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Kinetics and Mechanism of the Oxidation of Hydrogen Peroxide by Gold(III) in an Aqueous Hydrochloric Acid Medium

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The kinetics of the reaction between hydrogen peroxide and gold(III) in a hydrochloric acid medium has been studied. The reaction is first order with respect to $[\mathrm{Au^{III}}]$ as well as $[\mathrm{H_2O_2}]$. The reaction rate has an inverse dependence on $[\mathrm{H^+}]$ and $[\mathrm{Cl^-}]$. $\mathrm{AuCl_4^-}$, $\mathrm{AuCl_3(OH_2)}$, and $\mathrm{AuCl_3(OH)^-}$ are the reactive species of Au(III). A rate expression consistent with the experimental findings has been proposed.

The reactions between hydrogen peroxide and Mn(III),[1—3] Co(III),[4—7] Ce(IV),[8—10] Fe(II),[11] and Ag(II)[12] have already been investigated in an acid medium. All of the above-mentioned aqua-metal ions are known to be one-electron transfer oxidants. The reactions have been shown to occur through the intermediate formation of free radicals. Metal–hydrogen peroxide complexes have also been postulated in a few cases. There is no evidence for the formation of free radicals in the oxidation of $\mathrm{H_2O_2}$ by Ag(III)[13] and Tl(III)[14] in an acidic medium; rather, two-electron processes are reported to be involved in the reactions.

The presence of $\mathrm{AuCl_3(OH_2)}$ and $\mathrm{AuCl_3(OH)^-}$ in a solution of $\mathrm{AuCl_4^-}$ was postulated during a kinetic study[15—19] of the hydrolysis of $\mathrm{AuCl_4^-}$. Studies concerning the substitution reactions of Au(III) with ethylenediamine[20,21] and other polyamines,[22,23] as well as a few redox reactions[24—29] of Au(III), have also been reported. The reaction between hydrogen peroxide and gold(III) in a hydrochloric acid medium was undertaken in order to understand the reactivity of different Au(III) species towards $\mathrm{H_2O_2}$.

Experimental

Reagents. An Au(III) solution was prepared by dissolving solid tetrachloroauric(III) acid (Loba, India) in 0.1 mol dm^{-3} hydrochloric acid, and estimated gravimetrically.[30] Hydrogen peroxide (BDH) was used, and the solution was estimated by the addition of a known excess of Ce(IV) to an aliquot $\mathrm{H_2O_2}$ solution, followed by an estimation of unreacted Ce(IV) by titration against a standard ammonium iron(II) sulfate using ferroin as an indicator.[31] All other reagents were of analytical grade. Solutions were prepared in doubly distilled water.

Kinetic Measurements. The reaction rate was determined spectrophotometrically under pseudo-first-order conditions, where $[\mathrm{H_2O_2}] \gg [\mathrm{Au^{III}}]$. Gold(III) absorbs maximum at $\lambda = 313$ nm.[28] However, according to a number of authors, there is a possibility of colloidal gold formation[32] when aqueous solutions of $\mathrm{AuCl_3}$ or $\mathrm{HAuCl_4}$ 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, in order to avoid the possibility of the formation of colloidal gold, the kinetics were followed in the visible region at $\lambda = 400$ nm using higher gold(III) concentrations. All of the kinetic investigations were carried out on a Systronics (India) UV-vis spectrophotometer using a thermostatted cell of 1 cm path length. Generally, 8—10 experimental readings were taken in each run. The pseudo-first-order rate constant (k_{obs}) was determined from a plot of log (absorbance) versus time. The k_{obs} values were reproducible to within ±5%.

Evidence for the Formation of Free Radicals. A solution of Au(III) (8×10^{-4} mmol) was added to a solution containing $\mathrm{H_2O_2}$ (2.5×10^{-1} mmol) and acrylamide (3×10^{-3} dm^3, 40% (w/v)); each of the $[\mathrm{H^+}]$ and $[\mathrm{Cl^-}]$ was adjusted to 0.01 mol dm^{-3}. The total volume of the solution was adjusted to 1×10^{-2} dm^3. A white polymer resulted immediately. Control experiments showed that no polymerization of acrylamide took place under the experimental conditions with either Au(III) or $\mathrm{H_2O_2}$ alone.

