Kinetic Studies on the Oxidation of Ethylenediaminebis(pyridine)- and Bis(ethylenediamine)-platinum(II) Complexes by Hexachloroiridate(IV)

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The oxidation reactions of $[Pt(en)L_2]^{2+}$ [L = $\frac{1}{2}$ ethylenediamine (en) or pyridine (py)] by $IrCl_6^{2-}$ in the presence of chloride ions have been kinetically investigated in aqueous solution. In the absence of added $IrCl_6^{3-}$ the reactions obey the rate law: $-d[IrCl_6^{2-}]/dt = 2\,(k_a + k_b[Cl^-])[Pt(en)L_2^{2+}][IrCl_6^{2-}]$; a further rate term, second order in $[Cl^-]$, operates at high chloride concentrations. Hexachloroiridate(III) lowers the rates and its kinetic effect increases at lower $IrCl_6^{2-}$ and/or Cl^- concentrations. A consistent reaction mechanism is proposed. The complex $[Pt(en)_2]^{2+}$ reacts much faster than $[Pt(en)(py)_2]^{2+}$, *e.g.* at 20 °C k_b/dm^6 mol^{-2} s^{-1} = 2.81×10^4 (L = $\frac{1}{2}$ en) or 5.7×10^1 (L = py), owing to a very favourable activation enthalpy [$\Delta H^{\ddagger}$/kJ mol^{-1} = 2.0 (L = $\frac{1}{2}$ en) or 26.2 (L = py)]. The kinetic and thermodynamic tendencies towards the oxidation of such complexes appear to be correlated.

The most extensively studied oxidation reactions of platinum(II) complexes involve two-electron oxidizing agents which are believed to operate through inner-sphere atom-transfer mechanisms.[1-3] Conversely, studies of the mechanisms of non-complementary oxidations, involving one-electron oxidizing agents, appear to be far less advanced.[4-7]

This paper reports the results of a kinetic investigation on the oxidation of $[Pt(en)_2]^{2+}$ and $[Pt(en)(py)_2]^{2+}$ (en = ethylenediamine, py = pyridine) by $IrCl_6^{2-}$ in aqueous solution and in the presence of chloride ions.

Experimental

Materials.—Bis(ethylenediamine)platinum(II) dichloride, $[Pt(en)_2]Cl_2$, was prepared by a literature method[8] {Found: C, 12.4; H, 4.1; N, 14.4. Calc. for $[Pt(en)_2]Cl_2$: C, 12.4; H, 4.2; N, 14.5%}. Ethylenediaminebis(pyridine)platinum(II) diperchlorate, $[Pt(en)(py)_2][ClO_4]_2$, was prepared by heating an aqueous suspension of $[PtCl_2(en)]$ (1 g in 50 cm^3) with the equivalent amount of $Ag[ClO_4]$. The reaction mixture was stirred in the dark at 60 °C for 1 h. After cooling, it was filtered and treated with charcoal. The filtered solution was evaporated to *ca.* 10 cm^3 and an excess of pyridine (4:1) was added at 50 °C. The mixture was then evaporated almost to dryness. The colourless material obtained was dissolved in methanol. Subsequent addition of diethyl ether resulted in the separation of the required compound in the form of colourless microcrystals {Found: C, 23.5; H, 3.0; N, 9.1. Calc. for $[Pt(en)(py)_2][ClO_4]_2$: C, 23.5; H, 3.0; N, 9.2%}. The related platinum(IV) complexes, $[PtCl_2(en)_2]Cl_2$ and $[PtCl_2(en)(py)_2]Cl_2$, were prepared by chlorination of the related platinum(II) dichloride complexes, following previously described procedures.[9]

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 by a literature method.[10] Sodium chloride and perchlorate were reagent grade, dried before use. Twice distilled water was used.

