⁻³, [H⁺] = 8.9×10^{-5} mol dm⁻³, [Cl⁻] = 3×10^{-2} mol dm⁻³.



Figure 2 Variation of pseudo-first-order rate constant with acid concentration. Plots of k_{obs}^{-1} versus {K₁ + [H⁺]} for different substrates at 313K. [Au^{III}] = $2.2 \times 10^{-3} \text{ mol dm}^{-3}$, [substrate] = 0.2 mol dm^{-3} [Cl⁻] = $3 \times 10^{-2} \text{ mol dm}^{-3}$, $\mu = 0.3 \text{ mol dm}^{-3}$. ($\Delta = \text{GA}$; $\blacktriangle = \text{LA}$; $\blacksquare = \text{IB}$; $\square = \text{BA}$; $\bigcirc = \text{MA}$)



Figure 3 Variation of pseudo-first-order rate constant with chloride ion concentration. Plots of k_{obs}^{-1} versus [Cl⁻] for different substrates at 313K. [Au^{III}] = 2.2×10^{-3} mol dm⁻³, [substrate] = 0.2 mol dm⁻³ [H⁺] = 8.9×10^{-5} mol dm⁻³, $\mu = 0.4$ mol dm⁻³. ($\Delta = GA$; $\blacktriangle = LA$; $\blacklozenge = IB$; $\Box = BA$; $\bigcirc = MA$; $\blacksquare = AL$)

plot of $1/k_{obs}$ against [Cl⁻] is linear with a positive slope and positive intercept on the ordinate (Figure 3). The observation that Cl⁻ inhibits the rate is in keeping with step (8) of the suggested mechanism.

Effect of Ionic Strength

The reaction was studied at different ionic strengths maintained by the addition of NaClO₄ [(0.05–0.3) mol dm⁻³] but at constant [Au^{III}], [α -hydroxy acid], [H⁺], [Cl⁻] and temperature of 4 × 10⁻⁴, 0.1, 3.5 × 10⁻⁵, 2 × 10⁻² mol dm⁻³, and 308K, respectively. The pseudo-first-order rate constant increases with increase in salt concentrations (Figure 4). The observation is to be expected if the reactions occur between ions of like charge [25(a)].

Activation Parameters

The values of K_2 (equilibrium constant for the formation of the 1:1 complex between the reactants) and



Figure 4 Variation of pseudo-first-order rate constant with ionic strength. Plots of log k_{obs} versus $\sqrt{\mu}$ for different substrates at 308K. [Au^{III}] = 4×10^{-4} mol dm⁻³, [substrate] = 0.1 mol dm⁻³ [H⁺] = 3.5×10^{-5} mol dm⁻³, [Cl⁻] = 2×10^{-2} mol dm⁻³. ($\Delta = GA$; $\blacktriangle = LA$; $\blacksquare = IB$; $\square = BA$; $\bigcirc = MA$; $\blacksquare = AL$)

k (the disproportionation constant of the intermediate complex) as referred to in steps 8 and 9 for each substrate at four different temperatures have been evaluated from the plots of substrate effect. The results are in Table IV. Plots of log K₂ versus 1/T (Figure 5) are linear and the enthalpy change (Δ H°) associated with the equilibrium step was calculated followed by the estimation of Δ S° from relation (2).

$$\log K_2 = [\Delta S^\circ - (\Delta H^\circ/T)]/2.303R$$
 (2)

Plots of log(k/T) versus 1/T (Figure 6) are also linear.



Figure 5 Variation of equilibrium constant (K₂) with temperature. Plots of log K₂ versus T⁻¹. (Δ = GA; \blacktriangle = LA; \blacklozenge = IB; \Box = BA; \bigcirc = MA)

The values of ΔH^{\neq} were calculated from the respective slopes using relation (3), where R, N and h have their usual significances.

$$k = \frac{\mathrm{RT}}{\mathrm{Nh}} \,\mathrm{e}^{-\Delta \mathrm{H}^{\pm}/\mathrm{RT}} \,\mathrm{e}^{\Delta \mathrm{S}^{\pm}/\mathrm{R}} \tag{3}$$

The thermodynamic parameters associated with the equilibrium step and the activation parameters associated with the rate determining step are recorded in Table V. The fairly large and negative ΔS^{\neq} values may indicate a cyclic complex. However, for ions of same sign the transition state (T.S.) will be a more highly charged ion which would be expected to be strongly solvated so that more solvent molecules might be required than for the separate ions. This would lead to a decrease in entropy in forming the T.S. [25(b)].

