A Kinetic Investigation on the Oxidation of Platinum(II) Complexes by Hexachloroiridate(IV). Role of Steric Hindrance

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The oxidation reactions of platinum(II) complexes of the type $[Pt(en)L_2]^{2+}$ [en = $H_2NCH_2CH_2NH_2$, L = NH_3, NH_2R (R = Me, Et, Pr^n, CH_2Bu^t, CH_2Ph, Bu^n, C_4H_7, C_5H_9, or C_6H_{11}), 4-cyanopyridine, $\frac{1}{2}$ $MeHNCH_2CH_2NH_2$, $\frac{1}{2}$ $Me_2NCH_2CH_2NH_2$, or $\frac{1}{2}$ $Me_2NCH_2CH_2NMe_2$] and $[PtL_4]^{2+}$ [L = NH_3 or NH_2R (R = Me, Et, or Pr^n)] by $IrCl_6^{2-}$ in the presence of chloride ions have been kinetically investigated in aqueous perchlorate media (pH 2.0—3.0, I = 1.0 mol dm^{-3}). In the absence of $IrCl_6^{3-}$ the reactions obey the rate law $-d[IrCl_6^{2-}]/dt = 2\,(k_a + k_b[Cl^-])\,[complex][IrCl_6^{2-}]$. The iridium(III) reaction product, $IrCl_6^{3-}$, lowers the rates. The results obtained are consistent with a redox mechanism involving a five-co-ordinate platinum(II) intermediate and two successive one-electron-transfer steps. The reactivity of the complexes is strongly dependent on the ligands co-ordinated to platinum(II), steric hindrance being the most important factor in the observed trend.

In a previous paper[1] I reported the kinetic behaviour and reaction mechanism of the oxidation of $[Pt(en)_2]^{2+}$ and $[Pt(en)(py)_2]^{2+}$ by $IrCl_6^{2-}$ in aqueous perchlorate medium (I = 1.0 mol dm^{-3}) in the presence of chloride ions (en = ethylenediamine, py = pyridine). The replacement of one ethylenediamine by two pyridines in the co-ordination sphere of platinum(II) was found to cause a strong lowering (4.9 × 10^2 times) of the oxidation rate. Although a connection between kinetic and thermodynamic parameters ($\Delta G^\ddagger$ and ΔG°) was observed, the data were limited to two complexes and could not provide reliable information on which ligand properties are responsible for reactivity changes occurring in the oxidation of platinum(II) complexes by hexachloroiridate(IV) ions.

In order to try to elucidate this matter I have carried out a kinetic investigation on the oxidation by $IrCl_6^{2-}$ of complexes of the type $[Pt(en)L_2]^{2+}$ {L = NH_3, NH_2R [R = methyl, ethyl, n-propyl, neopentyl (CH_2Bu^t), benzyl, n-butyl, cyclobutyl, cyclopentyl, or cyclohexyl], 4-cyanopyridine (4CN-py), $\frac{1}{2}$ *N*-methylethylenediamine (meen), $\frac{1}{2}$ *N,N*-dimethylethylenediamine (dmen), or $\frac{1}{2}$ *N,N,N',N'*-tetramethylethylenediamine (tmen)} and $[PtL_4]^{2+}$ [L = NH_3 or NH_2R (R = Me, Et, or Pr^n)] in the presence of chloride ions.

Experimental

Materials.—Platinum(II) complexes of the type $[Pt(en)L_2]Cl_2$ (L = NH_2Me, NH_2Et, NH_2Pr^n, $NH_2CH_2Bu^t$, NH_2CH_2Ph, NH_2Bu^n, $NH_2C_4H_7$, $NH_2C_5H_9$, or $NH_2C_6H_{11}$) were prepared by treating an aqueous suspension of $[PtCl_2(en)]$ with an excess of the required amine, and heating at 50—70 °C until a clear and colourless solution was obtained. This solution was evaporated to dryness under vacuum and the crude material was dissolved in a small portion of methanol. The solution was then treated with charcoal, warmed, and filtered. Subsequent addition of acetone, acetonitrile, or diethyl ether caused the separation of the required platinum(II) complexes as white or very pale yellow solids (Table 1). Sometimes the addition of diethyl ether resulted in the separation of a sticky colourless liquid. However, when this was dissolved in a very small portion of methanol and then treated with an excess of diethyl ether the complexes