Results

Stoichiometry. The stoichiometry of the reaction was studied under different experimental conditions. The reaction mixture containing excess $[\mathrm{H_2O_2}]$, as compared to $[\mathrm{Au^{III}}]$, was kept for 24 h, and the unconsumed $\mathrm{H_2O_2}$ was determined using Ce(IV). The average stoichiometry for three different experiments was 1.00±0.045. A colorless gas was found to evolve during the reaction. The reaction took place according to the following equation

$$\mathrm{H_2O_2} + \mathrm{Au^{III}} \longrightarrow 2\mathrm{H^+} + \mathrm{O_2} + \mathrm{Au^{I}} \tag{1}$$

Effect of Reactant Concentration. The reaction was studied at varying concentrations of Au(III) [$(0.1—2.0)\times10^{-3}$ mol dm^{-3}], but at constant $[\mathrm{H_2O_2}]$, $[\mathrm{H^+}]$, $[\mathrm{Cl^-}]$, and temperature. The results (Table 1) show that the reaction rate is independent of the initial $[\mathrm{Au^{III}}]$. The reaction was also studied at different $[\mathrm{H_2O_2}]$ [$(0.2—2.0)\times10^{-1}$ mol dm^{-3}], but at constant $[\mathrm{Au^{III}}]$, $[\mathrm{H^+}]$, $[\mathrm{Cl^-}]$, and temperature. The plots of k_{obs} against $[\mathrm{H_2O_2}]$ are linear, passing through the origin (Fig. 1). The reaction follows the rate law

Table 1. Variation of Different Rate Constants with Oxidant Concentration at 303 K $[H_2O_2]=8\times10^{-2}$ mol dm^{-3}; $[H^+]=2\times10^{-2}$ mol dm^{-3}; $[Cl^-]=2\times10^{-2}$ mol dm^{-3}

$[Au^{III}]\times10^3$ mol dm^{-3}	$k_{obs}\times10^5$ s^{-1}	$k\times10^4$ dm^3 mol^{-1} s^{-1}
0.1	10.9	13.6
0.2	11.0	13.8
0.4	11.4	14.2
0.8	11.3	14.1
2.0	11.2	14.0

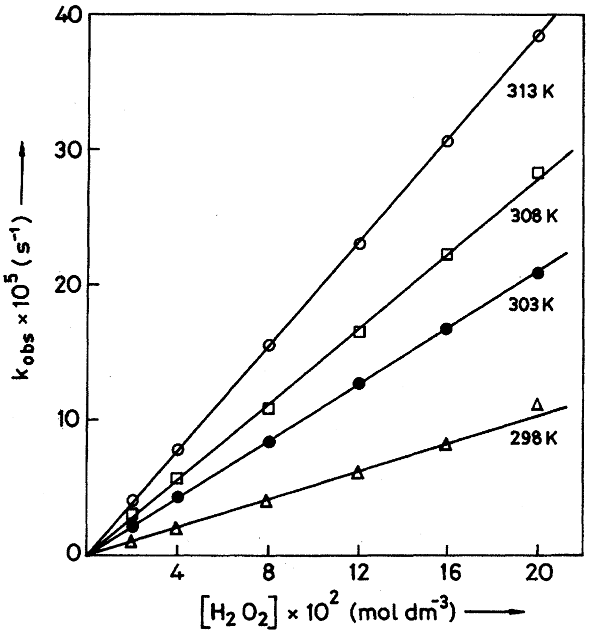

Fig. 1. Plots of k_{obs} against $[H_2O_2]$ at different temperatures. $[Au^{III}]=1.0\times10^{-3}$ mol dm^{-3}, $[H^+]=[Cl^-]=0.02$ mol dm^{-3}, $\mu=0.02$ mol dm^{-3}.

$$k_{obs} = -\frac{1}{[Au^{III}]}\cdot\frac{d[Au^{III}]}{dt} = k[H_2O_2], \tag{2}$$

where k is the second-order rate constant.

Effect of Ionic Strength. The reaction was studied at different ionic strengths maintained by the addition of $NaClO_4$, but at constant $[Au^{III}]$, $[H_2O_2]$, $[H^+]$, $[Cl^-]$, and temperature. It appears that the rate of the reaction in 1 mol dm^{-3} $NaClO_4$ decreases to half the value in the absence of the salt, and hence, the influence of $[H^+]$ and $[Cl^-]$ on the rate was studied at constant ionic strength.

Effect of $[H^+]$. The rate of the reaction was also determined at four different temperatures, but at different $[H^+]$ in the range (0.01—0.2) mol dm^{-3}, keeping $[Au^{III}]$, $[H_2O_2]$, $[Cl^-]$, and ionic strength constant. k_{obs} decreased with an increase in $[H^+]$. The plots of k_{obs} versus $1/[H^+]$ at different temperatures are straight lines with different slopes and different intercepts (Fig. 2). At a constant temperature and at constant $[Cl^-]$, k shows a linear variation with $1/[H^+]$; such straight lines at different $[Cl^-]$ have different slopes and different intercepts on the Y-axis (Fig. 3). Thus, the empirical rate expression for k may be written as

