Kinetics of the Reduction of Platinum(IV) by Tin(II) and Copper(I) in Aqueous Chloride Solutions

By **Kandasamy G. Moodley,*** Chemistry Department, University of Durban-Westville, P/B X54001, Durban 4000 South Africa
Michael J. Nicol, National Institute for Metallurgy, Johannesburg, South Africa

Rate constants for the Pt^{IV} + Sn^{II} and the Pt^{IV} + Cu^{I} redox reactions have been measured under various conditions using spectrophotometric and amperometric methods respectively. Rate equations (i) and (ii) describe the data for

$$-d[Pt^{IV}]/dt = k_{obs.}[Pt^{IV}][Sn^{II}] \tag{i}$$

$$\frac{-d[Cu^{I}]}{dt} = \frac{2k_1k_2[Pt^{IV}][Cu^{I}]^2}{k_{-1}[Cu^{II}] + k_2[Cu^{I}]} \tag{ii}$$

the two reactions. The rate of reduction of Pt^{IV} by Sn^{II} is much faster than the rate of formation of the 1 : 1 complex between Pt^{II} and Sn^{II}. The rate of reduction by Sn^{II} varies linearly with increasing chloride concentration in nitrate and sulphate solutions. A possible explanation is offered for the higher rates in perchlorate solutions. The data for the Pt^{IV} + Cu^{I} system indicate that the reaction proceeds *via* an intermediate containing Pt^{III}, but there is no evidence for the formation of Pt^{III} in the reduction of Pt^{IV} by Sn^{II}. The mechanisms for both reactions are discussed in terms of complementary and non-complementary processes.

COMPARATIVE studies involving complementary and non-complementary electron-transfer reactions have received very little attention. Wetton and Higginson [1] investigated the reducing reactions of Sn^{II} with one- and two-equivalent oxidizing agents. The main aim of their work was to determine the transient existence of Sn^{III} in non-complementary reactions by using cobalt(III) complexes as selective oxidants. Beattie and Basolo [2,3] studied the reduction of various platinum(IV) complexes by hexa-aquachromium(II) and tris(2,2′-bipyridine)-chromium(II). Their data suggested that platinum(IV) complexes were reduced by rate-determining one-electron steps with intermediate formation of Pt^{III}. Evidence for the formation of Pt^{III} as an intermediate has also been cited by Halpern and Pribanić [4] and Peloso and Basato [5,6] from data for the oxidation of platinum(II) complexes by hexachloroiridate(IV) and Fe^{III} respectively.

Higginson and Marshall [7] suggested that redox reactions between transition-metal ions and complexes or ions derived from non-transition elements may occur in either one- or two-equivalent steps with the two-equivalent process occurring more often. In all the studies referred to above, Pt^{IV} or Pt^{II} was treated with transition-metal ions. To our knowledge, the present work constitutes the first kinetic study of the reduction of Pt^{IV} by a non-transition-metal ion. In addition to the study of the reduction of Pt^{IV} by the two-equivalent reductant Sn^{II}, it was felt that data on the one-equivalent reductant Cu^{I}, under similar conditions, would enable a comparison to be made of both the rates and mechanisms of reduction by one- and two-equivalent reductants.

EXPERIMENTAL

A stock *ca.* 1.0 mol dm^{-3} solution of tin(II) chloride was prepared from $SnCl_2 \cdot 2H_2O$ (B.D.H. AnalaR) using deionized deaerated water and AnalaR grade hydrochloric acid. Pieces of tin foil were added and the solution was periodically purged with oxygen-free nitrogen. Diluted solutions were standardized iodometrically.[8] A platinum(IV) solution was prepared by dissolving 99.9% platinum foil in a mixture of concentrated hydrochloric and nitric acids (3 : 1). Residual HNO_3 was removed by repeated evaporation with concentrated HCl. A copper(I) solution (*ca.* 10^{-3} mol dm^{-3}) was obtained by dissolving May and Baker ' R ' CuCl in thoroughly deaerated deionized water containing 1.0 mol dm^{-3} AnalaR HCl. This solution was standardized by using Fe^{III} and Ce^{IV}.[8] All the acids used were prepared by dilution of AnalaR grade stock solutions. They were analysed by standard methods.[8] The salts used for adjusting the ionic strengths were all AnalaR grade materials and were used without further purification.

