Redox Reaction Mechanisms in Non-complementary Processes. Part II.[1] Kinetics of Platinum(II)–Iron(III) and Iron(II)–Platinum(IV) Interconversions

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The kinetics of the equilibration reactions (i) (L = NH_3, NH_2Me, NH_2Et, NH_2Pr, or ½en; X = Cl or Br) have been

$$cis\text{- or } trans\text{-}[PtL_2X_2] + 2Fe^{3+} + 2X^- \rightleftharpoons cis\text{- or } trans\text{-}[PtL_2X_4] + 2Fe^{2+} \qquad \text{(i)}$$

studied in water in the presence of 0·5M-perchloric acid at 1M ionic strength. The rate law for the reduction of the platinum(IV) complexes has the form: rate = $k_r[Pt^{IV}][Fe^{2+}]$. The rate law for the oxidation of the platinum(II) bromo-complexes, when no iron(II) is added to the reacting mixture, is: rate = $k_t[Pt^{II}][Fe^{3+}][Br^-] + k_{t'}[Pt^{II}][Fe^{3+}][Br^-]^2$. When an excess of iron(II) is added to the reacting mixtures the reactions do not go to completion and the rates of approach to equilibrium strongly depend on the amount of iron(II) added. The forms of the rate laws are consistent with a mechanism involving a platinum(III) intermediate and two one-electron redox steps. A five-co-ordinate platinum(II) complex, $[PtL_2Br_3]^-$, is postulated to be responsible for the $k_{t'}$ oxidation path. The free energies of activation for both oxidation of platinum(II) and reduction of platinum(IV) complexes are found to parallel the overall free-energy changes of the reactions. A change of the geometric form of the complexes has no effect on the reaction rate or the equilibrium constant of the redox reaction. *trans*-$[PtL_2Br_4]$ is 5—15 times less reactive than the corresponding chloro-complexes, mainly as a consequence of the formation of a more stable oxidation product, FeX^{2+}, when X is Cl rather than Br.

IN Part I of this series we reported a kinetic investigation of the reversible redox reaction (1) in water in the

$$trans\text{-}[Pt(NH_2Me)_2Br_2] + 2Fe^{3+} + 2Br^- \rightleftharpoons trans\text{-}[Pt(NH_2Me)_2Br_4] + 2Fe^{2+} \qquad (1)$$

presence of 0·5M-perchloric acid at 1M ionic strength. The reaction mechanism proposed is shown in equations (2a—c), where the ligands not involved in the reaction are omitted.

$$Fe^{3+} + Br^- \overset{K_1}{\rightleftharpoons} FeBr^{2+} \qquad \text{(2a)}$$

$$Pt^{II} + FeBr^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Pt^{III}Br + Fe^{2+} \qquad \text{(2b)}$$

$$Pt^{III}Br + FeBr^{2+} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Pt^{IV}Br_2 + Fe^{2+} \qquad \text{(2c)}$$

We have now performed a kinetic investigation on a series of reactions described by equation (3) (L = NH_3,

$$cis\text{- or } trans\text{-}[PtL_2X_2] + 2Fe^{3+} + 2X^- \rightleftharpoons cis\text{- or } trans\text{-}[PtL_2X_4] + 2Fe^{2+} \qquad (3)$$

NH_2Me, NH_2Et, NH_2Pr, or ½en; X = Cl or Br), in 0·5M-perchloric acid and 1M ionic strength. This study has been undertaken in order to determine the effects of changing L, X, and the geometric configuration of the complexes on both reaction rates and equilibria.