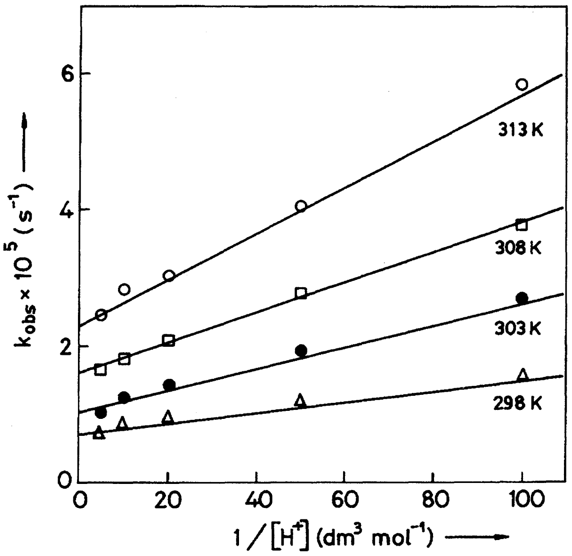

Fig. 2. Plots of k_{obs} against $1/[H^+]$ at different temperatures. $[Au^{III}]=1.0\times10^{-3}$ mol dm^{-3}, $[H_2O_2]=8.0\times10^{-2}$ mol dm^{-3}, $[Cl^-]=0.20$ mol dm^{-3}, $\mu=0.20$ mol dm^{-3}.

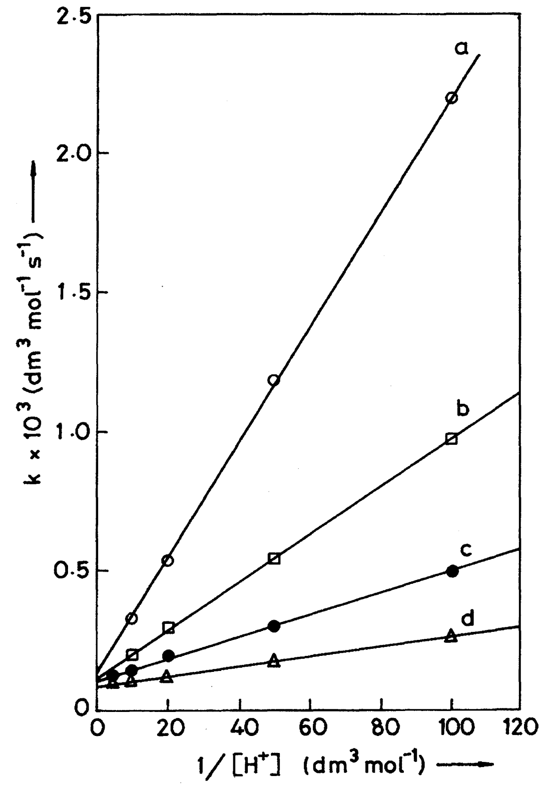

Fig. 3. Plots of second order rate constant, k, against $1/[H^+]$ at different $[Cl^-]$. $[Au^{III}]=1.0\times10^{-3}$ mol dm^{-3}, $\mu=0.20$ mol dm^{-3}, Temp=298 K, $[Cl^-]$: (a) 0.01, (b) 0.02, (c) 0.05, and (d) 0.10 mol dm^{-3}.

$$k = k_a + \frac{k_b}{[H^+]}, \tag{3}$$

where k_a and k_b are constants which are both dependent on $[Cl^-]$.

Effect of $[Cl^-]$. The reaction was studied at different $[Cl^-]$ [(0.01—0.1) mol dm^{-3}] maintained by the addition of NaCl, but at constant [Au^{III}], [H_2O_2], [H^+], and ionic strength. The ionic strength in each case was held constant by the addition of $NaClO_4$. The value of k_{obs} was found to decrease with an increase of [Cl^-]. The plots of k_{obs} against 1/[Cl^-] at four different temperatures are linear with different slopes and different intercepts on the Y-axis (Fig. 4). A linear plot was also obtained for k versus 1/[Cl^-] at a constant temperature and at constant pH. Such straight-line plots at different pH values have the same intercept on the Y-axis, despite the different slopes (Fig. 5). Thus, the relation between k and [Cl^-] can be given by the expression

$$k = k_c + \frac{k_d}{[Cl^-]}, \tag{4}$$

where, k_c = a constant independent of [H^+],

k_d = a constant dependent on [H^+].

Discussion

The following equilibria are known[19,24,25] to exist in a dilute solution of tetrachloroauric(III) acid:

