Kinetics of Reduction of Gold(III) by Platinum(II) and Iron(III) in Aqueous Chloride Solutions

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Rate constants for the gold(III)–platinum(II) and the gold (III)–iron(II) redox reactions in aqueous chloride solutions have been measured under various conditions using spectrophotometric and amperometric methods respectively. There is no evidence for the formation of gold metal at short times (1—2 h) after mixing of dilute solutions of the reactants. The data for the reduction of Au^{III} by Pt^{II} are consistent with a mechanism requiring a complementary two-electron transfer, whereas the data for reduction by Fe^{II} indicate that the reaction proceeds *via* the formation of an intermediate containing Au^{II}. For the gold(III)–iron(II) reaction the data for the dependence of the rate on chloride concentration have been interpreted in terms of a mechanism consisting of parallel paths involving Fe^{2+} and $[FeCl]^{+}$. A value for the dissociation constant of $HAuCl_4$ has been computed from the data for the hydrogen-ion dependence of the rate of this reaction.

THERE have been very few reports on the kinetics of oxidations by gold(III) and the majority of them [1-3] are concerned with reductions by non-metal ions and molecules. The reduction of Au^{III} by $[Fe(CN)_6]^{4-}$ appears to be the only study [4] in which a metal-ion complex was used as reductant. A possible reason for the paucity of kinetic studies on the reduction of Au^{III} is that gold metal is often produced. This not only complicates the measurements but also raises the prospect of heterogeneous catalysis. Gold metal can be generated by further reduction of the product gold(I) by excess of reductant and/or by disproportionation of Au^I according to equilibrium (1). Our experiments

$$3[AuCl_2]^- \rightleftharpoons [AuCl_4]^- + 2Au(s) + 2Cl^- \quad (K\ 10^{7.74})\ [5] \quad (1)$$
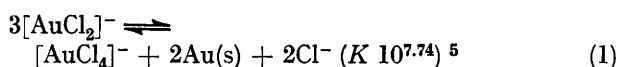
showed that no detectable amounts of gold metal were formed under the reaction conditions used (for time up to 2 h).

The choice of platinum(II) as a reductant for Au^{III} is of interest because the redox reaction involves iso-electronic and isostructural ions, $[AuCl_4]^-$ and $[PtCl_4]^{2-}$. The possibility of forming gold(II) as an intermediate during the reduction of Au^{III} makes the gold(III)–gold(I) system particularly suitable for investigating complementary and non-complementary electron-transfer reactions. We have therefore undertaken a kinetic study of the reduction of Au^{III} by a one- and a two-equivalent reductant under comparable conditions.

EXPERIMENTAL

Solutions of Au^{III} were prepared from B.D.H. tetrachloroauric(III) acid. The percentage of Au^{III} was determined gravimetrically.[6] Dilute platinum(II) solutions were prepared by dissolving the requisite amount of B.D.H. $K_2[PtCl_4]$ in 1.0 mol dm^{-3} HCl. More concentrated solutions of Pt^{II} were obtained by reducing platinum(IV) solutions, prepared from 99.9% B.D.H. platinum foil, with SO_2 solution. Fresh solutions of *ca.* 0.05 mol dm^{-3} iron(II) were prepared by dissolving AnalaR $FeCl_2 \cdot 4H_2O$ in AnalaR HCl. These solutions were standardised [6] against potassium dichromate. Stock solutions of iron(III) chloride were prepared in AnalaR HCl using B.D.H. $FeCl_3$. The solutions were analysed [6] by reducing the Fe^{III} to Fe^{II} in a Jones reductor and titrating [6] the Fe^{II} with potassium dichromate. All the acids were prepared by dilution of AnalaR grade stock solutions. They were analysed by standard methods.[6] All the salts used for adjusting the ionic strength were AnalaR grade materials and were used without further purification.

The gold(III)–platinum(II) reaction was monitored on a

[1] D. V. Sokol'skii, Ya. A. Dorfman, and V. S. Emel'yanova, *Kinetika i Kataliz,* 1973, **14(6),** 1573.

[2] V. P. Kazakov and M. V. Konovalova, *Zhur. Neorg. Khim.,* 1968, **13(9),** 2377.