EXPERIMENTAL

Materials.—The platinum complexes were prepared by literature methods, when available;[2] other complexes were prepared as follows. *trans*-$[Pt(NH_2Pr)_2Cl_2]$ Was prepared by refluxing (3 h) a concentrated solution of $[Pt(NH_2Pr)_4]Cl_2$ in 2M-hydrochloric acid. The product, which separated from the cool mixture as pale yellow crystals, was filtered off and extracted with chloroform in which the parent $[Pt(NH_2Pr)_4]Cl_2$ is insoluble (Found: C, 19·5; H, 5·0; Cl, 17·8; N, 7·6. *trans*-$[Pt(NH_2Pr)_2Cl_2]$ requires C, 18·8; H, 4·7; Cl, 18·4; N, 7·3%). *trans*-$[Pt(NH_2Pr)_2Br_2]$ Was prepared by treating (80 °C, 30 min) a concentrated aqueous solution of the dichloro-complex with a large

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

[2] Gmelins Handbuch der Anorganische Chemie, 1957, **68**, Teil D, Verlag Chemie; G. W. Watt and R. E. McCarley, *J. Amer. Chem. Soc.*, 1957; **79**, 3315; A. Peloso, G. Dolcetti, and R. Ettorre, *Inorg. Chim. Acta*, 1967, **1**, 403.

excess of sodium bromide. This treatment was repeated on the yellow product which separated from the cold solution (Found: C, 16·0; H, 4·2; Br, 32·6; N, 6·0. *trans*-$[\mathrm{Pt(NH_2Pr)_2Br_2}]$ requires C, 15·2; H, 3·85; Br, 33·8; N, 5·9%). The isomeric form of these complexes was assigned on the basis of the preparation method.

trans-$[\mathrm{Pt(NH_2Pr)_2Cl_4}]$ and -$[\mathrm{Pt(NH_2Pr)_2Br_4}]$ Were prepared by treating solutions of the corresponding platinum(II) complexes in chloroform with an excess of chlorine or bromine, respectively (Found for *trans*-$[\mathrm{Pt(NH_2Pr)_2Cl_4}]$: C, 16·5; H, 4·4; Cl, 31·0; N, 6·4. Required: C, 15·9; H, 4·0; Cl, 31·2; N, 6·15. Found for *trans*-$[\mathrm{Pt(NH_2Pr)_2Br_4}]$ C, 11·7; H, 3·1; Br, 50·8; N, 4·4. Required: C, 11·4; H, 2·9; Br, 50·5; N, 4·4%). *cis*-$[\mathrm{Pt(NH_2Me)_2Br_4}]$ and -$[\mathrm{Pt(NH_2Et)_2Br_4}]$ Were prepared by treating warm aqueous solutions of the corresponding platinum(II) complexes, in the presence of 0·1M-hydrobromic acid, with an excess of bromine; they were recrystallized from 0·01M-hydrobromic acid (Found for *cis*-$[\mathrm{Pt(NH_2Me)_2Br_4}]$: C, 4·4; H, 1·9; Br, 54·45; N, 4·7. Required: C, 4·2; H, 1·7; Br, 55·4; N, 4·85%. Found for *cis*-$[\mathrm{Pt(NH_2Et)_2Br_4}]$: C, 8·1; H, 2·6; Br, 50·95; N, 4·65. Required C, 7·9; H, 2·35; N, 4·6; Br, 52·7%). The isomeric form of the platinum(IV) complexes was assigned on the basis of the preparation method as well as from a comparison of their u.v. spectra with those known for *cis*- and *trans*-$[\mathrm{Pt(NH_3)_2Br_4}]$.

Sodium bromide, sodium chloride, sodium perchlorate, and perchloric acid (70%) were reagent grade. Iron(II) perchlorate (Schuchard) and iron(III) perchlorate (Fluka) were purified and analysed as described in Part I. Twice distilled water was used as solvent.

Preparation of the Reaction Mixtures and Evaluation of the Reaction Rates.—Stock solutions of the platinum complexes were prepared by weight in perchloric acid (0·5M) containing sodium halide ($8{\cdot}75 \times 10^{-2}$M) to prevent solvolysis. It was found that 0·02M sodium halide was in general enough to reduce the extent of solvolysis to less than 5%. Stock solutions of the other compounds were prepared as described in Part I and similar procedures for the preparation of the reaction mixtures and for the evaluation of the reaction rates were employed. The conventional spectrophotometric technique was suitable for the present investigation.