The Pt^{IV} + Sn^{II} reaction was monitored on a modified Hilger and Watts model 303 u.v.–visible spectrophotometer and on a Durrum–Gibson model D-110 stopped-flow spectrophotometer. The Pt^{IV} + Cu^{I} reaction was followed amperometrically using a rotating vitreous-graphite rod as the indicator electrode and silver–silver(I) chloride as the reference electrode. Temperature control *via* water-jacketed cells was accurate to 0.1 K. In the conventional spectrophotometric and amperometric methods the re-

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[1] E. A. M. Wetton and W. C. E. Higginson, *J. Chem. Soc.*, 1965, 5890.

[2] J. K. Beattie and F. Basolo, *Inorg. Chem.*, 1971, **10**, 486.

[3] J. K. Beattie and F. Basolo, *Inorg. Chem.*, 1967, **6**, 2069.

[4] J. Halpern and M. Pribanić, *J. Amer. Chem. Soc.*, 1968, **90**, 5942.

[5] A. Peloso and M. Basato, *J. Chem. Soc. (A)*, 1971, 725.

[6] A. Peloso and M. Basato, *J.C.S. Dalton*, 1972, 2040.

[7] W. C. E. Higginson and J. W. Marshall, *J. Chem. Soc.*, 1957, 447.

[8] A. I. Vogel, ' Quantitative Inorganic Analysis,' 3rd edn., Longmans, 1961.

action was initiated by injecting $\leqslant 0.1$ cm^3 of Sn$^{\text{II}}$ or Cu$^{\text{I}}$, from a graduated 0.5-cm^3 capacity syringe fitted with a Teflon needle, into a well stirred reaction vessel containing Pt$^{\text{IV}}$ in the desired medium. Mixing was complete in *ca.* 1 s. The monitoring wavelength in the spectral methods was 367 nm (where Pt$^{\text{IV}}$ absorbs to a considerably greater extent than any of the other reactants or products). The amperometric runs were carried out at a potential of 0.52 V *versus* the Ag–AgCl reference electrode. At this potential, oxidation of Cu$^{\text{I}}$ is mass-transport controlled and both Pt$^{\text{IV}}$ and Pt$^{\text{II}}$ are electroinactive.

RESULTS

The Pt$^{\text{IV}}$ + Sn$^{\text{II}}$ *Reaction*.—It is well known [9] that Pt$^{\text{II}}$ forms complexes with Sn$^{\text{II}}$. Experiments showed that these complexes absorb strongly at the wavelength used. In order to establish whether the rate of formation of the complex (for runs in which an excess of Sn$^{\text{II}}$ was present) would affect the measurement of the redox rate, it was necessary to compare the rate of formation of the 1 : 1 complex between Sn$^{\text{II}}$ and Pt$^{\text{II}}$ with the rate of reduction of Pt$^{\text{IV}}$ under similar conditions. The data in Table 1 show that the rate of reduction is considerably faster than that of complex formation.

The reaction rates were calculated from transmittance values read from the recorder chart or from the scale of the stopped-flow oscillogram. The rate expressions were obtained by integrating equation (i). Graphical methods

$$-d[\text{Pt}^{\text{IV}}]/dt = k_{\text{obs.}}[\text{Pt}^{\text{IV}}][\text{Sn}^{\text{II}}] \qquad \text{(i)}$$

were used to check for goodness of fit, but routine calculations were made using a computer program incorporating a least-squares subroutine.

