Reversible Non-complementary Redox Reactions involving Platinum Complexes

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The kinetics and equilibria of the reversible system (i) [L = NH_3, $NMeH_2$, $NEtH_2$, $NPrH_2$, or $\frac{1}{2}$en (en = ethylenediamine)] have been studied in aqueous 0.50 mol dm^{-3} perchloric acid at I = 1.0 mol dm^{-3}. The pseudo-first-order rate constants have the form $k_{obs.} = k_f[Fe^{3+}][Br^-] + k_f'[Fe^{3+}][Br^-]^2$ for the oxidation of platinum(II) complexes, and $k_{obs.} = k_r[Fe^{2+}]$ for the reduction of platinum(IV) derivatives. The rate of oxidation of the platinum(II) complexes by Fe^{III} is decreased by the presence of Fe^{II}. The results are consistent with a redox mechanism involving two successive one-electron-transfer steps. Changes of ligands are found to influence the kinetic and thermodynamic parameters in the same direction, the oxidation of the platinum(II) complexes being kinetically and thermodynamically favoured in the order $NPrH_2 < NEtH_2 < NMeH_2 < NH_3 <$ en. The steric hindrance of the amines is considered to be the factor responsible for the observed trends. The kinetic and thermodynamic parameters are linearly correlated with the steric constants of the amines.

$$[PtL_4]^{2+} + 2Fe^{3+} + 2Br^- \rightleftharpoons trans\text{-}[PtL_4Br_2]^{2+} + 2Fe^{2+} \qquad (i)$$

REDOX reactions involving platinum complexes have received considerable attention during the past few years.[1-8] However, few studies have been devoted to reversible systems, whose investigation would provide information on the influence of co-ordinated ligands both on the thermodynamics of the processes and the reactivity of platinum(II) towards oxidation and platinum(IV) towards reduction. The studies which have been carried out involved the use of reagents for the oxidation of platinum(II) complexes whose redox couples were different from that of the reagents employed for the reduction of the corresponding platinum(IV) species, thus preventing an unambiguous identification of the relevant factors.[1,2,7,9] Only two papers appear to have been concerned with reversible systems, one of which deals with complementary redox reactions (1) and the other with non-complementary reactions (2). Both

$$trans\text{-}[PtL_4Cl_2]^{2+} + [PtL'_4]^{2+} \rightleftharpoons [PtL_4]^{2+} + trans\text{-}[PtL'_4Cl_2]^{2+} \qquad (1)$$

$$cis\text{- or } trans\text{-}[PtL_2Br_2] + 2Fe^{3+} + 2Br^- \rightleftharpoons cis\text{- or } trans\text{-}[PtL_2Br_4] + 2Fe^{2+} \qquad (2)$$

these studies demonstrated the occurrence of interesting linear free-energy relationships between the kinetic and thermodynamic parameters.[10,11]

In order to determine which properties of the ligands are important in affecting both the reactivity and thermodynamics of redox reactions of platinum complexes, the investigation of systems of type (2) have now been extended to the redox reactions (3) [L = NH_3, $NMeH_2$, $NEtH_2$, $NPrH_2$, or $\frac{1}{2}$en (en = ethylenediamine)] in 0.50 mol dm^{-3} aqueous perchloric acid and at I = 1.0 mol dm^{-3}.

$$[PtL_4]^{2+} + 2Fe^{3+} + 2Br^- \rightleftharpoons trans\text{-}[PtL_4Br_2]^{2+} + 2Fe^{2+} \qquad (3)$$

EXPERIMENTAL

Materials.—The complexes $[PtL_4]Br_2$ and *trans*-$[PtL_4Br_2]Br_2$ were prepared by standard methods.[12] Platinum(II) perchlorates, $[PtL_4][ClO_4]_2$, were also prepared by treating cold aqueous concentrated solutions of the related bromides with either cold perchloric acid (70%) (L = NH_3 or $NMeH_2$) or cold aqueous saturated solutions of $Na[ClO_4]$ (L = NH_3, $NEtH_2$, or $NPrH_2$). Their u.v. and visible spectra were the same as those of the parent bromides, and analytical data (%) were consistent with the assigned formulation.