The concentrations of the platinum complexes in the silica cell, used as reaction vessel, were in the range 4×10^{-5}—1×10^{-4}M. The ranges of concentration for the other reagents were as follows: (i) reduction of *trans*-$[\mathrm{PtL_2Br_4}]$, $[\mathrm{Fe^{II}}] = 3{\cdot}38 \times 10^{-2}$—$16{\cdot}9 \times 10^{-2}$M, $[\mathrm{NaBr}] = 2{\cdot}80 \times 10^{-2}$—$8{\cdot}9 \times 10^{-2}$M; (ii) reduction of *cis*-$[\mathrm{PtL_2Br_4}]$, $[\mathrm{Fe^{II}}] = 6{\cdot}00 \times 10^{-2}$—$16{\cdot}9 \times 10^{-2}$M, $[\mathrm{NaBr}] = 2{\cdot}00 \times 10^{-2}$—$6{\cdot}00 \times 10^{-2}$M; (iii) reduction of *trans*-$[\mathrm{PtL_2Cl_4}]$, $[\mathrm{Fe^{II}}] = 2{\cdot}20 \times 10^{-2}$—$8{\cdot}30 \times 10^{-2}$M, $[\mathrm{NaCl}] = 1{\cdot}00 \times 10^{-2}$—$9{\cdot}00 \times 10^{-2}$M; (iv) oxidation of *cis*- and *trans*-$[\mathrm{PtL_2Br_2}]$, $[\mathrm{Fe^{III}}] = 2{\cdot}40 \times 10^{-3}$—$8{\cdot}00 \times 10^{-3}$M, $[\mathrm{NaBr}] = 2{\cdot}36 \times 10^{-2}$—$3{\cdot}39 \times 10^{-1}$M; (v) equilibration reactions of *cis*- and *trans*-$[\mathrm{Pt(NH_3)_2Br_2}]$ and *cis*- and *trans*-$[\mathrm{Pt(NH_2Me)_2Br_2}]$, $[\mathrm{Fe^{III}}] = 4{\cdot}80 \times 10^{-3}$—$9{\cdot}6 \times 10^{-3}$M, $[\mathrm{Fe^{II}}] = 2{\cdot}20 \times 10^{-2}$—$8{\cdot}27 \times 10^{-2}$M, $[\mathrm{NaBr}] = 4{\cdot}00 \times 10^{-2}$—$7{\cdot}00 \times 10^{-2}$M: (vi) equilibration reactions of *cis*- and *trans*-$[\mathrm{Pt(NH_2Et)_2Br_2}]$ and *trans*-$[\mathrm{Pt(NH_2Pr)_2Br_2}]$, $[\mathrm{Fe^{III}}] = 8{\cdot}00 \times 10^{-3}$—$1{\cdot}20 \times 10^{-2}$M, $[\mathrm{Fe^{II}}] = 2{\cdot}00 \times 10^{-2}$—$5{\cdot}50 \times 10^{-2}$M, $[\mathrm{NaBr}] = 6{\cdot}00 \times 10^{-2}$—$9{\cdot}00 \times 10^{-2}$M; (vii) equilibration reactions of $[\mathrm{Pt(en)Br_2}]$, $[\mathrm{Fe^{III}}] = 2{\cdot}40 \times 10^{-3}$—$4{\cdot}80 \times 10^{-3}$M, $[\mathrm{Fe^{II}}] = 2{\cdot}20 \times 10^{-2}$—$1{\cdot}38 \times 10^{-1}$M, $[\mathrm{NaBr}] = 4{\cdot}00 \times 10^{-2}$—$7{\cdot}00 \times 10^{-2}$M. The reaction mixture was 0·5M in perchloric acid. Constant ionic strength (1M) was maintained by adding the appropriate amount of sodium perchlorate. At least eight kinetic runs were carried out for each study.