Table 1. Elemental analyses (%) of platinum(II) complexes

Complex	C Found	C Calc.	H Found	H Calc.	N Found	N Calc.
(**1**) $[Pt(en)(NH_3)_2][ClO_4]_2$	4.90	4.90	2.90	2.90	11.40	11.50
(**2**) $[Pt(en)(NH_2Me)_2]Cl_2$	12.15	12.40	4.60	4.65	14.20	14.45
(**3**) $[Pt(en)(NH_2Et)_2]Cl_2$	17.25	17.30	5.20	5.35	13.30	13.45
(**4**) $[Pt(en)(NH_2Pr^n)_2]Cl_2$	21.25	21.65	5.95	5.85	12.50	12.60
(**5**) $[Pt(en)(NH_2CH_2Bu^t)_2]Cl_2$	28.90	28.80	6.85	6.85	11.15	11.20
(**6**) $[Pt(en)(NH_2CH_2Ph)_2]Cl_2$	35.40	35.55	4.90	4.85	10.25	10.35
(**7**) $[Pt(en)(NH_2Bu^n)_2]Cl_2$	25.35	25.45	6.40	6.40	11.70	11.85
(**8**) $[Pt(en)(NH_2C_4H_7)_2]Cl_2$	25.70	25.65	5.80	5.60	11.45	11.95
(**9**) $[Pt(en)(NH_2C_5H_9)_2]Cl_2$	28.50	29.05	6.05	6.10	11.40	11.30
(**10**) $[Pt(en)(NH_2C_6H_{11})_2]Cl_2$	31.30	32.05	6.75	6.55	10.00	10.70
(**11**) $[Pt(en)(4CN\text{-}py)_2][ClO_4]_2$	25.30	25.40	2.40	2.45	12.35	12.70
(**12**) $[Pt(en)(meen)][ClO_4]_2$	11.45	11.35	3.40	3.45	10.65	10.60
(**13**) $[Pt(en)(dmen)][ClO_4]_2$	13.30	13.30	3.70	3.70	10.35	10.35
(**14**) $[Pt(en)(tmen)]Cl_2$	20.45	21.70	5.60	5.45	12.35	12.65
(**15**) $[Pt(NH_3)_4][ClO_4]_2$			2.60	2.60	12.00	12.10
(**16**) $[Pt(NH_2Me)_4]Cl_2$	12.15	12.30	5.15	5.15	14.20	14.35
(**17**) $[Pt(NH_2Et)_4][ClO_4]_2$	16.50	16.75	4.85	4.90	9.55	9.75
(**18**) $[Pt(NH_2Pr^n)_4]Cl_2{\cdot}2H_2O$	26.70	26.75	7.50	7.50	10.35	10.40

separated as white flocculant materials. Platinum(II) complexes of the type $[Pt(en)L_2][ClO_4]_2$ (L = NH_3, 4CN-py, ½ meen, or ½ dmen) were prepared by treating a hot (80—90 °C) aqueous suspension of $[PtCl_2(en)]$ with 2 equivalents of $Ag[ClO_4]$, and warming at 80—90 °C for about 2 h. The silver chloride separated was filtered off and the resulting clear yellow solution was treated with an excess of the required amine and maintained at *ca.* 50 °C for about 30 min. The solution was then evaporated to dryness under vacuum. The crude material was washed with diethyl ether, and then dissolved in a little acetonitrile or water. The resulting solution was treated with charcoal, warmed, and filtered. Addition of acetone or diethyl ether (when acetonitrile was the solvent) caused separation of the required complexes as white materials (Table 1).