[3] G. Natile, E. Bordignon, and L. Cattalini, *Inorg. Chem.,* 1976, **15(1),** 246.

[4] V. A. Zakharov, O. S. Songina, and L. P. Kal'nitskaya, *Zhur. analit. Khim.,* 1971, **26(3),** 482.

[5] 'Stability Constants of Metal–Ion Complexes,' eds. L. G. Sillén and A. E. Martell, *Special Publ.,* The Chemical Society, London, 1964, No. 17.

[6] A. I. Vogel, 'Quantitative Inorganic Analysis,' Longmans, London, 1961.

modified Hilger–Watts model 303 u.v.–visible spectro-photometer. The monitoring wavelength was either 330 or 260 nm (when excess of Au^{III} was present). The gold(III)–iron(II) reaction was followed amperometrically using a rotating platinum electrode as the indicator electrode and silver–silver(I) chloride as the reference electrode. A potential of 0.8 V *versus* the reference electrode was used. At this potential the oxidation of Fe^{II} is mass-transport controlled and Au^{III} and Au^{I} are electroinactive. In both methods the reaction was initiated by injecting $\leqslant 0.1$ cm^3 of Pt^{II} or Fe^{II} into the well stirred reaction vessel containing Au^{III} in the desired medium. Temperature control was accurate to 0.1 K.

RESULTS

The Gold(III)*–Platinum*(II) *Reaction.*—The reaction rates were calculated from the transmittance values read from the recorder chart. The rate expressions were obtained by integrating equation (2). Graphical methods were used to

$$-\mathrm{d}[Au^{III}]/\mathrm{d}t = k[Au^{III}][Pt^{II}] \qquad (2)$$

check for goodness of fit, but routine calculations were made through a linear least-squares computer program.

The rate of the reaction was measured at various initial concentrations of Au^{III} and Pt^{II}. The rate constants and the conditions under which they were measured are given in Table 1. The constancy of the values of the second-order

TABLE 1

Dependence of the rate of the gold(III)–platinum(II) reaction on the gold(III) and platinum(II) concentrations at 298 K, [HCl] = 1.0 mol dm^{-3}, and ionic strength $I = 1.0$ mol dm^{-3}

$\dfrac{10^5[Au^{III}]}{\text{mol dm}^{-3}}$	$\dfrac{10^5[Pt^{II}]}{\text{mol dm}^{-3}}$	$\dfrac{k \ *}{\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$
5.0	5.0	829 ± 27 (8)
10	10	828 ± 28 (7)
20	20	834 ± 14 (19)
40	40	837 ± 16 (18)
40	30	830 ± 26 (8)
40	20	828 ± 20 (12)
40	10	819 ± 26 (9)
2.0	0.2	830 ± 27 (6)

* The figures in parentheses denote the number of determinations for which the mean and the standard deviation are quoted.

rate constant over a considerable range of reactant concentrations is good confirmation of the assumed first-order dependence of the rate on the concentrations of Au^{III} and Pt^{II}.
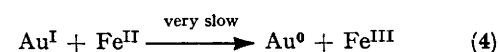
The influence of added chloride ions on the reaction rate was investigated by measuring the rate at constant pH and ionic strength (adjusted with sodium perchlorate) for different concentrations of added chloride. The results (first part of Table 2) show that added chloride does not affect the rate under the conditions specified. The effect of ionic strength on the reaction rate was checked by keeping the concentrations of chloride and hydrogen ions constant while varying the ionic strength using Na[ClO$_4$]. As shown in the second part of Table 2, the observed rate constant increased with ionic strength. The rate of the reaction was also measured at two different concentrations of hydrogen ions but constant chloride concentration and ionic strength. The data (last part of Table 2) indicate that the rate increases with decreasing hydrogen-ion concentration.