$$HAuCl_4 \overset{K_1}{\rightleftarrows} H^+ + AuCl_4^- \tag{5}$$

$$AuCl_4^- + H_2O \overset{K_2}{\rightleftarrows} AuCl_3(OH_2) + Cl^- \tag{6}$$

$$AuCl_3(OH_2) \overset{K_3}{\rightleftarrows} AuCl_3(OH)^- + H^+ \tag{7}$$

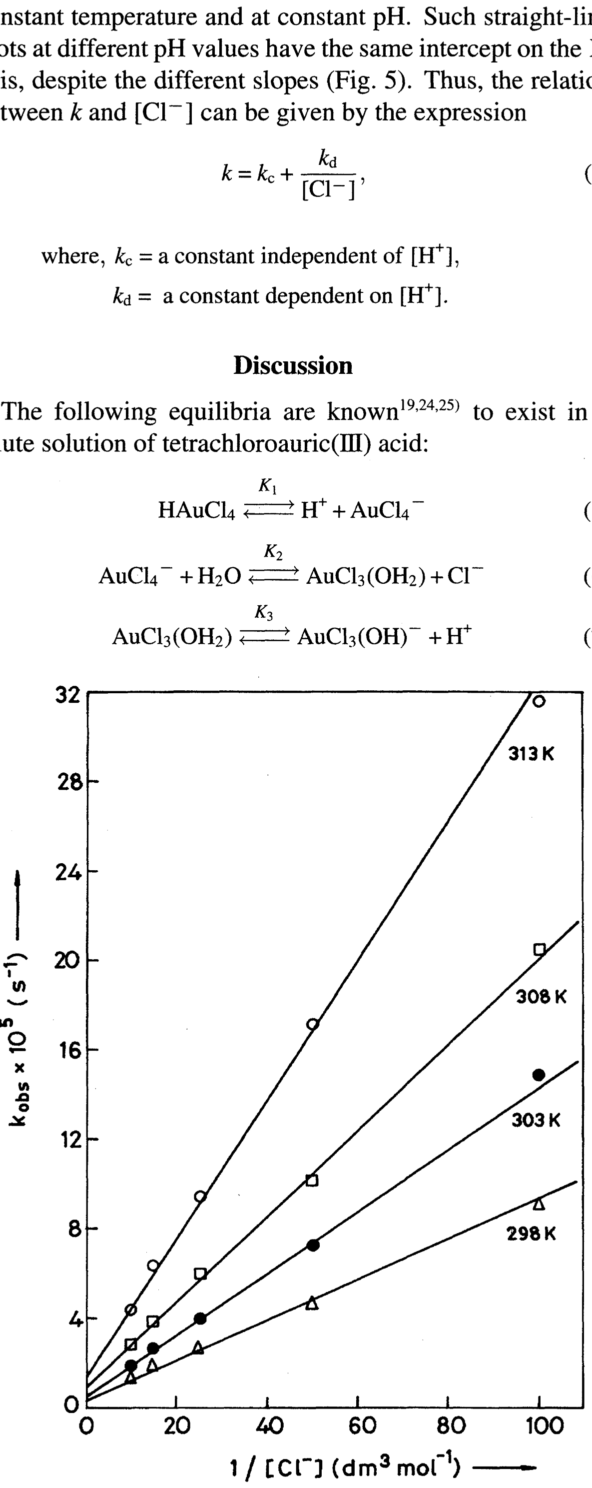

Fig. 4. Plots of k_{obs} against 1/[Cl^-] at different temperatures. [Au^{III}]=1.0×10^{-3} mol dm^{-3}, [H_2O_2]=5.0×10^{-2} mol dm^{-3}, [H^+]=0.01 mol dm^{-3}, μ=0.20 mol dm^{-3}.

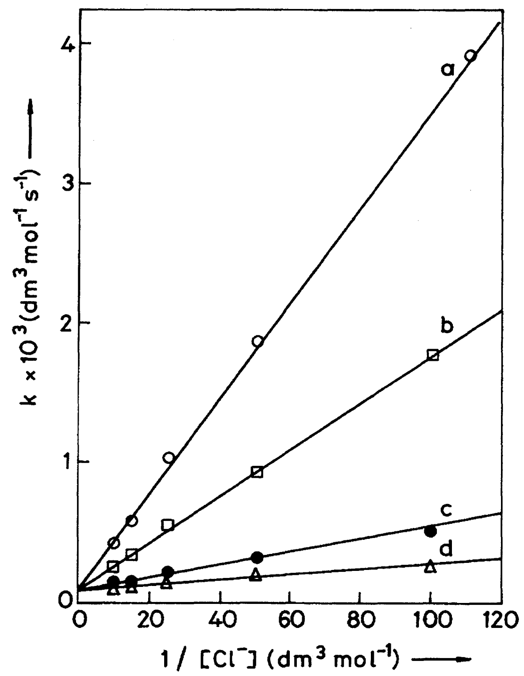

Fig. 5. Plots of second order rate constant, k, against 1/[Cl^-] at different [H^+]. [Au^{III}]=1.0×10^{-3} mol dm^{-3}, μ=0.20 mol dm^{-3}, Temp=298 K, [H^+]: (a) 0.005, (b) 0.01, (c) 0.05, and (d) 0.10 mol dm^{-3}.

In the above, K_1=1.0, K_2=9.5×10^{-6}, and K_3=0.25 at 298 K. Consequently, four different species, viz., $HAuCl_4$, $AuCl_4^-$, $AuCl_3$ (OH_2), and $AuCl_3$ $(OH)^-$, may act as oxidants under the present experimental condition. Again, the value of K_1 predicts that in a 10^{-2} mol dm^{-3} solution of HCl, [$HAuCl_4$] is practically insignificant compared to [$AuCl_4^-$].