Literature methods were followed for the preparation of $[Pt(en)(tmen)]Cl_2$,[2] $[Pt(NH_2Et)_4][ClO_4]_2$,[3] and $[Pt(NH_2Pr^n)_4]Cl_2{\cdot}2H_2O$.[4]

Disodium hexachloroiridate(IV), $Na_2[IrCl_6]{\cdot}6H_2O$, was reagent grade and used without further purification. Trisodium hexachloroiridate(III), $Na_3[IrCl_6]{\cdot}2H_2O$, was prepared according to a literature method.[5] Sodium chloride and perchlorate were reagent grade and dried before use. Twice distilled water was used as solvent.

Kinetic Measurements.—The reactions were carried out in water at $I = 1.0$ mol dm^{-3} and pH 2.0—3.0, using sodium perchlorate to adjust the ionic strength. The routine procedures for preparing stock solutions of reactants as well as mixtures for kinetic investigation were as described elsewhere.[1] The progress of the reactions was followed spectrophotometrically by scanning the spectrum of the reacting mixture in the 550—400 nm region, where hexachloroiridate(IV) exhibits a molar absorptivity [$\lambda_{max.}$ at 488 nm ($\varepsilon = 4.050 \times 10^3$ dm^3 mol^{-1} cm^{-1})] at least 20 times higher than those of the other reactants or reaction products. Some preliminary spectrophotometric experiments, carried out using an excess of $IrCl_6^{2-}$ and Cl^- over the platinum(II) complexes, showed that the overall absorbance changes observed in this region were fully consistent with a reaction implying the consumption of 1.9 ± 1 mol of hexachloroiridate(IV) per mol of platinum(II) initially present in the mixture. Thus, reactions (1) and (2) are suggested to occur.

$$[Pt(en)L_2]^{2+} + 2IrCl_6^{2-} + 2Cl^- \longrightarrow \textit{trans}\text{-}[PtCl_2(en)L_2]^{2+} + 2IrCl_6^{3-} \quad (1)$$

$$[PtL_4]^{2+} + 2IrCl_6^{2-} + 2Cl^- \longrightarrow \textit{trans}\text{-}[PtCl_2L_4]^{2+} + 2IrCl_6^{3-} \quad (2)$$

The actual composition of the platinum(IV) reaction products is postulated rather than confirmed since their very low absorbances prevent any identification under kinetic conditions. On the other hand their separation from the reacted mixture is very difficult owing to their very high solubility. The assumed structure takes into account the usual behaviour of platinum(II) complexes towards oxidation and is supported by the fact that similar reactions involving $[Pt(en)_2]^{2+}$ or $[Pt(en)(py)_2]^{2+}$ are known to yield *trans*-$[PtCl_2(en)_2]^{2+}$ and *trans*-$[PtCl_2(en)(py)_2]^{2+}$, respectively.[1]

Under kinetic conditions the starting platinum(II) concentrations usually ranged from *ca.* 1.0×10^{-4} to *ca.* 9.0×10^{-4} mol dm^{-3} and were stoicheiometrically always at least 10 times the concentration of hexachloroiridate(IV). The concentration ranges of chloride explored were (*i*) *ca.* 2.0×10^{-4}—5.0×10^{-3} [complexes (**2**) and (**12**)], (*ii*) *ca.* 2.0×10^{-4}—9×10^{-3} [complexes (**1**), (**3**), (**4**), (**7**), and (**15**)], (*iii*) *ca.* 2.0×10^{-4}—2.0×10^{-2} [complexes (**5**), (**8**), (**9**), (**13**), and (**16**)], (*iv*) *ca.* 4.0×10^{-4}—3.5×10^{-2} [complexes (**6**), (**10**), and (**17**)], and (*v*) *ca.* 4.0×10^{-4}—5.0×10^{-2} mol dm^{-3} [complexes (**11**), (**14**), and (**18**)]. The effective concentration ranges were sometimes dictated by the reactivity of the individual platinum(II) complex. In some cases [*i.e.* for some platinum(II) complexes prepared as perchlorates] reactions have been carried out even in the absence of chloride ions. In these cases reactions (1) and (2) should be replaced by similar reactions where water molecules occupy two *trans* sites in the platinum(IV) reaction product. Finally, for oxidations of $[Pt(en)(NH_3)_2]^{2+}$, $[Pt(NH_3)_4]^{2+}$, and $[Pt(en)(dmen)]^{2+}$ some kinetic runs were carried out on mixtures containing initially also variable amounts of hexachloroiridate(III) {1.33×10^{-4}—1.33×10^{-3} for $[Pt(en)(NH_3)_2]^{2+}$ and $[Pt(en)(dmen)]^{2+}$, and 6.89×10^{-5}—7.29×10^{-3} mol dm^{-3} for $[Pt(NH_3)_4]^{2+}$}.