TABLE 2

Dependence of the rate of the gold(III)–platinum(II) reaction on the chloride concentration, ionic strength, and acidity at 298 K and $[Au^{III}] = [Pt^{II}] = 4 \times 10^{-4}$ mol dm^{-3}

$\dfrac{[Cl^-]}{\text{mol dm}^{-3}}$	$\dfrac{I}{\text{mol dm}^{-3}}$	$\dfrac{[H^+]}{\text{mol dm}^{-3}}$	$\dfrac{k}{\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$
0.25	1.0	1.0	830 ± 20 (12)
0.50	1.0	1.0	825 ± 28 (12)
1.0	1.0	1.0	837 ± 16 (18)
1.0	1.5	1.0	927 ± 25 (18)
1.0	2.0	1.0	1 220 ± 85 (10)
1.0	1.0	0.1	999 ± 64 (13)
1.0	1.0	1.0	837 ± 16 (18)

The Gold(III)*–Iron*(II) *Reaction.*—Spectrophotometric measurements showed that no metallic gold was formed for at least 1 h after the final readings were recorded. This suggests that the reduction of Au^{III} to gold metal occurs in two stages, (3) and (4). Only the first stage is

$$Au^{III} + 2Fe^{II} \xrightarrow{\text{fast}} Au^{I} + 2Fe^{III} \qquad (3)$$

$$Au^{I} + Fe^{II} \xrightarrow{\text{very slow}} Au^{0} + Fe^{III} \qquad (4)$$

considered here. The rates of this reaction were calculated from the values of the current (i) due to the oxidation of Fe^{II} and the time read from the recorder traces. As all the measurements were made under conditions where Au^{III} and Fe^{III} were in large excess over Fe^{II}, the rate equation (5) was assumed and integrated to give (6) where

$$-\mathrm{d}[Fe^{II}]/\mathrm{d}t = k_{\text{obs.}}[Fe^{II}]^2 \qquad (5)$$

$$\frac{1}{i_t - i_\infty} - \frac{1}{i_0 - i_\infty} - \frac{k_{\text{obs.}}[Fe^{II}]_0 t}{i_0 - i_\infty} \qquad (6)$$

i_0, i_t, and i_∞ are the currents at times $t = 0$, $t = t$, and $t = \infty$ and $[Fe^{II}]_0$ is the initial concentration of Fe^{II}. Plots of $1/(i_t - i_\infty)$ against t yielded good straight lines confirming the second-order dependence of the rate on the concentration of Fe^{II}. In calculating $k_{\text{obs.}}$ from the gradients of such lines the values of $i_0 - i_\infty$, obtained by extrapolation to $t = 0$, were used.

As the reaction rate was sensitive to the presence of Fe^{III}, a systematic investigation of the effect of Fe^{III} was carried out by varying the iron(III) concentration while keeping the gold(III) and iron(II) concentrations constant. The results are shown in Table 3. The constancy of the

TABLE 3

Dependence of the rate of the gold(III)–iron(II) reaction on the iron(III) concentration at 298 K, [HCl] = 1.0 mol dm^{-3}, $I = 1.0$ mol dm^{-3}, $[Au^{III}] = 5.1 \times 10^{-5}$ mol dm^{-3}, and $[Fe^{II}] = 4.0 \times 10^{-5}$ mol dm^{-3}

$\dfrac{10^3[Fe^{III}]}{\text{mol dm}^{-3}}$	$\dfrac{k_{\text{obs.}}}{\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$	$\dfrac{10^{-3}k_{\text{obs.}}[Fe^{III}][Au^{III}]^{-1}}{\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$
4.18	471 ± 8 (12)	3.86
8.35	240 ± 6 (10)	3.93
16.7	119 ± 4 (11)	3.90
40.0	51 ± 2 (9)	4.00

values of $k_{\text{obs.}}[Fe^{III}]/[Au^{III}]$ (last column) points to an inverse first-order dependence of the rate on the concentration of Fe^{III}. The influence of added chloride on the reaction rate was studied by varying the chloride concentration from 0.05 to 1.0 mol dm^{-3} at constant ionic strength and acidity. Both the ionic strength and acidity were

adjusted with perchloric acid. The first part of Table 4 gives the data for these runs. The hydrogen-ion concentration was varied from 0.05 to 1.0 mol dm^{-3} at $I = 1.0$ mol dm^{-3} and a chloride concentration of 1.0 mol dm^{-3}. Sodium chloride was used to adjust both the ionic strength and chloride concentration. The second part of Table 4 gives the results obtained from these runs.