Hydrogen peroxide is known to be a very weak acid, and the dissociation constant (K_4) for the reaction,[33]

$$H_2O_2 \overset{K_4}{\rightleftarrows} H^+ + HO_2^-, \tag{8}$$

is 1.5×10^{-12} at 298 K. Therefore, in a solution of 10^{-2} mol dm^{-3} HCl, hydrogen peroxide exists mainly as molecular H_2O_2. Again, the equilibrium constant for the protonation[1] of H_2O_2 in 1.0 mol dm^{-3} $HClO_4$ has a value of ca. 10^{-3}:

$$H_2O_2 + H^+ \overset{K_5}{\rightleftarrows} H_3O_2^+. \tag{9}$$

Hence, in a solution of 10^{-2} mol dm^{-3} HCl, it may be assumed that [$H_3O_2^+$] is practically insignificant compared to [H_2O_2].

Gold(III) is known[24] to behave as a one- or two-electron transfer oxidant, depending upon the nature of the substrate and the experimental conditions. In the present investigation, the reaction mixture gave a polymeric suspension in the presence of acrylamide. This suggests that a free-radical intermediate is formed during the reaction, and that Au(III) behaves as a one-electron transfer oxidant. A free-radical intermediate may also be produced from a reaction of H_2O_2 with Au(I), or from a catalytic decomposition of H_2O_2 in presence of Au(I) or Au(0); however, such possibilities may be ruled out, since they would result in a stoichiometry of Au(III): H_2O_2 of less than 1, which is not in conformity with the observed stoichiometry under the kinetic conditions. Moreover, neither colloidal gold nor any precipitate of gold was detected under the kinetic conditions. The formation of unstable Au(II) as an intermediate has been predicted by a number of workers.[34—37] On the other hand, the removal of one electron from H_2O_2 in the rate-determining step leads to the formation of free radicals $(HO_2)^{\bullet}$ and/or $(H_2O_2)^{\bullet +}$. There is literature evidence[10,38] indicating that $(HO_2)^{\bullet}$ is formed during the oxidation of H_2O_2 by Ce(IV) in acidic media, and that $(H_2O_2)^{\bullet +}$ is formed during the oxidation of H_2O_2 by Mn(III).[1] These two species are in equilibrium in acidic solution,

$$(H_2O_2)^{\bullet +} \overset{K_6}{\rightleftharpoons} H^+ + (HO_2)^{\bullet} \tag{10}$$

The value of the equilibrium constant[1] (K_6) is ca. 10^{-1} in acidic solution. Thus, in ca. 10^{-2} mol dm^{-3} HCl, the $(HO_2)^{\bullet}$ concentration would be in large excess compared to the $(H_2O_2)^{\bullet +}$ concentration.

Again, since $(HO_2)^{\bullet}$ is known to react by fast steps (Eqs. 11 and 12), the respective rate constants[1] are 6.5×10^2 and 5.4×10^6 dm^3 mol^{-1} s^{-1}.

$$(HO_2)^{\bullet} + H_2O_2 \xrightarrow{\text{fast}} (OH)^{\bullet} + H_2O + O_2 \tag{11}$$

$$(HO_2)^{\bullet} + (HO_2)^{\bullet} \xrightarrow{\text{fast}} H_2O_2 + O_2 \tag{12}$$

The following steps may be proposed to explain the reaction:

$$AuCl_4^- + H_2O_2 \xrightarrow[\text{slow}]{k_1} AuCl_4^{2-} + (HO_2)^{\bullet} + H^+ \tag{13}$$

$$AuCl_3(OH_2) + H_2O_2 \xrightarrow[\text{slow}]{k_2} AuCl_3(OH_2)^- + (HO_2)^{\bullet} + H^+ \tag{14}$$

$$AuCl_3(OH)^- + H_2O_2 \xrightarrow[\text{slow}]{k_3} AuCl_3(OH_2)^{2-} + (HO_2)^{\bullet} + H^+ \tag{15}$$

Reaction (11) does not appear to be very fast, as is evident from the value of the rate constant, although reaction (12) appears to be very fast. Again, the $(HO_2)^{\bullet}$ concentration is very low, so that the rates of reactions (11) and (12) appear to be low. However, since $[Au^{III}]\approx10^{-3}$ mol dm^{-3}, the values of K_1, K_2, and K_3 suggest that in a 0.01 mol dm^{-3} HCl solution, although $[AuCl_4^-]\approx10^{-3}$ mol dm^{-3}, other Au^{III} species will be at a much lower concentration, viz., $[AuCl_3(OH_2)]\approx10^{-6}$ mol dm^{-3} and $[AuCl_3(OH)^-]\approx10^{-5}$ mol dm^{-3} or even less in a higher concentration of HCl. Again, the rate constant (evaluated later) for the elementary reaction (13) is very low compared to those for reactions (14) and (15). All of these facts suggest that elementary reactions (13)—(15) are much slower than reaction (12), if not (11).