The disappearance of hexachloroiridate(IV) was usually found to obey a pseudo-first-order rate law for at least 50—60% completion of the reaction only when high chloride concentrations are used, otherwise the gradients of plots of log $|A_t - A_\infty|$ *vs.* time smoothly decrease during the progress of the reaction, as a consequence of the inhibiting effect of hexachloroiridate(III) which accumulates in the course of the reaction. Deliberate addition of $IrCl_6^{3-}$ to the reacting mixture causes a lowering of the reaction rate, more marked at lower chloride-ion concentrations [see below; also rate law (4)]. In these cases early-stage pseudo-first-order rate constants, $k_{obs.}$, for the disappearance of $IrCl_6^{2-}$ were obtained from the gradients of plots of log $|A_t - A_\infty|$ *vs.* time corresponding only to the first 20—30% completion of the reaction, where the hexachloroiridate(III) concentration is still low enough to have little effect on the rate.

Results

The early-stage pseudo-first-order rate constant, $k_{obs.}$, for the individual platinum(II) complexes has always been found to depend on the chloride ion and platinum(II) concentrations according to rate law (3) {$[Pt(am)_4]^{2+} = [Pt(en)L_2]^{2+}$ or $[PtL_4]^{2+}$}. The pH (range 2.0—3.0, several reactions were tested also at pH 7) does not appear to affect the rates significantly. The second-order rate constant, k_a, usually contributes little to the early-stage pseudo-first-order rate constant. Moreover, this rate term, but not k_b, is poorly reproducible upon changing the stock of sodium perchlorate so that its value can be assigned only qualitatively. The values of k_b obtained for the complexes examined are reported in Table 2 together with the related activation parameters and with an estimate of k_a.

$$-\frac{d[IrCl_6^{2-}]}{dt} = -2\frac{d[Pt(am)_4^{2+}]}{dt} = k_{obs.}[IrCl_6^{2-}] = 2(k_a + k_b[Cl^-])[Pt(am)_4^{2+}][IrCl_6^{2-}] \quad (3)$$

It has been found (see Experimental section) that the slopes of plots of log $|A_t - A_\infty|$ *vs.* time become progressively flatter as expected if some reaction product lowers the rate. Accordingly, the rates of some reactions [*e.g.* with complexes (**1**), (**13**), and (**15**)] carried out on exhausted reaction mixtures of previous runs were much lower than of related reactions carried out in the absence of reaction products. It was found previously[1] that the rates of similar reactions with $[Pt(en)(py)_2]^{2+}$ are lowered by the addition of $IrCl_6^{3-}$ to the reacting mixture, the effect being more marked when low concentrations of $IrCl_6^{2-}$ and/or Cl^- are used. A similar sort of effect would explain the above mentioned kinetic effect of the reaction products. Therefore, in order to check whether a common rate law holds for the oxidation of all dipositive platinum(II) complexes by hexachloroiridate(IV) ions, series of kinetic runs were carried out with $[Pt(NH_3)_4]^{2+}$, $[Pt(en)(NH_3)_2]^{2+}$, and $[Pt(en)(dmen)]^{2+}$ using various concentrations of $IrCl_6^{2-}$, $IrCl_6^{3-}$, and Cl^-. These experiments showed that the early-stage pseudo-first-