Sodium bromide and perchlorate, iron(II) and iron(III) perchlorates, perchloric acid, and twice distilled water were purified and analysed as described previously.[13]

Preparation of the Reaction Mixtures and Evaluation of the Reaction Rates.—Stock solutions of platinum complexes (8.00×10^{-4}—4.00×10^{-3} mol dm^{-3}) were usually prepared by weight in 0.50 mol dm^{-3} $HClO_4$ and 0.50 mol dm^{-3} $Na[ClO_4]$. Some of the sodium perchlorate (5.00×10^{-2} mol dm^{-3}) in the solutions of platinum(IV) complexes was replaced by sodium bromide to prevent hydrolysis. For sparingly soluble platinum(IV) complexes (L = $NEtH_2$ or $NPrH_2$), saturated solutions were employed. Stock solutions of the other reagents were prepared as described elsewhere.[13] The reactions were followed spectrophotometrically by recording the spectrum over the range 280—360 nm, where large changes of absorbance occur. The platinum(IV) complexes exhibit maxima in this region [320 (L = en or NH_3), 325 ($NMeH_2$), and 330 nm ($NEtH_2$ or $NPrH_2$)]. The course of the reactions was also characterized by the presence of an isosbestic point in the 290—300 nm region, its wavelength depending on both the complex employed and the concentration of bromide.

Preparation of the reactant mixtures, determination of the form of the rate laws, and evaluation of the observed rate constants, $k_{obs.}$ were as described previously.[11,13] The concentrations of the platinum complexes in the mixtures were in the range 6×10^{-4}—1×10^{-3} mol dm^{-3}, apart from complexes with $NEtH_2$ and $NPrH_2$ whose concentrations never exceeded 1×10^{-4} mol dm^{-3}. The ranges of concentration for the other reagents were as follows: (*i*) oxidation of $[Pt(en)_2]^{2+}$, $[Fe^{3+}] = 3.57 \times 10^{-3}$—$2.38 \times 10^{-2}$, $[Br^-] = 1.43 \times 10^{-2}$—$2.86 \times 10^{-1}$; (*ii*) oxidation of $[Pt(NH_3)_4]^{2+}$, $[Fe^{3+}] = 3.57 \times 10^{-3}$—$2.38 \times 10^{-2}$, $[Br^-] = 5.71 \times 10^{-2}$—$3.86 \times 10^{-1}$; (*iii*) oxidation of $[Pt(NMeH_2)_4]^{2+}$, $[Fe^{3+}] = 1.52 \times 10^{-3}$—$4.76 \times 10^{-2}$, $[Br^-] = 4.29 \times 10^{-2}$—$3.22 \times 10^{-1}$; (*iv*) oxidation of $[Pt(NEtH_2)_4]^{2+}$ and $[Pt(NPrH_2)_4]^{2+}$,

$[Fe^{3+}] = 7.14 \times 10^{-3}$—$2.38 \times 10^{-2}$, $[Br^-] = 5.71 \times 10^{-2}$—$3.43 \times 10^{-1}$; (*v*) reduction of *trans*-$[Pt(NH_3)_4Br_2]^{2+}$, *trans*-$[Pt(NMeH_2)_4Br_2]^{2+}$, and *trans*-$[Pt(en)_2Br_2]^{2+}$, $[Fe^{2+}] = 2.86 \times 10^{-2}$—$1.43 \times 10^{-1}$; (*vi*) reduction of *trans*-$[Pt(NEtH_2)_4Br_2]^{2+}$ and *trans*-$[Pt(NPrH_2)_4Br_2]^{2+}$, $[Fe^{2+}] = 1.43 \times 10^{-2}$—$4.77 \times 10^{-2}$; (*vii*) equilibration reactions of $[Pt(en)_2]^{2+}$, $[Fe^{3+}] = 7.14 \times 10^{-3}$—$3.57 \times 10^{-2}$, $[Fe^{2+}] = 1.91 \times 10^{-2}$—$1.10 \times 10^{-1}$, $[Br^-] = 2.86 \times 10^{-2}$—$2.71 \times 10^{-1}$; (*viii*) equilibration reactions of $[Pt(NH_3)_4]^{2+}$, $[Fe^{3+}] = 7.14 \times 10^{-3}$—$1.36 \times 10^{-2}$, $[Fe^{2+}] = 2.39 \times 10^{-2}$—$1.10 \times 10^{-1}$, $[Br^-] = 5.71 \times 10^{-2}$—$2.57 \times 10^{-1}$; (*ix*) equilibration reactions of $[Pt(NMeH_2)_4]^{2+}$, $[Fe^{3+}] = 9.52 \times 10^{-3}$—$2.86 \times 10^{-2}$, $[Fe^{2+}] = 1.91 \times 10^{-2}$—$1.05 \times 10^{-1}$, $[Br^-] = 5.71 \times 10^{-2}$—$2.57 \times 10^{-1}$ mol dm^{-3}. The reaction mixtures were 0.50 mol dm^{-3} in perchloric acid. Constant ionic strength (1.0 mol dm^{-3}) was maintained using $Na[ClO_4]$ as supporting electrolyte.