Table IVEquilibrium Constants for the Fast Step and Disproportionation Constants for the Slow Step for DifferentEffects at 313K

Substrate	Effect of [S]		Effect of [H ⁺]		Effect of [Cl ⁻]	
	$\mathrm{K}_{2} imes 10^{2}$	$k imes 10^{3}$ (dm ³ mol ⁻¹ s ⁻¹)	$K_2 \times 10^2$	$k imes 10^{3}$ (dm ³ mol ⁻¹ s ⁻¹)	$K_{2} \times 10^{2}$	$k imes 10^{3}$ (dm ³ mol ⁻¹ s ⁻¹)
Glycolic acid	8.759	2.33	9.452	2.16	9.541	2.02
Lactic acid	8.225	3.03	8.374	3.03	8.228	3.00
α -Hydroxy isobutyric acid	7.578	3.37	6.497	3.78	6.883	3.5
Mandelic acid	4.327	6.0	4.243	6.0	4.476	5.95
Atrolactic acid		7.57		7.9		7.50
Benzilic acid	5.47	4.3	5.48	4.33	5.087	4.21



Figure 6 Variation of disproportionation constant (*k*) with temperature. Plots of $\log(k/T)$ versus T^{-1} . ($\Delta = GA$; $\blacktriangle = LA$; $\bullet = IB$; $\Box = BA$; $\bigcirc = MA$; $\blacksquare = AL$)

The enthalpy of activation is linearly related to the entropy of activation (r = 0.99, Figure 7) and the isokinetic temperature is 291K. This indicates that a similar mechanism may be operative in all the reactions. The isokinetic behavior is also supported by the linear plot of log k versus log k' (r = 0.98, Figure 7) where k and k' are the disproportionation constants of the complex at temperature 303K (T_1) and 308K(T_2), respectively. The isokinetic temperature was calculated from the relation $\beta = T_1T_2(1 - f)/(T_1 - T_2f)$, where f is the slope of the Exner plot [26]. The value of β was found to be 276K which is lower than T, (mid point of the experimentally used range of temperatures). Although in most cases, β is found to exceed T, there is literature evidence [27] for a large number of reactions for which β is lower than T. The rates of such reactions for which β – T is negative, are believed to be entropy controlled.

The kinetic isotope effect using mandelic and α deutero mandelic acids was carried out at [substrate],



Figure 7 Isokinetic plots for the oxidations of α -hydroxy carboxylates by Au^{III} in buffer medium. (a, a'): plot of ΔS^{\neq} vs ΔH^{\neq} (b, b'): plot of log k' vs log k (1 = GA; 2 = LA; 3 = IB; 4 = MA; 5 = BA; 6 = AL)

[Au^{III}], [H⁺], [Cl⁻] and temperature of 4.5 × 10⁻¹, 2.2 × 10⁻³, 8.9 × 10⁻⁵, 3 × 10⁻² mol dm⁻³, and 318K respectively. The $k_{\rm H}/k_{\rm D}$ value has been found to be 1.02. This indicates that C—H bond cleavage does not occur.

In a solution of tetrachloroauric(III) acid the following equilibria exist [28–30]:

$$HAuCl_4 \xleftarrow{K_3} H^+ + AuCl_4^-$$
(4)

$$\operatorname{AuCl}_4^- + \operatorname{H}_2O \xrightarrow{K_4} \operatorname{AuCl}_3(OH_2) + \operatorname{Cl}^-$$
 (5)

$$\operatorname{AuCl}_{3}(\operatorname{OH}_{2}) \xrightarrow{K_{5}} \operatorname{AuCl}_{3}(\operatorname{OH})^{-} + \operatorname{H}^{+} \qquad (6)$$

where $K_3 = 1.0$, $K_4 = 9.5 \times 10^{-6}$ and $K_5 = 0.25$ at

Table V Thermodynamic Data Associated with the Complex and the Activation Parameters Associated with the Slowest Steps