Table 2. Rate constants[a] [equation (3)] and activation parameters[b] for the oxidations of platinum(II) complexes by hexachloroiridate(IV) ions in aqueous perchlorate medium at $I = 1.0$ mol dm^{-3}

Complex	θ_c/°C	k_a/dm^3 mol^{-1} s^{-1}	k_b/dm^6 mol^{-2} s^{-1}	$\Delta H_b^\ddagger$/kJ mol^{-1}	$\Delta S_b^\ddagger$/J K^{-1} mol^{-1}
$[Pt(en)(NH_3)_2]^{2+}$	20.0	<3	1.15×10^4	9.1	−136
	30.0	<4	1.32×10^4		
	40.0	<4	1.56×10^4		
$[Pt(en)(NH_2Me)_2]^{2+}$	20.0	<2	1.36×10^4	8.4	−137
	30.0	<3	1.58×10^4		
	40.0	<3	1.81×10^4		
$[Pt(en)(NH_2Et)_2]^{2+}$	20.0	<0.8	4.65×10^3	7.8	−148
	30.0	<1	5.32×10^3		
	40.0	<1.5	6.10×10^3		
$[Pt(en)(NH_2Pr^n)_2]^{2+}$	20.0	<0.8	5.01×10^3	8.6	−147
	30.0	<1	5.79×10^3		
	40.0	<1.3	6.70×10^3		
$[Pt(en)(NH_2CH_2Bu^t)_2]^{2+}$	20.0	<0.6	3.21×10^3	10.3	−149
	30.0	<0.8	3.83×10^3		
	40.0	<1	4.49×10^3		
$[Pt(en)(NH_2CH_2Ph)_2]^{2+}$	20.0	<0.5	1.38×10^3	10.5	−149
	30.0	<0.5	1.65×10^3		
	40.0	<1	1.94×10^3		
$[Pt(en)(NH_2Bu^n)_2]^{2+}$	20.0	<0.3	3.64×10^3	10.6	−141
	30.0	<0.5	4.32×10^3		
	40.0	<0.5	5.13×10^3		
$[Pt(en)(NH_2C_4H_7)_2]^{2+}$	20.0	<0.5	2.29×10^3	11.2	−142
	30.0	<0.5	2.74×10^3		
	40.0	<0.7	3.28×10^3		
$[Pt(en)(NH_2C_5H_9)_2]^{2+}$	20.0	<0.3	1.07×10^3	12.8	−143
	30.0	<0.5	1.33×10^3		
	40.0	<0.5	1.60×10^3		
$[Pt(en)(NH_2C_6H_{11})_2]^{2+}$	20.0	<0.1	2.29×10^2	19.5	−133
	30.0	<0.2	3.14×10^2		
	40.0	<0.3	4.08×10^2		
$[Pt(en)(4CN\text{-}py)_2]^{2+}$	20.0	<0.2	8.91×10^1	17.8	−147
	30.0	<0.4	1.18×10^2		
	40.0	<0.4	1.52×10^2		
$[Pt(en)(meen)]^{2+}$	20.0	<8	2.39×10^4	2.4	−153
	30.0	<9	2.52×10^4		
	40.0	<9	2.73×10^4		
$[Pt(en)(dmen)]^{2+}$	20.0	<0.5	2.33×10^3	10.8	−144
	30.0	<0.8	2.77×10^3		
	40.0	<1	3.30×10^3		
$[Pt(en)(tmen)]^{2+}$	20.0	$<6 \times 10^{-2}$	4.50×10^1	19.7	−146
	30.0	$<7 \times 10^{-2}$	6.31×10^1		
	40.0	$<8 \times 10^{-2}$	8.05×10^1		
$[Pt(NH_3)_4]^{2+}$	20.0	<2.5	4.93×10^3	12.9	−130
	30.0	<3.5	6.14×10^3		
	40.0	<4.5	7.39×10^3		
$[Pt(NH_2Me)_4]^{2+}$	20.0	<0.2	3.63×10^3	12.3	−135
	30.0	<0.3	4.43×10^3		
	40.0	<0.4	5.35×10^3		
$[Pt(NH_2Et)_4]^{2+}$	20.0	<0.1	4.50×10^2	15.2	−142
	30.0	<0.15	5.66×10^2		
	40.0	<0.15	7.16×10^2		
$[Pt(NH_2Pr^n)_4]^{2+}$	20.0	$<3 \times 10^{-2}$	2.43×10^2	17.3	−140
	30.0	$<5 \times 10^{-2}$	3.19×10^2		
	40.0	$<5 \times 10^{-2}$	4.08×10^2		