Series of at least four kinetic runs were carried out using different iron(II) concentrations in the reductions of each platinum(IV) complex at 50.0 °C. The oxidations of platinum(II) complexes were studied by carrying out at least three sets of kinetic runs using different iron(III) concentrations, each set involving at least four runs at different sodium bromide concentrations. In the case of the equilibrium reactions, each series was repeated using at least three different concentrations of Fe^{II}.

Stoicheiometry of the Reactions and Evaluation of the Equilibrium Constants.—The absorption spectrum of the reaction mixture at the end of the reaction for the oxidations of platinum(II) complexes showed that Pt^{II} was quantitatively converted into *trans*-$[PtL_4Br_2]^{2+}$. On the other hand, the concentration of Fe^{III} formed in the reduction of platinum(IV) complexes, determined as described elsewhere,[13] was found to be twice that of the Pt^{IV} consumed. These results are in agreement with stoicheiometry (3). The equilibrium constants, K, of the reactions were evaluated from the changes of absorbance of series of oxidation reactions of platinum(II) complexes, carried out using a constant starting concentration of Pt^{II} and variable amounts of the other species, both reactants and reaction products, in concentration such as to prevent reaction (3) from going to completion. The reactant mixtures were thermostatted at 50.0 °C and their spectra were recorded at suitable time intervals until equilibrium conditions were attained. The values of K are not very accurate, mainly because in the long time required for equilibration (some days in the case of complexes with en and NH_3) significant amounts of Fe^{II} are oxidized to Fe^{III} in a secondary reaction.

RESULTS

Under the experimental conditions adopted the oxidations of all the platinum(II) complexes examined go to completion in the absence of added Fe^{II}. The reactions follow stoicheiometry (3) and the disappearance of Pt^{II} obeys a pseudo-first-order rate law. In each case, the pseudo-first-order rate constant, $k_{obs.}$, has the form (4), as illustrated by the examples in Figure 1.

$$k_{obs.} = k_f[Fe^{3+}][Br^-] + k_f'[Fe^{3+}][Br^-]^2;$$
$$k_{obs.}/[Fe^{3+}][Br^-] = k_f + k_f'[Br^-] \quad (4)$$

The reductions of the platinum(IV) complexes also go to completion if Fe^{III} is not added to the reacting mixture, again following a pseudo-first-order rate law. In this case $k_{obs.}$ is a function only of the iron(II) concentration, according to relation (5).

$$k_{obs.} = k_r[Fe^{2+}] \quad (5)$$

The rates of oxidation of the platinum(II) complexes (examined only for L = NH_3, $NMeH_2$, or $\frac{1}{2}$en) is lowered by Fe^{II}. The reactions obey a pseudo-first-order rate law and still go to completion, except for the oxidations of $[Pt(NMeH_2)_4]^{2+}$ carried out in the presence of low concentrations of both Fe^{III} and bromide and high concentrations of Fe^{II}. For L = NH_3 and $NMeH_2$, the pseudo-first-order rate constant has the form (6), the contribution of the k_r term being significant only for the reactions of $[Pt(NMeH_2)_4]^{2+}$ which do not go to completion. The validity of relation (6) is supported by the example of Figure 2 where the data were calculated according to