Å

Substrate	ΔH° (kJ mol ⁻¹)	ΔS° (JK ⁻¹ mol ⁻¹)	ΔH^{\neq} (kJ mol ⁻¹)	ΔS^{\neq} (JK ⁻¹ mol ⁻¹)
Glycolic acid	20 ± 4	45 ± 13	38 ± 2	-173 ± 7
Lactic acid	9 ± 4	8 ± 13	46 ± 2	-146 ± 7
α -Hydroxy isobutyric acid	25 ± 4	59 ± 13	48 ± 2	-139 ± 7
Mandelic acid	11 ± 4	9 ± 13	53 ± 4	-118 ± 14
Atrolactic acid	_	_	57 ± 2	-101 ± 7
Benzilic acid	13 ± 4	19 ± 13	54 ± 2	-116 ± 7

298K. Since the reactions were studied at a very low $[H^+]$ (~10⁻⁵ mol dm⁻³), $[HAuCl_4]$ will be practically insignificant compared to $[AuCl_4^-]$. Again, in a solution where $[Cl^-] \sim 10^{-2}$ mol dm⁻³, the value of K₄ suggests that $[AuCl_3(OH)_2]$ and hence $[AuCl_3(OH)^-]$ will be negligibly small compared to $[AuCl_4^-]$. Consequently, under the present experimental condition, $AuCl_4^-$ may only act as the oxidizing species.

Gold(III) is known [29] to behave as a one- or twoelectron transfer oxidant, depending upon the nature of the substrate and the experimental conditions. In the present investigation, the reaction mixture did not produce any polymeric suspension in presence of acrylonitrile. This suggests that gold(III) possibly behaves as a two-electron transfer oxidant in the present reaction. The observation is similar to that noticed in the oxidation of glycolaldehyde by gold(III) [31].

The acid dissociation constants [32] of some α -hydroxy acids at 298K are known, the values are 1.47×10^{-4} , 1.38×10^{-4} , 2.2×10^{-4} , 3.89×10^{-4} , and 9.1×10^{-4} for glycolic, lactic, α -hydroxy/isobutyric, mandelic and benzilic acids, respectively. Since the reactions were carried out at low acidities, the dissociation constant (K₁) values [32] of the α -hydroxy acids suggest that they will remain dissociated to a large extent (Eq. 7). The substrate anion enter into the coordination sphere of square planar gold(III) complex and replaces a chloride ligand to give an intermediate complex (X). This is further supported by the spectrophotometric evidence for the intermediate complex(X) formation. The absorbance of the reaction mixture ini-



Figure 8 Spectrophotometric evidence for intermediate complex formation between mandelic acid and gold(III) at 400 nm. [Au^{III}] = 2.2×10^{-3} mol dm⁻³, [H⁺] = 8.9×10^{-5} mol dm⁻³, [Cl⁻] = 3×10^{-2} mol dm⁻³, Temp = 318K, [MA] are \Box , 3×10^{-1} ; \blacktriangle , 4×10^{-1} ; \bigtriangleup , 5×10^{-1} ; \blacklozenge , 6×10^{-1} and 0, 7×10^{-1} mol dm⁻³.

tially increases and then decreases gradually (Figure 8). The initial increase in absorbances indicates that an intermediate complex is formed between the reactants. The latter then decomposes to give products as mentioned in steps (9) and (10), where R = R' = -H for glycolic, R' = -H for lactic and mandelic acid. The observed kinetic isotopic effect suggests that the oxidation occurs via C—C bond cleavage and not by C—H bond breaking.