Kinetic Measurements.—The reactions were carried out in water at I = 1.00 mol dm^{-3} and pH 3.0, using sodium perchlorate to adjust the ionic strength. A 1-cm silica cell maintained in the thermostatted cell compartment of a UV-VIS Lambda 5 Perkin-Elmer spectrophotometer was used as a reaction vessel. Stock solutions of the reactants were prepared by weight. Those of hexachloroiridate-(III) and -(IV) were standardized spectrophotometrically.[10] The progress of slow reactions was followed by scanning at suitable time intervals the absorption spectrum of the reacting mixture in the 550—400 nm region, where hexachloroiridate(IV) exhibits an absorbance ($\lambda_{max.}$ 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. Fast reactions were followed at a constant wavelength (488 nm) by means of conventional or stopped-flow techniques. The concentration ranges explored for the reactions of $[Pt(en)(py)_2]^{2+}$ carried out without added $IrCl_6^{3-}$ were: (*i*) $IrCl_6^{2-}$, 1.99×10^{-5}—7.00×10^{-5}; (*ii*) $[Pt(en)(py)_2]^{2+}$, 1.80×10^{-4}—2.49×10^{-3}; (*iii*) Cl^-, 1.00×10^{-3}—6.67×10^{-1} mol dm^{-3}. For the reactions of $[Pt(en)_2]^{2+}$ the concentration ranges explored were: (*i*) $IrCl_6^{2-}$, 1.56×10^{-5}—3.64×10^{-5}; (*ii*) $[Pt(en)_2]^{2+}$, 1.13×10^{-4}—3.39×10^{-4}; (*iii*) Cl^-, 2.26×10^{-4}—8.54×10^{-3} and 5.00×10^{-2}—4.00×10^{-1} mol dm^{-3}. Whenever possible, the concentration of the platinum(II) complexes was at least eight times higher than that of hexachloroiridate(IV). At least 30 kinetic runs (40 for the reactions studied at 20 °C) were carried out for the reactions of each platinum(II) complex, at each temperature, using various concentrations of iridium(IV), platinum(II), and chloride ions. The concentration ranges explored for the reactions of $[Pt(en)(py)_2]^{2+}$ (3.00×10^{-4} mol dm^{-3}) carried out in the presence of added $IrCl_6^{3-}$ were: (*i*) $IrCl_6^{2-}$, 1.99×10^{-5}—7.98×10^{-5}; (*ii*) $IrCl_6^{3-}$, 3.34×10^{-4}—4.67×10^{-3}; (*iii*) Cl^-, 6.67×10^{-3}—6.67×10^{-2} mol dm^{-3}. More than 40 kinetic runs were carried out, using various concentrations of iridium-(III) and -(IV) and chloride ions. In these experiments the concentration of $[Pt(en)(py)_2]^{2+}$ was maintained rather low (3.00×10^{-4} mol dm^{-3}) in order to avoid separation of violet microcrystals, likely $[Pt(en)(py)_2][IrCl_6]$, when the highest concentration of hexachloroiridate(IV) was used. Therefore, in these cases pseudo-first-order conditions were not fulfilled and only the first 10—30% of the progress of the reaction was taken into account for an evaluation of the early stage pseudo-first-order rate constant, $k_{obs.}$.

As a general procedure, only the first 20—30% of the progress of the reaction was considered for the evaluation of the early stage pseudo-first-order rate constant, $k_{obs.}$, since the gradient of log $|A_t - A_\infty|$ *vs.* time plots smoothly decreases during the course of the reaction, particularly when low concentrations of chloride ions are used, as a consequence of the particular rate law operating (see Results section).