TABLE 1

Comparison of the rate constants for the complex formation and redox reactions of Pt$^{\text{II}}$ and Pt$^{\text{IV}}$ with Sn$^{\text{II}}$ at 297 K, [HCl] = 1.0 mol dm^{-3}, and I = 1.0 mol dm^{-3}

10^4[Pt$^{\text{II}}$] / mol dm^{-3}	10^4[Sn$^{\text{II}}$] / mol dm^{-3}	10^4[Pt$^{\text{IV}}$] / mol dm^{-3}	Rate constant / dm^3 mol^{-1} s^{-1}
4.0	4.0		13 ± 1 (8) *
	4.0	4.0	473 ± 22 (10)

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

TABLE 2

Dependence of the rate of the Pt$^{\text{IV}}$ + Sn$^{\text{II}}$ reaction on the concentrations of Pt$^{\text{IV}}$ and Sn$^{\text{II}}$

10^4[Pt$^{\text{IV}}$] / mol dm^{-3}	10^4[Sn$^{\text{II}}$] / mol dm^{-3}	$k_{\text{obs.}}$ / dm^3 mol^{-1} s^{-1}
4.0	4.0	924 ± 35 (12)
8.0	8.0	906 ± 42 (9)
4.0	2.0	895 ± 32 (14)
	6.0	906 ± 50 (8)
	8.0	892 ± 39 (10)
6.0	8.0	923 ± 36 (11)
4.0	40.0	955 ± 41 (11)
2.0	40.0	956 ± 37 (12)

The rate of the reaction was measured at various initial concentrations of Pt$^{\text{IV}}$ and Sn$^{\text{II}}$. The rate constants and the conditions under which they were measured are given in Table 2. Runs in which a large excess of Sn$^{\text{II}}$ was used were feasible only if the chloride concentration was at least 1.0 mol dm^{-3}. When the added chloride concentration was much lower than this, the platinum(II)–tin(II) complex began to form before the reduction of Pt$^{\text{IV}}$ was complete. As rapid mixing and fast detection are crucial to the success of such experiments, the stopped-flow method was used in all the pseudo-first-order runs. These data are shown in the last two rows of Table 2.

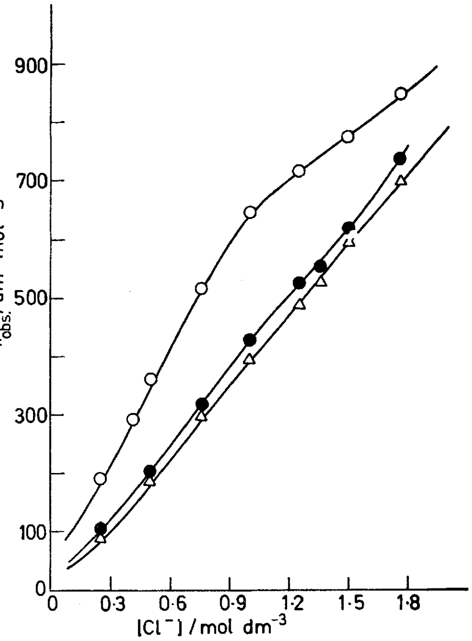

FIGURE 1 Plot of $k_{\text{obs.}}$ against chloride concentration for the reaction of Pt$^{\text{IV}}$ with Sn$^{\text{II}}$ in perchlorate (○), nitrate (●), and sulphate solutions (△) respectively

Preliminary investigations showed that addition of chloride ions produced a marked increase in the rate of reaction and a detailed investigation of the effect of chloride on the rate, in solutions containing sulphate, nitrate, or perchlorate electrolytes, was therefore carried out. The ionic strength was maintained at 2.0 mol dm^{-3} and the acidity at 1.0 mol dm^{-3}. In sulphate solutions, a value * of 10^{-2} mol dm^{-3} for the dissociation constant of [HSO$_4$]$^-$ was assumed in calculating the concentration required to maintain the constant ionic strength. A plot of $k_{\text{obs.}}$ against the concentration of chloride is shown in Figure 1. The approximate linearity of the plots in sulphate and nitrate media over such a wide range of added chloride concentrations suggests that $k_{\text{obs.}}$ incorporates a term which is first order in chloride concentration. The plot of the data obtained in perchlorate medium was initially linear but began to curve at *ca.* 1.0 mol dm^{-3} chloride. The reason for the higher rates in perchlorate solutions will be considered at a later stage. Variations of the acid concentration from 0.1 to 2.0 mol dm^{-3} in chloride solutions and the ionic strength (I) from 1.0 to 3.0 mol dm^{-3} had no noticeable effect on the rate as shown by the data in Table 3.