The rate of disappearance of Au^{III} may be expressed as

$$-d[Au^{III}]/dt = k[X]$$
(11)

Now
$$[X] = \frac{K_2[A^-][Au^{III}]_f}{[Cl^-]}$$

where $[A^-] = \frac{K_1}{K_1 + [H^+]} [S]$
 $\therefore [X] = \frac{K_2K_1 [S] [Au^{III}]_f}{\{K_1 + [H^+]\}[Cl^-]}$ (12)

and
$$[Au^{III}]_{t} = [Au^{III}]_{f} + \frac{K_{2}K_{1} [S] [Au^{III}]_{f}}{\{K_{1} + [H^{+}]\}[Cl^{-}]}$$

so that $[Au^{III}]_f =$

$$\frac{[Au^{m}]_{t}}{1 + \frac{K_{1}K_{2}[S]}{(K_{1} + [H^{+}])[Cl^{-}]}}$$
(13)

Equation (10) can be transformed into

$$= \frac{k K_1 K_2 [S]}{\{K_1 + [H^+]\}[Cl^-]} \frac{[Au^{III}]_t}{\left\{1 + \frac{K_2 K_1 [S]}{(K_1 + [H^+])[Cl^-]}\right\}}$$
(14)

so that the pseudo-first-order rate constant

$$k_{obs} = -\frac{1}{[Au^{III}]_{t}} \frac{d[Au^{III}]_{t}}{dt}$$
$$= \frac{kK_{1}K_{2}[S]}{\{K_{1} + [H^{+}]\}[Cl^{-}] + K_{2}K_{1}[S]} \quad (15)$$

Rearranging equation (15), we obtain

$$1/k_{\rm obs} = \frac{\{K_1 + [H^+]\}[Cl^-]}{kK_1K_2[S]} + 1/k$$
(16)

Thus equation (16) can explain the linear plot (Figure 1) of $1/k_{obs}$ versus 1/[S] and from the intercept of the plot at each temperature the value of the disproportionation constant (k) at that temperature was evaluated and using the literature value of K₁, the value of K_2 at that temperature was calculated from the slope (Table IV). We are unable to calculate the value of K_2 in case of atrolactic acid, since the dissociation constant at that temperature is not available in the literature. Figure 2 shows an inverse dependence of the rate on $[H^+]$ which conforms to the rate law (16). The values of k and K_2 at 313K evaluated from the plot of $1/k_{obs}$ against {K₁ + [H⁺]} at that temperature (Figure 2) are found to be in agreement with those obtained from the substrate effect as well as effect of [Cl⁻] at that temperature (Table IV).

It is evident that in the slow step (9), the transition state will be much more polar than the intermediate complex (X) and the former will be more stabilized by the presence of ion atmosphere than the latter. Thus an increase in ionic strength will favor the transition state, thereby increasing the value of k (step 9) and consequently an increase in k_{obs} is expected as observed in the present investigation (Figure 4).

Introduction of a methyl group at the α -carbon of

glycolic acid stabilizes the anion through stronger intramolecular H-bonding and the value of K2 diminishes in the order GA > LA > IB (Table IV). Introduction of a phenyl group decreases the nucleophilicity of the anion thereby further diminishing the value of K₂. Again, introduction of a methyl group at the α -carbon of glycolic acid increases the electron density on the α -carbon, thus rendering the C-C bond breaking easier in the order GA < LA <IB. Also, introduction of bulky methyl groups at the α -carbon facilitates the C—C bond breaking in the slow step due to release of steric strain in the product carbonyl compounds with sp² hybridization at that α carbon atom. From the same reasoning, introduction of a phenyl group should decrease the electron density on the α -carbon and the decrease in k (step 9) is expected. On the contrary, the value of k is higher for mandelic acid than for α -hydroxy isobutyric acid which can be explained only by the fact that carbonium ion formed on the α -carbon after removal of CO₂ is stabilized through resonance in the benzene ring. The value, however, slightly diminishes after introduction of a second phenyl group (viz, benzilic acid) possibly due to the fact that the benzene rings go slightly out of plane (that is, twisted) making resonance stabilization of the positively charged intermediate slightly difficult. In case of atrolactic acid, the α carbon of the -OH group is attached to one -Ph group and one — Me group. The — Ph group attached to the α -carbon stabilizes the carbonium ion formed in the intermediate through resonance while the -Me group stabilizes the system through hyperconjugation. The *k* values which are in the order GA < LA < IB< BA < MA < AL are in conformity with the suggested mechanism.

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