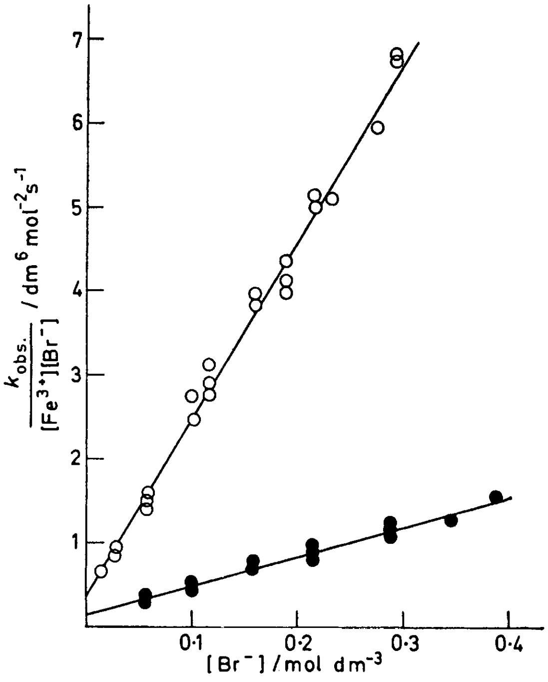

FIGURE 1 Dependence of $k_{obs.}/[Fe^{3+}][Br^-]$ on bromide-ion concentration for the oxidations of $[Pt(en)_2]^{2+}$ (○) and $[Pt(NH_3)_4]^{2+}$ (●) by Fe^{III} at 50.0 °C

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

expression (7), which may be derived from the former. Relationships (6) and (7) account also for the kinetic effect

$$\frac{k_{obs.}([Fe^{2+}] = 0)}{k_{obs.} - \Delta} = 1 + \frac{k[Fe^{2+}]}{[Fe^{3+}][Br^-]} \quad (7)$$

$$k_{obs.}([Fe^{2+}] = 0) = (k_f + k_f'[Br^-])[Fe^{3+}][Br^-];$$

$$\Delta = \frac{k_r[Fe^{2+}]}{1 + ([Fe^{3+}][Br^-]/k[Fe^{2+}])}$$

of Fe^{II} on the oxidation of $[Pt(en)_2]^{2+}$. However, in this case the gradients, k', obtained by plotting the left-hand side of equation (7) against $[Fe^{2+}]/[Fe^{3+}]$ are not linearly

TABLE 1

Rate constants and activation parameters * for the reactions: $[PtL_4]^{2+} + 2Fe^{3+} + 2Br^- \longrightarrow$ *trans*-$[PtL_4Br_2]^{2+} + 2Fe^{2+}$

L	θ_c/°C	k_f/dm^6 mol^{-2} s^{-1}	k_f'/dm^9 mol^{-3} s^{-1}	$\Delta H_f'^{\ddagger}$/kJ mol^{-1}	$\Delta S_f'^{\ddagger}$/J K^{-1} mol^{-1}
½ en	30	3.3×10^{-2}	3.98		
	40	9.5×10^{-2}	9.85	67.8	−10
	50	3.6×10^{-1}	22.4		
NH_3	30	2.2×10^{-2}	5.58×10^{-1}		
	40	5.0×10^{-2}	1.56	73.5	−8
	50	1.6×10^{-1}	3.60		
$NMeH_2$	30	1.0×10^{-2}	4.21×10^{-1}		
	40	4.0×10^{-2}	1.09	77.4	+5
	50	1.0×10^{-1}	3.01		
$NEtH_2$	30	3.0×10^{-3}	9.81×10^{-2}		
	40	9.0×10^{-3}	2.87×10^{-1}	85.9	+19
	50	3.0×10^{-2}	8.63×10^{-1}		
$NPrH_2$	30	2.7×10^{-3}	1.16×10^{-1}		
	40	2.0×10^{-2}	3.10×10^{-1}	76.1	−12
	50	4.1×10^{-2}	8.00×10^{-1}		

* Errors: k_f ±20%; k_f' ±3%; $\Delta H_f'^{\ddagger}$ ±4 kJ mol^{-1}; $\Delta S_f'^{\ddagger}$ ±10 J K^{-1} mol^{-1}.