Identification of the Reaction Products.—The products of the reactions of platinum(II) bromo-complexes with $\mathrm{Fe^{3+}}$ and platinum(IV) bromo-complexes with $\mathrm{Fe^{2+}}$ were identified as described in Part I for the reaction of methylamine–platinum bromo-complexes. No change of the position of the ligand L accompanied the redox reactions. *cis*- or *trans*-$[\mathrm{PtL_2Br_2}]$ Was formed in the reduction of the platinum(IV) complexes and *cis*- or *trans*-$[\mathrm{PtL_2Br_4}]$ was formed in the oxidation of the platinum(II) complexes. In both oxidation of platinum(II) and reduction of platinum(IV) complexes the stoicheiometry was such that 2 g-ions of iron reacted with 1 mole of platinum complex. The formation of iron(III) in the reaction of *trans*-$[\mathrm{PtL_2Cl_4}]$ was detected by comparing the u.v. spectrum of the reaction mixture at the end of the reaction, with that of a standard solution containing iron(III) and chloride in the same medium as the reaction mixture. This was possible because the platinum product did not significantly contribute to the observed absorbance in the range of wavelength chosen for the comparison. Two moles of iron(III) were formed for 1 mole of platinum(IV) consumed. The reduction product of these reactions is expected to be a platinum(II) complex, as required by the stoicheiometry related to the reactants. However, this could not be identified in solution, owing to the high absorbance of the iron(III) species, formed during the reaction, and its separation from the reaction mixture was unsuccessful, presumably because of its high solubility.

RESULTS

The stoicheiometry of the reactions of the bromo-complexes is as described in equation (3). The reversibility of these reactions was shown directly by the fact that the amount of platinum(II) oxidized by iron(III) in the presence of bromide and iron(II) was strongly dependent upon the concentration of iron(II) added to the reacting mixture. In fact, the platinum(II) oxidation reactions do not go to completion when an excess of iron(II) is present in the reaction mixture and, at a given iron(III) concentration, either an increase in the concentration of iron(II), or a lowering of the concentration of bromide, lowers the extent of oxidation. Quantitative measurements of the concentrations of the different species present at equilibrium at 50 °C, performed as described elsewhere,[1] allowed us to evaluate the values of the equilibrium constants, K_{eq}, of the reactions examined (see the Table).

The stoicheiometry of the reduction of the tetrachloro-complexes was not fully determined because the reduced product containing platinum(II) was not identified. The fact that 2 g-ions of iron(III) are formed for 1 mole of platinum(IV) consumed is in agreement with equation (3). Thus, reasonably, *trans*-$[\mathrm{PtL_2Cl_2}]$ can be assumed to be the reduced product. The reversibility of the reaction was shown, in non-kinetic conditions, by allowing *trans*-$[\mathrm{PtL_2Cl_2}]$ (5×10^{-3}M) to react with iron(III) (5×10^{-2}M) in the presence of sodium chloride (0·2M) in 0·5M-perchloric acid at 60 °C for 3 h. Yellow crystals of *trans*-$[\mathrm{PtL_2Cl_4}]$ slowly separated from the warm solution directly or on cooling.

The reduction reactions of platinum(IV) complexes were carried out using concentrations of iron(II) at least 30 times higher than that of the platinum complex. Moreover, the concentrations of iron(II) and halide were such that the reactions went to completion. In these conditions the disappearance of the platinum(IV) complexes follow a pseudo-first-order rate law. The pseudo-first-order rate constant, k_{obs}, has the form (4) over the entire range of

$$k_{obs} = k_r[Fe^{2+}] \qquad (4)$$

concentration explored. The specific rate constants, k_r, for the complexes examined, and the related activation parameters, $\Delta H^‡_r$ and $\Delta S^‡_r$, are collected in the Table.