Although reaction (12) has a very high rate constant, the possibility of reactions (16) and (17), viz.,

$$Au^{III} + (HO_2)^{\bullet} \xrightarrow{\text{fast}} Au^{II} + HO_2^+ \tag{16}$$

$$HO_2^+ \xrightarrow{\text{fast}} H^+ + O_2 \tag{17}$$

occurring to a small extent cannot be totally ruled out, since Au(III) is present at a comparatively greater concentration compared to $(HO_2)^{\bullet}$ itself. Au(II) would undergo a fast disproportionation into Au(I) and Au(III),

$$2\,Au^{II} \xrightarrow{\text{fast}} Au^{I} + Au^{III}, \tag{18}$$

and hence, the possibility of a reaction between Au(II) and $(HO_2)^{\bullet}$ may be ignored. The rate of the disappearence of Au(III) may be expressed as

$$-\frac{d[Au^{III}]}{dt} = \{k_1[AuCl_4^-] + k_2[AuCl_3(OH_2)] + k_3[AuCl_3(OH)^-]\}[H_2O_2]. \tag{19}$$

If $C_0=[Au^{III}]$, $x=[AuCl_3(OH_2)]$, and $y=[AuCl_3(OH)^-]$, Eq. 19 may be written as

$$\begin{aligned} -\frac{d[Au^{III}]}{dt} &= \{k_1(C_0-x-y)+k_2x+k_3y\}[H_2O_2] \\ &= \{k_1C_0+(k_2-k_1)x+(k_3-k_1)y\}[H_2O_2]. \end{aligned} \tag{20}$$

Again, the value of K_2 indicates that $C_0 \gg x$, y, so that

$$K_2 = \frac{x[Cl^-]}{C_0-x-y} \approx \frac{x[Cl^-]}{C_0}$$

$$\text{and } K_3 = \frac{y[H^+]}{x} = \frac{y[H^+][Cl^-]}{K_2C_0}.$$

Substitution of x and y in Eq. 20 gives

$$\begin{aligned} k_{\text{obs}} &= -\frac{1}{[Au^{III}]}\frac{d[Au^{III}]}{dt} \\ &= \{k_1 + \frac{(k_2-k_1)K_2}{[Cl^-]} + \frac{(k_3-k_1)K_2K_3}{[Cl^-]}\frac{1}{[H^+]}\}[H_2O_2]. \end{aligned} \tag{21}$$

Reactions involving $AuCl_3(OH_2)$ or $AuCl_3(OH)^-$ with oxalate[28] and polyamines[22,23] are found to be much faster than those involving $AuCl_4^-$ species, owing to the easier displacement of an OH^-/OH_2 group than a Cl^- ion. Hence, assuming that $k_1 \ll k_2$, k_3 Eq. 21 changes to Eq. 22,

$$k_{\text{obs}} = (k_1 + \frac{k_2K_2}{[Cl^-]} + \frac{k_3K_2K_3}{[H^+][Cl^-]})[H_2O_2]. \tag{22}$$

Comparing Eq. 22 with empirical Eqs. 3 and 4, it becomes evident that

$$k_a = (k_1 + \frac{k_2K_2}{[Cl^-]}), \tag{23}$$

$$k_b = (k_3K_2K_3/[Cl^-]), \tag{24}$$

$$k_c = k_1, \tag{25}$$

$$\text{and } k_d = (k_2K_2 + \frac{k_3K_2K_3}{[H^+]}). \tag{26}$$

The value of k_c has been calculated to be 8.5×10^{-5} dm^3 mol^{-1} s^{-1} at 298 K. The values of k_a, k_b, and k_d (Table 2) were calculated from the slopes and intercepts of the lines in Fig. 5. The values recorded in Table 2 indicate that there is an inverse dependence of k_d on $[H^+]$ and of k_a and k_b on $[Cl^-]$, which are in keeping with the plots as shown in Fig. 6.

Among the different gold(III) species, $AuCl_3(OH)^-$ appears to be the most reactive, since the reaction is found

Table 2. Values of Empirical Constants k_a, k_b, and k_d for Various [H$^+$] and [Cl$^-$]
Temperature=298 K