TABLE 2

Rate constants for the reduction of *trans*-$[PtL_4Br_2]^{2+}$ by Fe^{2+}, competition constant, k, and equilibrium constants for reactions (3) at 50.0 °C [a]

L	k_r/dm^3 mol^{-1} s^{-1}	k/mol dm^{-3}	K/dm^6 mol^{-2}
½ en	5.1×10^{-5}	[b]	4×10^7
NH_3	2.43×10^{-4}	1.3×10^{-2}	5×10^5
$NMeH_2$	6.03×10^{-4}	1.9×10^{-2}	5×10^4
$NEtH_2$	2.20×10^{-3}		8×10^3
$NPrH_2$	8.75×10^{-4}		3×10^3

[a] Errors: k_r ±3%; k ±5%; K ±50%. [b] $k' = 4 \times 10^{-2}$ ($[Br^-] = 2.86 \times 10^{-2}$), 3.5×10^{-2} ($[Br^-] = 5.71 \times 10^{-2}$), 3.1×10^{-2} ($[Br^-] = 1.14 \times 10^{-1}$), 2.8×10^{-2} ($[Br^-] = 1.71 \times 10^{-1}$), and 3.0×10^{-2} ($[Br^-] = 2.29 \times 10^{-1}$ mol dm^{-3}).

correlated with $1/[Br^-]$, as is required by such a relation (some values of k' are in Table 2).

The values of k_f, k_f', k_r, and k at the temperatures employed are listed in Tables 1 and 2 together with the activation parameters, whenever determined. The equilibrium constants of the reactions are also listed in Table 2.

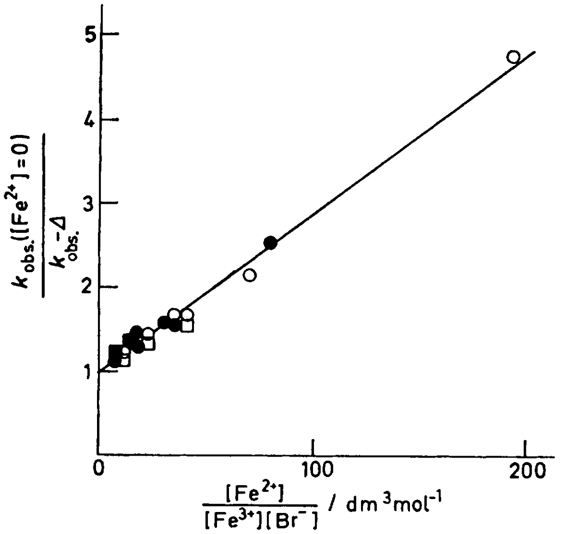

FIGURE 2 Kinetic data for the oxidation of $[Pt(NMeH_2)_4]^{2+}$ by Fe^{III} in the presence of Fe^{II} and bromide ions [5.72×10^{-2} (○), 1.14×10^{-1} (●), 1.71×10^{-1} (□), and 2.57×10^{-1} mol dm^{-3} (■)] at 50.0 °C

DISCUSSION

The rate laws followed by the redox systems considered in this paper have the same form as those previously obtained for the similar system (2), so that the same mechanism probably operates in both systems. The overall mechanism may be depicted by equations (8a)—(8e), and leads to a pseudo-first-order rate constant of the approach to equilibrium of the form (9). This

$$Fe^{3+} + Br^- \xrightleftharpoons{K_{Fe}} [FeBr]^{2+} \quad (8a)$$

$$[PtL_4]^{2+} + Br^- \xrightleftharpoons{K_{Pt}} [PtL_4Br]^+ \quad (8b)$$

$$[Pt^{II}L_4]^{2+} + [FeBr]^{2+} \xrightleftharpoons[k_{-1}]{k_1} [Pt^{III}L_4Br]^{2+} + Fe^{2+} \quad (8c)\ *$$

$$[Pt^{II}L_4Br]^+ + [FeBr]^{2+} \xrightarrow{k_2} [Pt^{III}L_4Br]^{2+} + Fe^{2+} + Br^- \quad (8d)\ *$$

$$[Pt^{III}L_4Br]^{2+} + [FeBr]^{2+} \xrightleftharpoons[k_{-3}]{k_3} [Pt^{IV}L_4Br_2]^{2+} + Fe^{2+} \quad (8e)$$