Table 4 compares the rate constants obtained with and without added Sn$^{\text{IV}}$ and Pt$^{\text{II}}$. It is clear that both products have no influence on the rate of the reaction.

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* As pointed out by one of the referees, this value is that for infinite dilution. However, use of the value appropriate to the conditions of the above experiment will result in only a relatively small variation in ionic strength, which, as demonstrated by the results in Table 3, will in any case have no noticeable effect on the rate constants.

[9] A. S. Meyer and H. G. Ayres, *J. Amer. Chem. Soc.*, 1955, **77**, 2671.

The reaction was studied at five different temperatures in sulphate medium containing 0.5 mol dm^{-3} chloride. The data for these measurements are shown as an Arrhenius plot in Figure 2. Values for the enthalpy ($\Delta H^‡$) and entropy ($\Delta S^‡$) of activation were calculated from this plot by using equation (ii): $\Delta H^‡ = 29$ kJ mol^{-1}; $\Delta S^‡ = -101$ J K^{-1} mol^{-1}.

$$k_{\text{obs.}} = (\boldsymbol{k}T/\boldsymbol{h})\exp(-\Delta H^‡/RT)\exp(\Delta S^‡/R) \qquad \text{(ii)}$$

The Pt$^{\text{IV}}$ + Cu$^{\text{II}}$ *Reaction*.—The reaction rates were computed from the values of current (i) due to the oxidation of Cu$^{\text{I}}$ and the time read from the recorder traces.

TABLE 3

Effects of acidity and ionic strength on the rate of the Pt$^{\text{IV}}$ + Sn$^{\text{II}}$ reaction at 297 K, [Pt$^{\text{IV}}$] = 4.0×10^{-4} mol dm^{-3}, and [Sn$^{\text{II}}$] = 6.0×10^{-4} mol dm^{-3}

[H$^+$] / mol dm^{-3}	[Cl$^-$] / mol dm^{-3}	I / mol dm^{-3}	$k_{\text{obs.}}$ / dm^3 mol^{-1} s^{-1}
0.10	2.0	2.0	892 ± 37 (10)
0.25	2.0	2.0	886 ± 42 (9)
0.50	2.0	2.0	894 ± 35 (11)
1.00	2.0	2.0	888 ± 45 (8)
2.00	2.0	2.0	906 ± 50 (8)
1.00 *	0.50	1.0	187 ± 7 (11)
	0.50	2.0	190 ± 10 (8)
	0.50	3.0	188 ± 8 (9)

* At 293 K.

TABLE 4

Effects of added Sn$^{\text{IV}}$ and Pt$^{\text{II}}$ on the rate of the Pt$^{\text{IV}}$ + Sn$^{\text{II}}$ reaction at I = 2.0 mol dm^{-3}

10^4[Pt$^{\text{IV}}$] / mol dm^{-3}	10^4[Sn$^{\text{II}}$] / mol dm^{-3}	[Pt$^{\text{II}}$] / mol dm^{-3}	[Sn$^{\text{IV}}$] / mol dm^{-3}	$k_{\text{obs.}}$ / dm^3 mol^{-1} s^{-1}
4.0 ^{a}	6.0	0	0	191 ± 10 (8)
	6.0	0	0.02	189 ± 7 (13)
2.0 ^{b}	4.0	0	0	402 ± 22 (7)
	4.0	4.0×10^{-4}	0	406 ± 18 (9)

^{a} 293.5 K, [H$^+$] = 1.36 mol dm^{-3}, and [Cl$^-$] = 0.50 mol dm^{-3}. ^{b} 294.5 K, [H$^+$] = 1.00 mol dm^{-3}, and [Cl$^-$] = 1.00 mol dm^{-3}.