Specific rate constants, activation parameters, and equilibrium constants for the redox reactions: *cis*- or *trans*-$[PtL_2X_2] + 2Fe^{3+} + 2X^- \rightleftharpoons$ *cis*- or *trans*-$[PtL_2X_4] + 2Fe^{2+}$

Geometric config.	Substrates L	X	t / °C	K_{eq} [a] / l^2 mol^{-2}	K_{eq} [b] / l^2 mol^{-2}	k_f / l^2 mol^{-2} s^{-1}	$\Delta H^‡_f$ / kJ mol^{-1}	$\Delta S^‡_f$ / J mol^{-1} K^{-1}	$k_{f'}$ / l^3 mol^{-3} s^{-1}	$\Delta H^‡_{f'}$ / kJ mol^{-1}	$\Delta S^‡_{f'}$ / J mol^{-1} K^{-1}	k_r / l mol^{-1} s^{-1}	$\Delta H^‡_r$ / kJ mol^{-1}	$\Delta S^‡_r$ / J mol^{-1} K^{-1}	k / mol l^{-1}
trans	NH_3	Br	50	1.4×10^5	1.0×10^5	2·42			5·30			1.78×10^{-3}			1.0×10^{-2}
			30			1.80×10^{-1}	103	81	1·04	64	−33	2.90×10^{-4}	71	−78	
cis	NH_3	Br	50	1.8×10^5	2.1×10^5	1·82			7·15			8.40×10^{-4}			1.2×10^{-2}
			30			1.25×10^{-1}	106	88	1·16	71	−9	1.46×10^{-4}	68	−94	
trans	NH_2Me	Br	50	6.5×10^4	6.2×10^4 [c]	3·22			4·97			4.10×10^{-3} [c]			1.2×10^{-2} [c]
			30			2.41×10^{-1}	108	83	9.00×10^{-1}	67	−25	6.40×10^{-4} [c]	72 [c]	−67 [c]	
cis	NH_2Me	Br	50	1.4×10^5	1.2×10^5	2·15			3·56			1.39×10^{-3}			1.1×10^{-2}
			30			1.40×10^{-1}	105	95	5.55×10^{-1}	73	−9	2.45×10^{-4}	68	−90	
trans	NH_2Et	Br	50	1.7×10^4	1.6×10^4	2·09			2·63			7.26×10^{-3}			1.7×10^{-2}
			30			1.50×10^{-1}	104	83	4.86×10^{-1}	66	−33	1.15×10^{-3}	72	−63	
cis	NH_2Et	Br	50	2.9×10^4	2.5×10^4	1·21			2·13			2.44×10^{-3}			1.7×10^{-2}
			30			7.25×10^{-2}	112	103	3.75×10^{-1}	68	−29	4.12×10^{-4}	70	−79	
trans	NH_2Pr	Br	50	1.3×10^4	1.2×10^4	2·08			2·30			8.20×10^{-3}			2.0×10^{-2}
			30			1.40×10^{-1}	107	92	4.00×10^{-1}	68	−28	1.45×10^{-3}	68	−75	
(*cis*)	½en	Br	50	1.8×10^6	1.9×10^6	2·62			11·8			2.47×10^{-4}			5.9×10^{-3}
			30			2.14×10^{-1}	99	69	1·76	75	+7	4.56×10^{-5}	66	−110	
trans	NH_3	Cl	50									2.50×10^{-2}			
			30									5.40×10^{-3}	60	−90	
trans	NH_2Me	Cl	50									2.60×10^{-2}			
			30									5.10×10^{-3}	64	−78	
trans	NH_2Et	Cl	50									3.91×10^{-2}			
			30									8.00×10^{-3}	62	−80	
trans	NH_2Pr	Cl	50									4.28×10^{-2}			
			30									9.75×10^{-3}	58	−92	

Errors: (i) $K_{eq} \pm 10\%$; (ii) k_f, $k_{f'}$, and $k_r \pm 3\%$; (iii) $k \pm 8\%$; and (iv) $\Delta H^‡ \pm 4$ kJ mol^{-1}, $\Delta S^‡ \pm 10$ J mol^{-1} K^{-1}. [a] From kinetic data. [b] From concentrations at equilibrium. [c] From ref. 1.