[Cl$^-$] mol dm^{-3}	[H$^+$] mol dm^{-3}	$k_d \times 10^5$ s^{-1}	$k_a \times 10^5$ dm^3 mol^{-1} s^{-1}	$k_b \times 10^5$ s^{-1}
0.005	0.005	3.61	20.4	3.75
	0.01	1.92		
	0.02	0.93		
	0.05	0.42		
	0.10	0.25		
0.01	0.005	3.61	14.0	1.89
	0.01	1.92		
	0.02	0.93		
	0.05	0.42		
	0.10	0.25		
0.02	0.005	3.61	11.0	0.95
	0.01	1.92		
	0.02	0.93		
	0.05	0.42		
	0.10	0.25		
0.05	0.005	3.61	10.2	0.379
	0.01	1.92		
	0.02	0.93		
	0.05	0.42		
	0.10	0.25		
0.10	0.005	3.61	9.3	0.190
	0.01	1.92		
	0.02	0.93		
	0.05	0.42		
	0.10	0.25		

to be inhibited by H$^+$ ions at a constant [Cl$^-$]. The plots of k_{obs} versus 1/[H$^+$] at four different temperatures (Fig. 2) conform to Eq. 22. From the slope of the straight line at 298 K, the value of k_3 was evaluated to be $(8.0\pm0.2)\times10^{-2}$ dm^3 mol^{-1} s^{-1}. It is evident from Eq. 6 that the addition of Cl$^-$ decreases the concentrations of $AuCl_3(OH_2)$ and $AuCl_3(OH)^-$, thereby increasing the concentration of less-reactive species, $AuCl_4^-$; it can thus explain the retarding effect of the Cl$^-$ ion on the reaction rate. Equation 22 predicts a linear plot of k_{obs} versus 1/[Cl$^-$], which was found to be experimentally true at four different temperatures (Fig. 4). The value of k_2, evaluated from the slope of such straight line plot at 298 K, using the k_3 (as obtained earlier from Fig. 2), equals $(6.0\pm0.3)\times10^{-2}$ dm^3 mol^{-1} s^{-1}. Again, using the value of k_2, k_1 determined from the plot of k_{obs} versus 1/[H$^+$] (Fig. 2) at 298 K has been found to be $(8.5\pm0.2)\times10^{-5}$ dm^3 mol^{-1} s^{-1}, while from the plot of k_{obs} versus 1/[Cl$^-$] (Fig. 4) at 298 K, k_1 is found to have the same value. The two values are in good agreement. The values of k_1, k_2, and k_3 at 298 K are 8.5×10^{-5}, 6.0×10^{-2}, and 8.0×10^{-2} dm^3 mol^{-1} s^{-1} respectively, which justify our previous assumption that $k_1 \ll k_2$, k_3. Although the values of k_1 were evaluated (Table 3) at four different temperatures, those of k_2 and k_3 cannot be determined, except at 298 K, since the values of K_2 and K_3 are known only at 298 K. From a plot of log k_1 against $1/T$, the value of the enthalpy of activation for step (13) has been evaluated to be (55±2) kJ mol^{-1} and the entropy of activation is (−137±7) J K^{-1} mol^{-1}. However, the values of constants k_2K_2 and $k_3K_2K_3$ were determined

Table 3. Values of Composite Constants at Different Temperatures

Temperature K	$k_1 \times 10^4$	$k_2K_2 \times 10^6$	$k_3K_2K_3 \times 10^7$
298	0.85	0.60	1.84
303	1.26	1.00	2.78
308	1.92	1.60	3.75
313	2.56	2.40	6.99

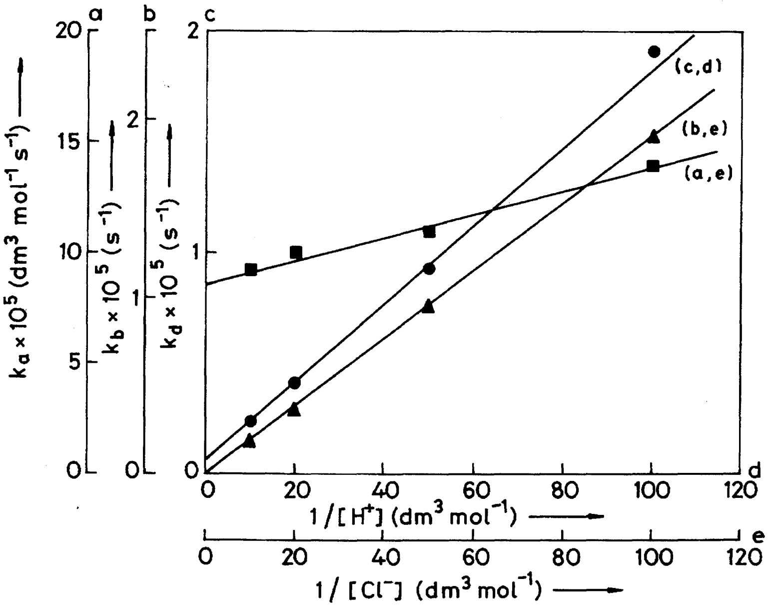

Fig. 6. Plots of k_a and k_b against 1/[Cl$^-$] and plot of k_d against 1/[H$^+$]. Temp=298 K.