[a] The coefficients of variation for k_b are within ±2 and ±3%. [b] Estimated errors (from average errors in rate constants) for $\Delta H_b^\ddagger$ and $\Delta S_b^\ddagger$ are within ±2 and ±3 kJ mol^{-1} and ±7 and ±10 J K^{-1} mol^{-1}, respectively.

order rate constant, $k_{obs.}$, decreases with increasing hexachloroiridate(III) concentration, more markedly when low concentrations of hexachloroiridate(IV) and/or chloride ions are used. If the usually slight contribution to the rate due to the k_a rate term is neglected, the results obtained are consistent with rate law (4),* previously found to hold[1] for the oxidation of $[Pt(en)(py)_2]^{2+}$.

$$-\frac{d[IrCl_6{}^{2-}]}{dt} = \frac{2k_b[IrCl_6{}^{2-}]^2[Pt(am)_4{}^{2+}][Cl^-]^2}{k_d[IrCl_6{}^{3-}] + [IrCl_6{}^{2-}][Cl^-]} \quad (4)$$

Discussion

The disappearance of hexachloroiridate(IV) arises mainly from a reduction path whose rate is dependent on the chloride-ion concentration (k_b rate term). Therefore, the following discussion will centre on this path.

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* The addition of the rate term $2k_a[IrCl_6{}^{2-}]^2[Pt(am)_4{}^{2+}]/(k[IrCl_6{}^{3-}] + [IrCl_6{}^{2-}])$ would satisfactorily account also for the kinetic effect experienced by hexachloroiridate(III) on the reaction step independent of chloride ions.

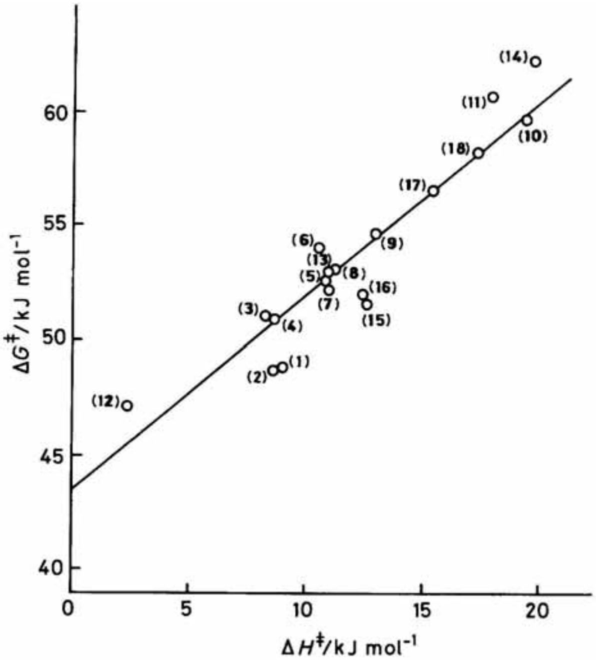

Figure 1. Correlation between the free energy of activation ($\Delta G^{\ddagger}$) and the enthalpy of activation ($\Delta H^{\ddagger}$) for reactions (1) or (2). For complex numbering see Table 1