The oxidation rates of the platinum(II) bromo-complexes were obtained in the presence of concentrations of iron(III) and bromide at least 30 times higher than those of platinum(II), and high enough for the reaction to go to completion. Under these conditions the reactions follow a pseudo-first-order rate law. The pseudo-first-order rate constant, k_{obs}, has the form (5) over the entire range of concentrations

$$k_{obs} = k_f[Fe^{3+}][Br^-] + k_{f'}[Fe^{3+}][Br^-]^2 \qquad (5)$$

explored. The specific rate constants, k_f and $k_{f'}$, and the related activation parameters are collected in the Table.

The oxidation of the platinum(II) bromo-complexes does not go to completion when an excess of iron(II) is added to the reacting mixture. Under these conditions the rate of approach to equilibrium is still of pseudo-first-order type and is consistent with a reversible process implying forward and reverse pseudo-first-order reactions. The pseudo-first-order rate constant of approach to equilibrium, k_{obs}, is strongly dependent on the concentration of iron(II), as previously found for the reactions of *trans*-$[Pt(NH_2Me)_2Br_2]$.[1] Values of k_{obs} at 50 °C were determined at different concentrations of iron(III), iron(II), and bromide (see Experimental section), in the range of bromide concentration in which the term $k_{f'}[Fe^{3+}][Br^-]^2$ in equation (5) does not strongly contribute to the rate. They obey the relation (6). The values of k are collected in the last column of the Table.

$$k_{obs} = \frac{k_f[Fe^{3+}][Br^-]}{1 + (k[Fe^{2+}]/[Fe^{3+}][Br^-])} + \frac{k_r[Fe^{2+}]}{1 + ([Fe^{3+}][Br^-]/k[Fe^{2+}])} \qquad (6)$$

DISCUSSION

The inner-sphere atom-transfer redox mechanism (2) appears to be consistent with the kinetic results for the reactions of all the bromo-complexes, carried out using low bromide concentrations. In fact, according to this mechanism, the full form (7) [1] of the pseudo-first-order rate constant, k_{obs}, is consistent with expression (6), and also with (4) and (5), obtained experimentally, provided that we place $k_f = k_1K_1$, $k_r = k_4$, and $k = k_2/k_3K_1$. The agreement of the experimental results with mechanism (2) is also consistent with the values obtained for

$$k_{obs} = \frac{k_1K_1[Fe^{3+}][Br^-]}{1 + (k_2[Fe^{2+}]/k_3K_1[Fe^{3+}][Br^-])} + \frac{k_4[Fe^{2+}]}{1 + (k_3K_1[Fe^{3+}][Br^-]/k_2[Fe^{2+}])} \qquad (7)$$

the equilibrium constants of our reactions. According to this mechanism the equilibrium constant of the overall reaction, K_{eq}, is related to the specific rate constants of the single steps by the relation $K_{eq} = k_1k_3K_1^2/k_2k_4 = k_f/kk_r$. The values of K_{eq} calculated from such a relationship are reported in the Table and the good agreement of these values with those derived from the concentrations of the different species present at equilibrium strongly supports the proposed mechanism.