As all the experiments were carried out with at least a tenfold excess of Pt$^{\text{IV}}$ and Cu$^{\text{II}}$ over Cu$^{\text{I}}$, the rate equation (iii) was integrated to give, on substitution, (iv) where i_0,

$$-d[\text{Cu}^{\text{I}}]/dt = k_{\text{obs.}}[\text{Cu}^{\text{I}}]^2 \qquad \text{(iii)}$$

$$\frac{(i_0 - i_\infty)}{(i_t - i_\infty)} \cdot \frac{1}{[\text{Cu}^{\text{I}}]_0} - \frac{1}{[\text{Cu}^{\text{I}}]_0} = k_{\text{obs.}}t \qquad \text{(iv)}$$

i_t, and i_∞ are the currents at times $t = 0$, t, and ∞ and [Cu$^{\text{I}}$]$_0$ is the initial concentration of Cu$^{\text{I}}$. 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 Cu$^{\text{I}}$. In calculating $k_{\text{obs.}}$ from the gradients of such lines the extrapolated values of $(i_0 - i_\infty)$, *i.e.* the value at $t = 0$, were used. All the experiments were carried out at 297.5 K in 1.0 mol dm^{-3} HCl solution.

Preliminary experiments showed that the reaction rate was quite sensitive to the presence of Cu$^{\text{II}}$. A systematic investigation of the effect of Cu$^{\text{II}}$ was carried out by varying the copper(II) concentration while keeping the platinum(IV) and copper(I) concentrations constant. Similar experiments were carried out with various platinum(IV) concentrations and constant copper(II). The results are shown in Table 5. The constancy of the values of $k_{\text{obs.}}[\text{Cu}^{\text{II}}]_0/[\text{Pt}^{\text{IV}}]_0$ (in the last column) points to an inverse first-order dependence of the rate on the concentration of Cu$^{\text{II}}$ and a first-order dependence on the platinum(IV) concentration.

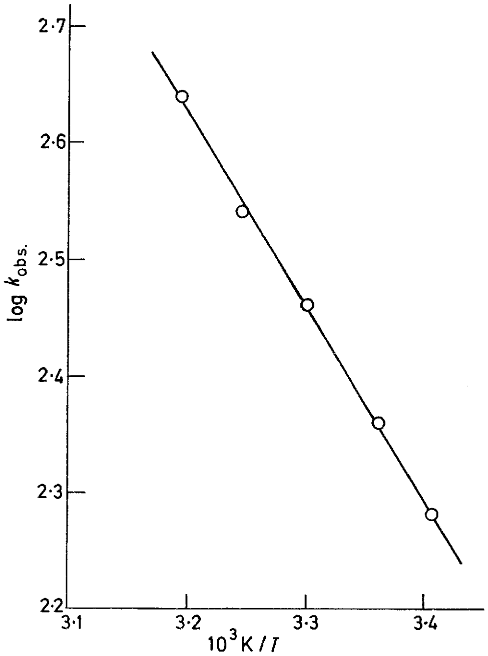

FIGURE 2 Plot of $\log_{10} k_{\text{obs.}}$ against $1/T$ for the reaction of Pt$^{\text{IV}}$ with Sn$^{\text{II}}$

DISCUSSION

The kinetic results show that, although Sn$^{\text{II}}$ and Cu$^{\text{I}}$ reduce Pt$^{\text{IV}}$ by overall complementary and non-complementary processes respectively, the rate-determining elementary steps involve complementary mechanisms for both reactions: a two-electron complementary step for reduction by Sn$^{\text{II}}$, and one-electron complementary steps for Cu$^{\text{I}}$ as the reductant. The Pt$^{\text{IV}}$ + Sn$^{\text{II}}$ reaction will be considered first. Reaction (v) most

$$[\text{PtCl}_6]^{2-} + [\text{SnCl}_3]^- \longrightarrow [\text{PtCl}_4]^{2-} + \text{SnCl}_4 + \text{Cl}^- \qquad \text{(v)}$$

probably proceeds through a transition state resembling $([\text{Cl}_5\text{Pt}\cdots\text{Cl}\cdots\text{SnCl}_3]^{3-})^‡$. The strong chloride dependence coupled with the fact that changes in hydrogen-ion concentration do not affect the reaction rate is evidence that only the chloro-complexes of both reactants are involved. The high propensity of Sn$^{\text{II}}$ for forming