TABLE 4

Effect of chloride and hydrogen-ion concentrations on the rate of the gold(III)–iron(II) reaction at 298 K, $[Au^{III}] = 5.1 \times 10^{-4}$ mol dm^{-3}, $[Fe^{II}] = 4.0 \times 10^{-5}$ mol dm^{-3}, $[Fe^{III}] = 8.35 \times 10^{-3}$ mol dm^{-3}, and $I = 1.0$ mol dm^{-3}

$\dfrac{[Cl^-]}{\text{mol dm}^{-3}}$	$\dfrac{[H^+]}{\text{mol dm}^{-3}}$	$\dfrac{k_{\text{obs.}}}{\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$
0.05	1.0	107 ± 3 (10)
0.10	1.0	115 ± 3 (9)
0.25	1.0	145 ± 5 (10)
0.50	1.0	195 ± 6 (8)
1.0	1.0	240 ± 6 (10)
1.0	0.05	438 ± 10 (9)
1.0	0.10	418 ± 9 (11)
1.0	0.25	375 ± 9 (10)
1.0	0.50	315 ± 8 (9)
1.0	1.0	240 ± 6 (10)

DISCUSSION

For the gold(III)–platinum(II) reaction the first-order dependence of the rate on the concentration of each reactant is interpreted as support for the two-electron complementary mechanism (7) where X represents a transition state.
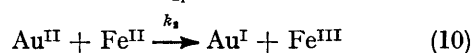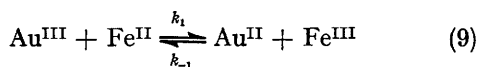
$$Au^{III} + Pt^{II} \xrightarrow{k} X \longrightarrow Au^{I} + Pt^{IV} \qquad (7)$$
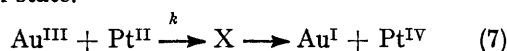
In chloride medium, Au^{III} is predominantly in the form $[AuCl_4]^-$. In the presence of hydrogen ions, protonation occurs according to the equilibrium (8).[5]
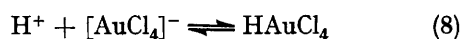
$$H^+ + [AuCl_4]^- \rightleftharpoons HAuCl_4 \qquad (8)$$

The increase in the magnitude of $k_{\text{obs.}}$ with decrease in hydrogen-ion concentration indicates that $[AuCl_4]^-$ is more effective than $HAuCl_4$ as the oxidising species. The observation that added chloride does not affect the reaction rate suggests that paths involving higher chloro-complexes of the reactants are not significant. Thus it appears that the reacting species are $[PtCl_4]^{2-}$ and $[AuCl_4]^-$. The increase in reaction rate with increase in ionic strength is also consistent with a reaction involving ions of the same charge type.

The question of whether the reaction occurs by an inner-sphere or outer-sphere mode cannot be answered unequivocally with the present data. On the basis that the stable products of the reaction are $[AuCl_2]^-$ and $[PtCl_6]^{2-}$, it is conceivable that the reaction could occur via a transition state in which a chloride from $[AuCl_4]^-$ acts as a bridge between Au^{III} and one of the two vacant co-ordination sites on $[PtCl_4]^{2-}$.

For the gold(III)–iron(II) reaction, our data point to a mechanism [equations (9) and (10)] involving one-

$$Au^{III} + Fe^{II} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Au^{II} + Fe^{III} \qquad (9)$$

$$Au^{II} + Fe^{II} \xrightarrow{k_2} Au^{I} + Fe^{III} \qquad (10)$$

equivalent steps. On the assumption that the steady-state approximation for the intermediate Au^{II} is valid, the rate law (11) can be derived. Under conditions such

$$\frac{-d[Fe^{II}]}{dt} = \frac{2k_1k_2[Fe^{II}]^2[Au^{III}]}{k_{-1}[Fe^{III}] + k_2[Fe^{II}]} \qquad (11)$$

that $[Fe^{III}]$, $[Au^{III}] \gg [Fe^{II}]$ we obtain (5), where $k_{\text{obs.}} = 2k_1k_2[Au^{III}]/[Fe^{III}]$.