Equation (5) shows that the oxidation of the platinum(II) bromo-complexes also involves a path implying two bromide ions in the activated complex. This path is accounted for by equations (8a) and (8b), involving a five-co-ordinate platinum(II) complex of the type

$$Fe^{3+} + Br^- \overset{K_1}{\rightleftharpoons} FeBr^{2+} \qquad (8a)$$

$$Pt^{II} + Br^- \overset{K_{Pt}}{\rightleftharpoons} Pt^{II}Br^- \qquad (8b)$$

$$Pt^{II}Br^- + FeBr^{2+} \underset{k_6}{\overset{k_5}{\rightleftharpoons}} Pt^{III}Br + Fe^{2+} + Br^- \qquad (8c)$$

$$[\text{or } Pt^{III}Br_2^- + Fe^{2+}]$$

$[PtL_2Br_3]^-$.* The existence of complexes of this kind has been postulated to occur, at least in the cases of *cis*- and *trans*-$[Pt(NH_3)_2Br_2]$,[3] to explain the failure in applying an anionic exchange separation technique to the system of *cis*- and *trans*-$[Pt(NH_3)_2Br_2]$ with bromide.[4] The alternative reaction paths (9a—c), whenever

$$Fe^{3+} + Br^- \overset{K_1}{\rightleftharpoons} FeBr^{2+} \qquad (9a)$$

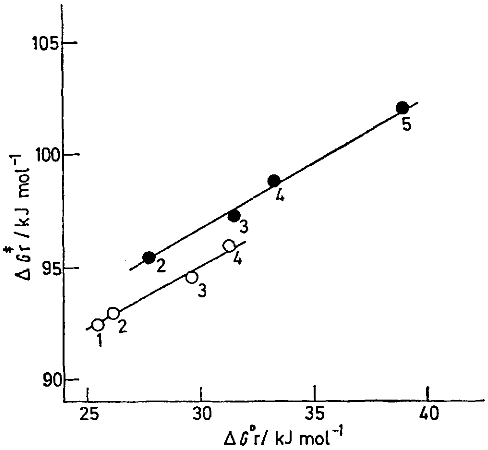
$$FeBr^{2+} + Br^- \overset{K_2}{\rightleftharpoons} FeBr_2^+ \qquad (9b)$$

$$Pt^{II} + FeBr_2^+ \underset{k_8}{\overset{k_7}{\rightleftharpoons}} Pt^{III}Br + Fe^{2+} + Br^- \qquad (9c)$$

occurring, are in our opinion of minor importance. Oxidation of platinum(II) through this reaction path ought to exhibit an entropy of activation, $\Delta S^{\ddagger}_{f'}$, more positive than that for the path occurring through mechanism (2), *i.e.* $\Delta S^{\ddagger}_{f}$, mainly because of the high positive contribution from the formation of $FeBr_2^+$ from $FeBr^{2+}$ and bromide.† A large positive entropy for the formation of $FeBr_2^+$ is expected because of the high desolvation accompanying a net neutralization of charges. As an example the reaction $FeF^{2+} + F^- \rightleftharpoons FeF_2^+$ in 0·5M-sodium perchlorate exhibits a reaction entropy of +88 J mol^{-1} K^{-1}.[5] The experimental results show that $\Delta S^{\ddagger}_{f'}$ is always 67—117 J mol^{-1} K^{-1} lower than $\Delta S^{\ddagger}_{f}$, in disagreement with the expectation for the occurrence of reaction paths (9a—c).

The reduction rate constants of the platinum(IV) complexes possessing the same geometric configuration and bonded halide, depend slightly upon the ligand L. The reactivity sequence is en < NH_3 < NH_2Me < NH_2Et < NH_2Pr. The Figure shows that linear free-energy relationships are found at 50 °C on plotting the activation free energy, $\Delta G^{\ddagger}_r$ corresponding to the second-order rate constants for the reactions of Fe^{2+} with $[PtL_2Br_4]$, against the overall free-energy change, ΔG°_r, for the reactions $[PtL_2Br_4] + 2Fe^{2+} \longrightarrow [PtL_2Br_2] + 2Fe^{3+} + 2Br^-$, evaluated from the equilibrium constants in the Table. The slopes are a little higher than 0·5. From the Table it is found that the reactivity order for the oxidation of the platinum(II) complexes also roughly parallels the order of the overall free-energy change. The occurrence of these relationships for both forward and reverse reactions, leads us to suggest that in both cases the activated complex has more pronounced reactant character when the reaction is thermodynamically favoured.