$$k_{obs.} = \frac{(k_1K_{Fe} + k_2K_{Fe}K_{Pt}[Br^-])[Fe^{3+}][Br^-]}{1 + (k_{-1}[Fe^{2+}]/k_3K_{Fe}[Fe^{3+}][Br^-])} + \frac{k_{-3}[Fe^{2+}]}{1 + (k_3K_{Fe}[Fe^{3+}][Br^-]/k_{-1}[Fe^{2+}])} \quad (9)$$

equation coincides with the experimental results provided assignments (10) are introduced. The kinetic

$$k_f = k_1K_{Fe},\ k_f' = k_2K_{Fe}K_{Pt},\ k_r = k_{-3},\ k = k_{-1}/k_3K_{Fe} \quad (10)$$

effect displayed by bromide in the equilibration reactions of $[Pt(en)_2]^{2+}$ indicates that the above mechanism is not fully satisfactory for the reactions of this complex. However, this problem is related to the occurrence of other fast reaction steps and does not rule out the correctness of the mechanism also for this complex as far as the slow steps are concerned.

The first conclusion which can be drawn from the data in Tables 1 and 2 is that the kinetic and thermodynamic parameters are influenced in the same way by changes of the ligands bonded to platinum. Thus, the reduction of platinum(IV) complexes is thermodynamically and kinetically enhanced in the direction L = ½en < NH_3 < $NMeH_2$ < $NEtH_2$ ~ $NPrH_2$, whereas the opposite order is observed for the oxidation of the corresponding platinum(II) complexes. The σ-donor ability of the amines (which slightly increases on going from NH_3 to $NPrH_2$) does not appear to be an adequate property for explaining the observed trends. In fact, on the basis of previous information indicating that an increase in the σ-donor ability of L would make Pt^{IV} more inert towards reduction,[7,9] such a property would lead to a reactivity trend opposite to that experimentally

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* For alternative reaction steps, see refs. 11 and 13.

found. On the other hand, there are good reasons to take into account the steric hindrance of the amines as a possible factor responsible for destabilizing Pt^{IV} towards reduction.[14] Such a possibility may be quantitatively tested by taking the values of the steric constants of the amines, E_N, recently proposed as a measure of their steric hindrance.[15-17]

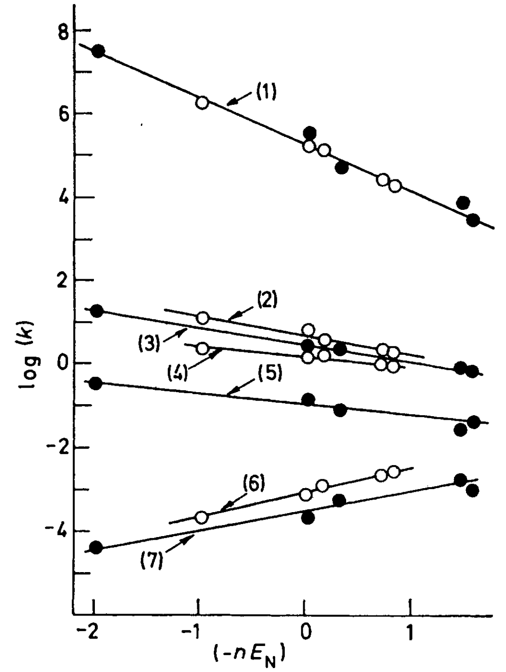

FIGURE 3 Dependence of log (k) on steric hindrance, ($-nE_N$), of amines for the redox systems: $[PtL_nBr_{4-n}]^{n-2} + 2\ Fe^{3+} + 2\ Br^- \rightleftharpoons [PtL_nBr_{6-n}]^{n-2} + 2\ Fe^{2+}$ at 50.0 °C: $n = 2$ (○) or 4 (●); (k) = K[(1)], k_f' [(2) and (3)], k_f [(4) and (5)], and k_r [(6) and (7)]; $E_N = -0.39$ ($NPrH_2$), -0.36 ($NEtH_2$), -0.07 ($NMeH_2$), 0.00 (NH_3), and 0.50 ($\frac{1}{2}$ en)