TABLE 5

Effects of copper(II) and platinum(IV) concentrations on the rate of the Pt$^{\text{IV}}$ + Cu$^{\text{II}}$ reaction at [Cu$^{\text{I}}$] = 5.0×10^{-5} mol dm^{-3} and [Pt$^{\text{IV}}$] = 2.0×10^{-4} mol dm^{-3}

10^4[Pt$^{\text{IV}}$] / mol dm^{-3}	10^3[Cu$^{\text{II}}$] / mol dm^{-3}	$k_{\text{obs.}}$ / dm^3 mol^{-1} s^{-1}	$10^4 k_{\text{obs.}}[\text{Cu}^{\text{II}}]_0/[\text{Pt}^{\text{IV}}]_0$ / dm^3 mol^{-1}s^{-1}
2.0	2.8	1 480 ± 50 (5)	2.07
	3.0	1 360 ± 42 (6)	2.04
	3.5	1 080 ± 39 (6)	1.89
	10	388 ± 13 (7)	1.94
	15	270 ± 10 (6)	2.03
	25	155 ± 6 (5)	1.95
	30	146 ± 5 (6)	2.09
	20	198 ± 6 (7)	1.98
4.0	20	405 ± 11 (6)	2.03
6.0	20	584 ± 16 (7)	1.95
8.0	20	785 ± 23 (6)	1.96
10.0	20	970 ± 46 (6)	1.94

labile chloro-complexes, and the absence of hydrolysis of $[PtCl_6]^{2-}$ and Sn^{II} in the pH range used, provide further support for this proposal.

As Pt^{IV} does not form higher chloro-complexes than $[PtCl_6]^{2-}$, it appears that chloride catalyses the reaction through the participation of chloro-complexes of Sn^{II} as the reducing species. Equilibria (1)—(3) must be considered in deducing the relative roles of the various tin(II) complexes. The values[10] used for K_1, K_2, and

$$Sn^{2+} + Cl^- \overset{K_1}{\rightleftharpoons} [SnCl]^+ \quad (1)$$

$$[SnCl]^+ + Cl^- \overset{K_2}{\rightleftharpoons} SnCl_2 \quad (2)$$

$$SnCl_2 + Cl^- \overset{K_3}{\rightleftharpoons} [SnCl_3]^- \quad (3)$$

K_3 are respectively 14.12, 3.54, and 0.89 dm^3 mol^{-1}. Figure 3 shows plots of the fractions of total Sn^{II} as the various complexes against the chloride concentration. Comparison of Figures 1 and 3 shows that there is a close similarity between the curves depicting the chloride dependence in sulphate and nitrate media on the one hand and the curve showing the fraction of total Sn^{II} as $[SnCl_3]^-$ on the other. This suggests that $[SnCl_3]^-$ is involved in a predominant path for the reaction. The deviation at low chloride concentrations may be ascribed to paths provided by lower species, whereas the deviation at high chloride may be attributable to a contribution from a path involving $[SnCl_4]^{2-}$. A non-complementary mechanism would yield either Pt^{III} or Sn^{III} as one of the products of the first step. As the rate was unaffected by addition of Pt^{II} or Sn^{IV} to the initial reaction mixture, a complementary mechanism involving a two-electron transfer is favoured.

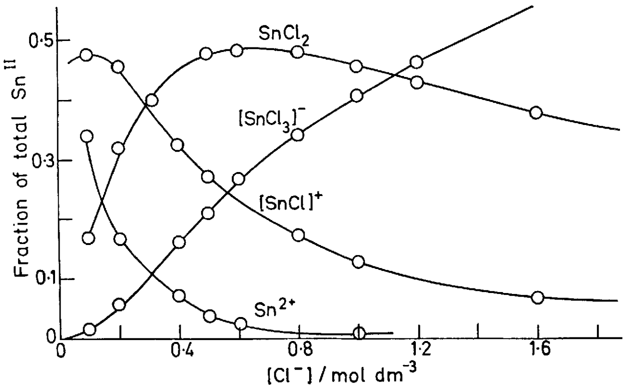

FIGURE 3 Plots of the concentrations of the different tin(II) species (as fractions of total Sn^{II} concentration) against chloride concentration