Rate law (4), as well as the k_b term of rate law (3), is consistent with mechanism (5)* ($k_b = k_1K_1$), previously inferred[1] for the oxidation of $[Pt(en)(py)_2]^{2+}$ and $[Pt(en)_2]^{2+}$ by hexachloroiridate(IV).

$$[Pt(am)_4]^{2+} + Cl^- \xrightleftharpoons{K_1} [PtCl(am)_4]^+ \quad (5a)$$

$$[PtCl(am)_4]^+ + IrCl_6^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [PtCl(am)_4]^{2+} + IrCl_6^{3-} \quad (5b)$$

$$[PtCl(am)_4]^{2+} + Cl^- + IrCl_6^{2-} \xrightarrow{k_2'} trans\text{-}[PtCl_2(am)_4]^{2+} + IrCl_6^{3-} \quad (5c)$$

$$-\frac{d[IrCl_6^{2-}]}{dt} = \frac{2k_1K_1[IrCl_6^{2-}]^2[Pt(am)_4^{2+}][Cl^-]^2}{(k_{-1}/k_2')[IrCl_6^{3-}] + [IrCl_6^{2-}][Cl^-]} \quad (6)$$

The results obtained (Table 2) show that the reactivity of platinum(II) complexes is strongly dependent on the co-ordinated ligands, changes in the enthalpy of activation being the most important factor, as shown by a plot of $\Delta G^{\ddagger}$ *vs.* $\Delta H^{\ddagger}$ (Figure 1) which is linear with a slope of *ca.* 1 (*i.e.* 0.88).

By focusing attention on the four in-plane ligands it appears that reactivity changes of platinum(II) complexes towards oxidation by $IrCl_6^{2-}$ are little dependent on the basicity of such ligands. The complexes $[Pt(en)(4CN\text{-}py)_2]^{2+}$ and $[Pt(en)(py)_2]^{2+}$ (k_b at 20 °C = 57 $dm^6 mol^{-2} s^{-1}$)[1] display very similar reactivity though the basicity of the pyridines linked to platinum(II) differs by more than 3 pK units [pK_a at 25 °C = 5.23 (py)[6] and 1.7—1.9 (4CN-py, estimated)[7,8]]. The variable reactivity of the investigated platinum(II) complexes can be ascribed to steric hindrance restrictions. Thus, the replacement of N-bonded hydrogen atoms by up to four methyl groups in one chelate ligand of bis(ethylenediamine) complexes entails a reactivity lowering of related complexes of up to *ca.* 620 times {k_b for $[Pt(en)_2]^{2+}$ at 20 °C = 2.81×10^4 $dm^6 mol^{-2} s^{-1}$},[1] even though only moderate basicity changes are occurring in the ligands [pK_{a1}, pK_{a2} at 25 °C = 6.84 and 9.93 (en); 5.58 and 9.15 (tmen)].[9] Again, the second complex of the pairs $[Pt(en)(NH_2Me)_2]^{2+}$ and $[Pt(en)(NH_2C_6H_{11})_2]^{2+}$ or $[Pt(NH_2Me)_4]^{2+}$ and $[Pt(NH_2Et)_4]^{2+}$ is significantly less reactive than the first (*ca.* 60 and 8 times, respectively), even though the basicity of the primary amines involved is the same (pK_a = 10.64).[6] In previous papers[3,10,11] it was found that the steric hindrance caused by a primary amine, NH_2R, on platinum(II) can be satisfactorily quantified by the negative value of a steric constant, E_N, which is assumed to coincide with Taft's steric constant, E_s, of the related CH_2R group.[12,†] Moreover,[11] I found that, at least for the oxidation of some platinum(II) complexes by the two-electron oxidant *trans*-$[PtCl_4(NH_3)_2]$, the sum of the negative values of the four in-plane groups, $\Sigma(-E_N)$, can be taken as a measure of the overall steric hindrance surrounding platinum(II). If this is true also for the oxidation of platinum(II) complexes by the one-electron oxidant $IrCl_6^{2-}$, a relationship of type (7) would correlate the reactivity with the steric hindrance.