Stoicheiometry of the Reactions.—The reactions carried out in the presence of chloride ions under kinetic conditions lead to

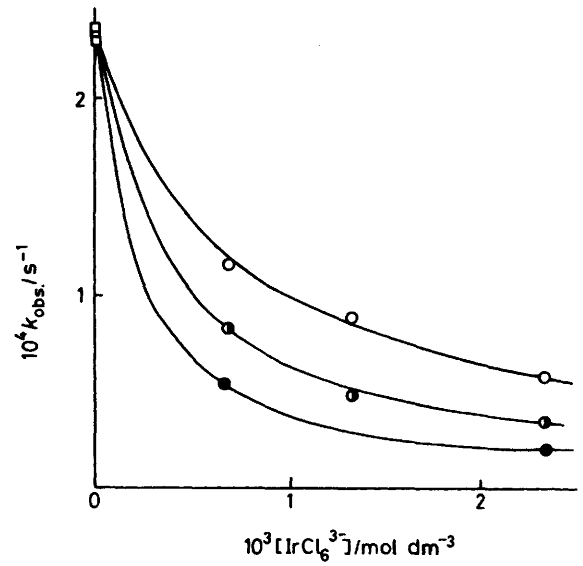

Figure 1. Effect of $[IrCl_6^{3-}]$ on the rates of the oxidation of $[Pt(en)(py)_2]^{2+}$ (3.00×10^{-4} mol dm^{-3}) by $IrCl_6^{2-}$ [1.99×10^{-5} (●), 3.99×10^{-5} (◑), or 7.98×10^{-5} mol dm^{-3} (○)] at 20 °C in water (I = 1.0 mol dm^{-3}, pH 3.0) and in the presence of 6.67×10^{-3} mol dm^{-3} chloride ions

quantitative disappearance of $IrCl_6^{2-}$. Conversely, some reactions carried out using an excess of $IrCl_6^{2-}$ (5.6×10^{-4} mol dm^{-3}) over platinum(II) complexes (6.00×10^{-5}—1.50×10^{-4} mol dm^{-3}) showed that the reactions progress to the consumption of 1.9 ± 0.1 mol of $IrCl_6^{2-}$ per mol of platinum(II) initially present in the reacting mixture. The reaction products could not be recognized using the concentrations employed for kinetic purposes, due to their very low absorbances. However, reliable information could be obtained from the spectrophotometric behaviour of reacting mixtures of $[Pt(en)(py)_2]^{2+}$ (1.0×10^{-3} mol dm^{-3}) and $IrCl_6^{2-}$ (2.0×10^{-3} mol dm^{-3}) and an excess of Cl^- in the 380—320 nm region. Two isosbestic points (360 and 328 nm) were found to occur and persist almost to the end of the reaction, when seemingly colourless microcrystals begin to separate. The wavelengths where the isosbestic points occur, together with the stoicheiometry found for the reactants, are consistent with the occurrence of reaction (1). A similar reaction (2) is inferred for the oxidation of $[Pt(en)_2]^{2+}$

$$[Pt(en)(py)_2]^{2+} + 2\,IrCl_6^{2-} + 2\,Cl^- \longrightarrow \textit{trans-}[PtCl_2(en)(py)_2]^{2+} + 2\,IrCl_6^{3-} \quad (1)$$

$$[Pt(en)_2]^{2+} + 2\,IrCl_6^{2-} + 2\,Cl^- \longrightarrow \textit{trans-}[PtCl_2(en)_2]^{2+} + 2\,IrCl_6^{3-} \quad (2)$$