In connection with the thermodynamics of the processes examined, a fair linear relationship between log K and ($-nE_N$) [equation (11); (k) = K] is indeed found (Figure 3) for $L = NH_3$,

$$\log(k) = \alpha(-nE_N) + \beta \qquad (11)$$

$NMeH_2$, $NEtH_2$, and $NPrH_2$, n being the number of ligands L bonded to platinum and the negative sign is introduced because E_N decreases with increasing steric hindrance of the amine. Interestingly, such a relation also gives a quantitative fit to data pertaining to system (2) (Figure 3), if the steric hindrance of bromide is considered to be comparable to that of ammonia, as suggested by the literature.[15,18] Unfortunately, the value of E_N for en cannot be evaluated from the literature. Nevertheless, relation (11) also gives a good fit to data for reactions of $[Pt(en)_2]^{2+}$ and $[Pt(en)Br_2]$ (Figure 3) when a value of +0.50 is assigned to E_N for a CH_2NH_2 moiety co-ordinated to platinum. Such a low steric hindrance for CH_2NH_2 may be explained by the fact that chelation constrains the methylenes to a position far from platinum, thus decreasing the steric crowding near the reaction centre. In this connection it is worth noting that, as a rule, cyclization of organic systems strongly reduces their steric hindrance.[18]

The reactivity of Pt^{II} and Pt^{IV} in both classes of complexes is also linearly related to the steric constants of the amines by relation (11) (Figure 3). The values of α and β found in each case are collected in Table 3. It is found that the value of α for a common reaction path is independent of the type of complex examined, within experimental error. Therefore, the changes of β observed for the same reaction step on changing the type of complex must arise from some property of the complexes as a whole, rather than of the ligands. Thus, the lower values of β observed for charged compared with uncharged complexes in the reaction paths k_f and k_r can be entirely ascribed to the extra repulsive coulombic free energy required to bring the charged complexes and the dipositive iron reactants together, at the ionic strength adopted.[19] On the other hand, the values of β for the oxidative path k_f are nearly the same for both classes of complexes. In this case, a higher stability of $[PtL_4Br]^+$ with respect to $[PtL_2Br_3]^-$ is likely to compensate for the more unfavourable coulombic free energy associated with the reactions of the positively charged, five-co-ordinate, platinum(II) complexes.

The values of α, which quantify the role played by the steric hindrance of the co-ordinated amines, show that this property is the factor which decreases the reactivity of Pt^{II} towards oxidation. The effect observed in the k_f' reaction path is twice that observed in the k_f path (Table 3), in agreement with and fully substantiating the proposed mechanism. In fact, the effect observed in the k_f' oxidation path (*i.e.* $k_2K_{Fe}K_{Pt}$) also reflects the influence of steric hindrance on the stability constant of the five-co-ordinate platinum(II) adduct (besides the effect on the oxidative attack of $[FeBr]^{2+}$ to Pt^{II}, which is common to both oxidation paths).

The positive value of α for the reduction of platinum(IV) complexes implies that the steric hindrance of amines enhances the reactivity of these complexes towards reduction, which is the expected behaviour in view of the

TABLE 3

Values of α and β calculated from relation (11) at 50.0 °C for the redox reactions $[PtL_nBr_{4-n}]^{n-2} + 2Fe^{3+} + 2Br^- \rightleftharpoons [PtL_nBr_{6-n}]^{n-2} + 2Fe^{2+}$

	K		k_f		k_f'		k_r	
$[PtL_nBr_{4-n}]^{n-2}$	α	β	α	β	α	β	α	β
cis-$[PtL_2Br_2]$	−1.09	5.25	−0.220	0.250	−0.460	0.670	0.570	−3.024
	±0.16	±0.13	±0.060	±0.040	±0.080	±0.055	±0.040	±0.027
$[PtL_4]^{2+}$	−1.09	5.25	−0.295	−0.955	−0.410	0.550	0.410	−3.474
	±0.16	±0.13	±0.045	±0.060	±0.010	±0.015	±0.080	±0.098

fact that steric crowding would strain the Pt^{IV}–Br bonds, thus promoting a decrease in co-ordination number which may be achieved by the reduction of Pt^{IV}.

It is worth noting that the σ-donor ability of amines has not been considered in this discussion. This property may have some influence on the reactivity of platinum complexes, as observed previously,[7,9] but in the present case steric effects clearly outweigh its opposite contribution to the rate.

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