(Table 3) at four different temperatures from Figs. 2 and 4. All of this kinetic evidence, as well as the polymerization test, are in favor of a mechanism in which three different Au(III) species react with H_2O_2 to give products through the intermediate formation of free radicals and Au(II).

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References

1) G. Davies, L. J. Kirschenbaum, and K. Kustin, *Inorg. Chem.*, **7**, 146 (1968).

2) T. E. Jones and R. E. Hamm, *Inorg. Chem.*, **13**, 1940 (1974).

3) C. F. Wells and D. Mays, *J. Chem. Soc. A*, **1968**, 665.

4) N. S. Rowan, C. Y. Price, W. Benjamin, and C. B. Storm, *Inorg. Chem.*, **18**, 2044 (1979).

5) I. Bodek and G. Davies, *Inorg. Chem.*, **14**, 2580 (1975).

6) C. F. Wells and M. Husain, *Trans. Faraday Soc.*, **67**, 760 (1971).

7) G. Davies and K. O. Watkins, *J. Phys. Chem.*, **74**, 3388 (1970).

8) C. F. Wells and M. Husain, *J. Chem. Soc. A*, **1970**, 1013.

9) H. A. Mahlman, R. W. Mathews, and T. J. Sworski, *J. Phys. Chem.*, **75**, 250 (1971).

10) P. B. Sigler and B. J. Masters, *J. Am. Chem. Soc.*, **79**, 6353 (1957).

11) W. J. Barb, J. H. Baxendale, P. George, and K. R. Hangrave, *Trans. Faraday Soc.*, **47**, 591 (1951).

12) C. F. Wells and D. Fox, *J. Inorg. Nucl. Chem.*, **38**, 107 (1976).

13) R. Banerjee, A. Das, and S. Dasgupta, *J. Chem. Soc., Dalton Trans.*, **1989**, 1645.

14) M. S. Prasada Rao, A. R. Mohan Rao, R. Kalavathi, T. Siva Rao, and P. Vani., *J. Chem. Soc., Dalton Trans.*, **1993**, 2238.

15) L. R. Rich and H. Taube, *J. Phys. Chem.*, **58**, 1 (1954).

16) H. Chateau, C. M. Gadet, and J. Pouvadier, *J. Chem. Phys.*, **63**, 269 (1966).

17) F. H. Fry, A. G. Hamilton, and J. Turkevich, *Inorg. Chem.*, **5**, 1943 (1966).

18) W. Robb, *Inorg. Chem.*, **6**, 382 (1967).

19) P. Van Z. Bekker, W. J. Louw, and W. Robb, *Inorg. Nucl. Chem. Lett.*, **8**, 849 (1972).

20) W. J. Louw and W. Robb, *Inorg. Chim. Acta*, **3**, 29 (1969).

21) P. Van Z. Bekker, W. J. Louw, and W. Robb, *Inorg. Chim. Acta*, **6**, 564 (1972).

22) W. J. Louw and W. Robb, *Inorg. Chim. Acta*, **3**, 303 (1969).

23) W. J. Louw and W. Robb, *Inorg. Chim. Acta*, **8**, 253 (1974).

24) K. G. Moodley and M. J. Nicol, *J. Chem. Soc., Dalton Trans.*, **1977**, 993.

25) H. G. Forsberg, H. Widdel, and L. G. Erwall, *J. Chem. Educ.*, **37**, 44 (1960).

26) K. K. Sen Gupta and B. Basu, *Polyhedron*, **23**, 805 (1984).

27) B. S. Maritz, R. Van Eldik, and A. J. Van Den Berg, *J. S. Afr. Chem. Inst.*, **28**, 14 (1975).

28) B. S. Maritz and R. Van Eldik, *Inorg. Chim. Acta*, **17**, 21 (1976).

29) B. S. Maritz and R. Van Eldik, *J. Inorg. Nucl. Chem.*, **39**, 1035 (1977).

30) S. C. Sundar Rajan and N. Appala Raju, *J. Indian Chem. Soc.*, **50**, 110 (1973).

31) "Vogel's Textbook of Quantitative Inorganic Analysis," 4th ed, Revised by J. Bassett, R. C. Denney, G. H. Jeffry, and J. Mendham, ELBS (Longman), England (1986), p. 369.

32) V. Balzavi and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, London (1970), p. 273.

33) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 5th ed, John Wiley and Sons, New York (1988), p. 457.

34) S. Komiya, T. A. Albright, R. Hoffman, and J. K. Kochi, *J. Am. Chem. Soc.*, **99**, 8440 (1977).

35) R. L. Rich and H. Taube, *J. Phys. Chem.*, **58**, 6 (1954).

36) A. Johnson and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, **1975**, 115; **1976**, 1360.

37) R. Kaptein, P. W. N. M. Van Leevween, and R. Huis, *J. Chem. Soc., Chem. Commun.*, **1975**, 568.

38) E. Saito and B. H. J. Bielski, *J. Am. Chem. Soc.*, **83**, 4467 (1961).