In terms of activated complexes the reaction could occur by the inner- or outer-sphere mode. A third possibility is one which combines an inner- and an outer-sphere mode. For inner-sphere activation the intermediate could be a chloride-bridged structure between $[PtCl_6]^{2-}$ and $[SnCl_3]^-$. Support for inner-sphere activation stems from considerations such as: (*i*) the fact[11] that $[SnCl_3]^-$ forms complexes with a number of transition-metal ions, indicating the presence of a suitably labile site for interaction with a chloride from $[PtCl_6]^{2-}$; (*ii*) $[SnCl_3]^-$ is known[12] to be a strong *trans* activator, and labilization of the chloride *trans* to the chloride being attacked by $[SnCl_3]^-$ would facilitate subsequent loss of chloride from $[PtCl_5]^{3-}$ to give $[PtCl_4]^{2-}$.

A possible explanation for the higher rates in solutions containing sodium perchlorate, relative to those containing sulphate and nitrate anions, could involve the formation of the presumably less reactive complexes of sulphate and nitrate ions. On this basis, it is the lowering of the rate in solutions containing nitrate and sulphate ions rather than the increase in rate in solutions containing perchlorate salt that has to be considered. The lowered rate could be ascribed to the reduction in the concentration of the more effective tin(II) complex, $[SnCl_3]^-$. However, the similar rates in nitrate and sulphate solutions and the absence of any published data[10] on the existence of complexes of Sn^{II} or Pt^{IV} with nitrate suggest that this explanation should be regarded as tentative.

The effect of platinum(IV) and copper(II) concentrations on the rate of the $Pt^{IV} + Cu^I$ reaction can be accounted for in terms of equations (6) and (7). Assuming that the steady-state approximation for $[Pt^{III}]$ is valid, the rate law (8) can be derived. At high copper(II)

$$Cu^I + Pt^{IV} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cu^{II} + Pt^{III} \quad (6)$$

$$Cu^I + Pt^{III} \xrightarrow{k_2} Cu^{II} + Pt^{II} \quad (7)$$

$$\frac{-d[Cu^I]}{dt} = \frac{2k_1k_2[Pt^{IV}][Cu^I]^2}{k_{-1}[Cu^{II}] + k_2[Cu^I]} \quad (8)$$

and low copper(I) concentrations $k_{-1}[Cu^{II}] \gg k_2[Cu^I]$ and equation (8) becomes (9). The dependence of

$$\frac{-d[Cu^I]}{dt} = \frac{2k_1k_2\,[Pt^{IV}][Cu^I]^2}{k_{-1}\,[Cu^{II}]} \quad (9)$$
$$= k[Cu^I]^2 \text{ (if } [Cu^{II}], [Pt^{IV}] \gg [Cu^I])$$

$$k = k_{obs.} = \frac{2k_1k_2[Pt^{IV}]}{k_{-1}[Cu^{II}]} \quad (10)$$

$k_{obs.}$ on the concentrations of Pt^{IV} and Cu^{II} has already been substantiated by the data in Table 5.

Evidence for the existence of Pt^{III} as a reaction intermediate has been cited in various studies.[2-4] It is clear that the results of the present work also support the expectation that stoicheiometrically non-complementary reactions with Pt^{IV} or Pt^{II} as one of the reactants would be characterized by the formation of Pt^{III} as an intermediate. This work has revealed that the rate of reduction of a two-equivalent oxidant by a one-equivalent reductant can be faster than the reduction of the same oxidant by a two-equivalent reductant under comparable conditions. This provides evidence against

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

[11] J. F. Young, *Adv. Inorg. Chem. Radiochem.*, 1968, **11**, 92.

[12] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' John Wiley, London, 1972, p. 1037.

the generalization[13] that stoicheiometrically non-complementary redox reactions are slow.

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[13] P. A. Shaffer, *J. Amer. Chem. Soc.*, 1953, **55**, 2169; *J. Phys. Chem.*, 1936, **40**, 1021.