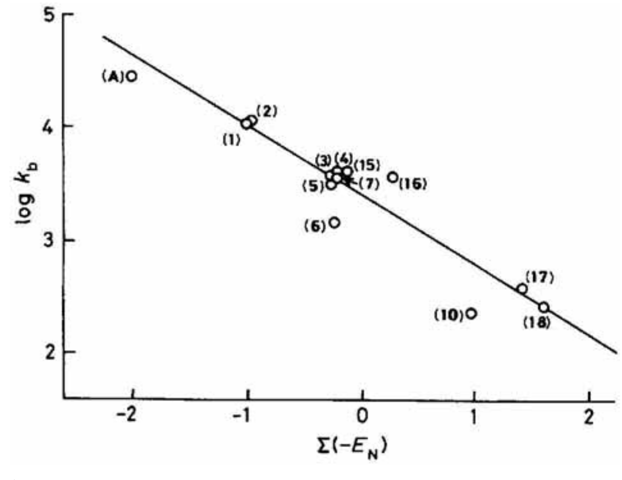

Figure 2. Effect of the overall steric hindrance [$\Sigma(-E_N)$] of co-ordinated ligands on the reactivity of platinum(II) complexes (log k_b at 20 °C) towards oxidation by hexachloroiridate(IV) [reactions (1) or (2)]. For complex numbering see Table 1; (A) = $[Pt(en)_2]^{2+}$, from ref. 1

$$\log k_b = \alpha + \rho_s[\Sigma(-E_N)] \quad (7)$$

Data available for E_N‡ allow such a relationship to be tested for thirteen complexes {*i.e.* (**1**)—(**7**), (**10**), (**15**)—(**18**), and $[Pt(en)_2]^{2+}$}. A rough consistency (α = 3.4, ρ_s = −0.62) seems to be suggested by the results in Figure 2. Though the relationship is not entirely satisfactory, the trend appears to be unequivocable. On the other hand, a better fit of the data is hardly expected in view of the fact that idealizations are introduced§ and any other factors are neglected [*e.g.* (*i*)

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* Parallel oxidative reaction paths involving $[Pt(am)_4]^{2+}$ instead of $[PtCl(am)_4]^+$ could account also for the k_a term of rate law (3), provided that this is a true reaction path independent of chloride.

† Negative values of E_N are better used since E_s values, and therefore E_N, decrease with increasing steric hindrance.

‡ E_N (from E_s values)[13] = 0.00 (NH_3), −0.07 (NH_2Me), −0.36 (NH_2Et), −0.39 (NH_2Pr^n), −0.34 ($NH_2CH_2Bu^t$), −0.38 (NH_2CH_2Ph), −0.40 (NH_2Bu^n), and −0.98 ($NH_2C_6H_{11}$). A formal estimate of +0.50 for ½ en has been obtained from kinetic data.[3]

§ For example, (*i*) no account is taken of the platinum(II) reaction centre being different both in size and geometric environment from the reaction centre involved in the determination of E_s values and (*ii*) the assumption that steric contributions are purely additive.

solvation effects and (*ii*) the contribution of σ-donor effects of amines on the rates].

The recognition that steric contributions are important in the reactivity of platinum(II) complexes towards oxidation allows us to explain the observed reactivity trend of both (*i*) N-substituted bis(ethylenediamine) complexes (*i.e.* en ~ meen > dmen > tmen) and (*ii*) complexes containing primary amines bearing cyclic R groups (*i.e.* $NH_2C_4H_7 > NH_2C_5H_9 > NH_2C_6H_{11}$). In the first group of complexes platinum(II) is progressively more hindered by the increasing number of methyl groups in its proximity. In the second group of complexes, the presence of a progressively bulker cyclic R group linked to the co-ordinated nitrogen would increasingly make more difficult an attack on the central metal atom.

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