The relatively high (1 mol dm^{-3}) fixed chloride concentration used in the investigation of the acid dependence of the reaction rate ensures that the reactants are predominantly present as chloro-complexes of Fe^{II} and Au^{III}. (The values of the formation constants $K_1 = 0.35$ dm^{-3} mol^{-1} (ref. 7) and $K_1K_2K_3K_4 = 24$ dm^{12} mol^{-4} (ref. 5) for the chloro-complexes of Fe^{II} and Au^{III} respectively supported this assumption.) The acid dependence should be explicable on the basis of equilibrium (8).[5]

$$k_{\text{obs.}}[Au^{III}]_T = k_3[AuCl_4^-] + k_4[HAuCl_4] \qquad (12)$$

Thus, one can write (12) where $[Au^{III}]_T$ is the total gold(III) concentration. The concentrations of $[AuCl_4]^-$ and $HAuCl_4$ can be written in terms of total Au^{III} to give expression (13) where K_a is the acid-dissociation constant of $HAuCl_4$.

$$k_{\text{obs.}} = \frac{k_3}{1 + ([H^+]/K_a)} + \frac{k_4[H^+]}{K_a\{1 + ([H^+]/K_a)\}} \qquad (13)$$

If it is assumed that the second term (the k_4 path) in equation (13) is negligible, then the approximate relation between $k_{\text{obs.}}$, $[H^+]$, and K_a can be written in the form (14). The good linearity of a plot of $1/k_{\text{obs.}}$ against

$$\frac{1}{k_{\text{obs.}}} = \frac{1}{k_3} + \frac{[H^+]}{K_a k_3} \qquad (14)$$

$[H^+]$ supports the assumption that the contribution of the k_4 path is very small at low acid concentrations. The values of k_3 and K_a derived from this plot are 457 dm^3 mol^{-1} s^{-1} and 1.11 mol dm^{-3} respectively. Considering the approximate nature of equation (14) this value of K_a compares well with that (1.35 mol dm^{-3}) obtained from data for the distribution of $HAuCl_4$ between water and diethyl ether.[8]

As Fe^{II} and Fe^{III} both form complexes with chloride, the increase in the rate with increase in free-chloride concentration could be due to: (a) the greater effectiveness of chloro-complexes over uncomplexed Fe^{II} in reducing Au^{III} and/or (b) the removal of Fe^{III} through complex formation (on the assumption that uncomplexed Fe^{III} is dominant in retarding the rate). A plot of $k_{\text{obs.}}$ against added chloride concentration is non-linear and shows that $k_{\text{obs.}}$ has a finite value at zero chloride concentration. This implies that the reaction can occur by a path involving uncomplexed Fe^{II}. A recent report[7] shows that there is no evidence for the formation of $FeCl_2$ under conditions comparable to that

[7] K. Ashurst, National Institute for Metallurgy, South Africa, personal communication.
[8] H. G. Forsberg, B. Widdel, and L. G. Erwall, *J. Chem. Educ.*, 1960, **37**, 44.

used in the present experiments. Hence the mass balance for Fe^{II} is given by equation (15) where $[Fe^{II}]_T$ is the total concentration of Fe^{II}.

$$[Fe^{II}]_T = [Fe^{2+}] + [FeCl^+] \qquad (15)$$

Expression (16) (which is based on the assumptions that $[FeCl]^+$ participates in the first or the second electron-transfer step and that there is a reaction path using uncomplexed Fe^{II}) may be used to describe the

$$k_{obs.}[Fe^{II}]_T^2 = k_5[Fe^{2+}][FeCl^+] + k_6[Fe^{2+}]^2 \qquad (16)$$

dependence of the rate on chloride concentration. Substitution from equation (15) into (16) gives (17). The linearity of a plot of $k_{obs.}(1 + K_1[Cl^-])^2$ against $[Cl^-]$

seems to suggest that chloride catalyses the reaction predominantly by enhancing the reactivity of Fe^{II} in

$$k_{obs.} = \frac{k_5 K_1[Cl^-]}{(1 + K_1[Cl^-])^2} + \frac{k_6}{(1 + K_1[Cl^-])^2} \qquad (17)$$

one of the steps. It should be emphasised that this suggestion is, to some extent, speculative and there are alternatives based on (a) and/or (b) above.