The *cis*- or *trans*-position of the ligands L has no effect on the reactivity of both platinum(II) and platinum(IV) complexes, and on the equilibrium constants of the reactions. In fact the differences in rate constant and equilibrium data between *cis*- and *trans*-isomers (see the Table) are mainly accounted for by statistical effects.[6] Different behaviour was encountered previously in the reduction of *cis*- and *trans*-$[Pt(PR_3)_2Cl_4]$ (R = Et or Pr^n) by I^-, SCN^-, $SeCN^-$, or $S_2O_3^{2-}$.[7,8] In these cases the *cis*-isomers react about 20—100 times faster than the corresponding *trans*-isomers. The difference in reactivity was explained on the basis of a different π interaction between the central metal atom and the phosphines *cis*- or *trans*-bonded.[7,9] In the cases of the complexes studied in the present paper the aliphatic amines cannot π interact with platinum and this accounts for the similar reactivity of the related *cis*- and *trans*-isomers. Moreover, the independence of the rates on the isomeric forms of the complexes also indicates that the role played by σ effects in determining the reaction rates is independent of the position of the ligands not involved in the reaction.



Relationship between the activation free energy, $\Delta G^{\ddagger}_r$, and the overall free-energy change, ΔG°_r, for the reduction of *cis*- (●) and *trans*- (○) platinum(IV) bromo-complexes by Fe^{2+} at 50 °C. L = NH_2Pr (1); NH_2Et (2); NH_2Me (3); NH_3 (4); and ½en (5)

The Table shows that *trans*-$[PtL_2Br_4]$ complexes always react with Fe^{2+} 5—15 times faster than the corresponding chloro-complexes. To our knowledge this appears to be the first case in which the reactivity trend $k_{Pt^{IV}Cl} > k_{Pt^{IV}Br}$ is observed, platinum(IV) bromo-complexes always reacting faster than the corresponding

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* A direct attack of Fe^{3+} on $[PtL_2Br_3]^-$ could represent an alternative to mechanism (2) in accounting for the k_f term. However, a path involving $FeBr^{2+}$ and $[PtL_2Br_2]$, equations (2a) and (2b), rather than a five-co-ordinate intermediate, $[PtL_2Br_3]^-$, is believed to be favoured since complexing of Br^- to Fe^{3+} is likely to be more extensive than that to $[PtL_2Br_2]$. This does not necessarily exclude contributions from the latter path, since kinetically the two paths are indistinguishable.

† It is assumed here that the entropies of activation of the elementary steps (2b) and (9c) are similar. This is expected from the similarity of the related intimate mechanisms which involve, in each case, a bridged activated complex of the type $Pt^{II} \cdots Br \cdots Fe^{III}$.

[3] D. R. Gano, G. F. Vandergrift, and D. S. Martin, jun., *Inorg. Chim. Acta*, 1968, **2**, 219.

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chloro-complexes, regardless of the mechanism involved.[10-13] We think that the main reason for this behaviour is the higher stability of $FeCl^{2+}$ with respect to $FeBr^{2+}$, these ions being the first oxidation products in the two cases. Literature data show that in water $FeCl^{2+}$ is about 5 kJ mol^{-1} more stable than $FeBr^{2+}$.[5] This extra kinetic-energy term lowers the activation free energy of reaction of the chloro-complexes with respect to the bromo-complexes, making the former more reactive.*

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* A full discussion on this point ought to also take into account the thermodynamic contribution of the processes $[PtL_2Br_4] + e \longrightarrow [PtL_2Br_3] + Br^-$ and $[PtL_2Cl_4] + e \longrightarrow [PtL_2Cl_3] + Cl^-$; this cannot be carried out at the present time.

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