Results

Oxidation Reactions carried out without Addition of $IrCl_6^{3-}$. —The early stage pseudo-first-order rate constants, $k_{obs.}$, for reactions carried out in the presence of an excess of the platinum(II) complex and at chloride-ion concentrations lower than *ca.* 5×10^{-2} mol dm^{-3} are consistent with relationship (3b). The second-order rate term, k_a, is rather small {for $[Pt(en)_2]^{2+}$: 24 (20), 25 (30), and 26 dm^3 mol^{-1} s^{-1} (40 °C); for $[Pt(en)(py)_2]^{2+}$: 3.0×10^{-2} (20), 4×10^{-2} (30), and 5×10^{-2} dm^3 mol^{-1} s^{-1} (40 °C)} and its values, obtained by an extrapolation method, are therefore not very accurate, in particular for the reactions of $[Pt(en)(py)_2]^{2+}$ (±15%). The values of the third-order rate term, k_b (±3%), and the related activation parameters for the two complexes are: (*i*) $[Pt(en)_2]^{2+}$, $k_b = 2.81 \times 10^4$ (20), 3.00×10^4 (30), and 3.16×10^4 dm^6 mol^{-2} s^{-1} (40 °C), $\Delta H^\ddagger = 2.0 \pm 1.5$ kJ mol^{-1}, $\Delta S^\ddagger = -153 \pm 5$ J K^{-1} mol^{-1}; (*ii*) $[Pt(en)(py)_2]^{2+}$, $k_b = 5.70 \times 10^1$ (20), 8.52×10^1 (30), and 1.21×10^2 dm^6 mol^{-2} s^{-1} (40 °C), $\Delta H^\ddagger = 26.2 \pm 1.5$ kJ mol^{-1}, $\Delta S^\ddagger = -122 \pm 5$ J K^{-1} mol^{-1}.

$$-\frac{d[IrCl_6^{2-}]}{dt} = -\frac{2\,d[Pt(en)L_2^{2+}]}{dt} = k_{obs.}[IrCl_6^{2-}] \quad (3a)$$

$$k_{obs.} = 2\,(k_a + k_b[Cl^-])[Pt(en)L_2^{2+}] \quad (3b)$$

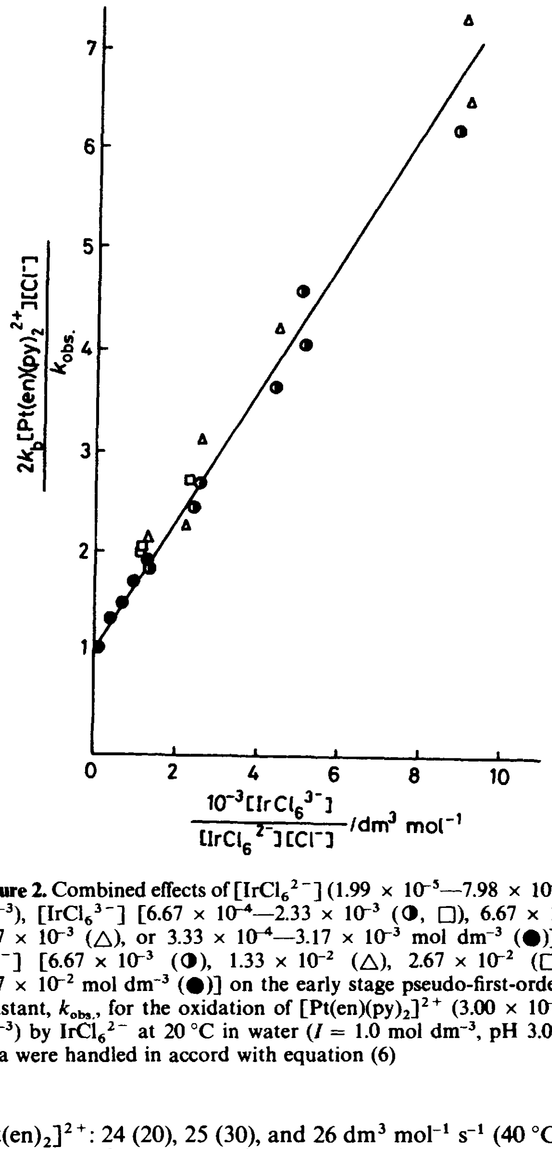

Figure 2. Combined effects of $[IrCl_6^{2-}]$ (1.99×10^{-5}—7.98×10^{-5} mol dm^{-3}), $[IrCl_6^{3-}]$ [6.67×10^{-4}—2.33×10^{-3} (◑, □), 6.67×10^{-4}—4.67×10^{-3} (△), or 3.33×10^{-4}—3.17×10^{-3} mol dm^{-3} (●)], and $[Cl^-]$ [6.67×10^{-3} (◑), 1.33×10^{-2} (△), 2.67×10^{-2} (□), or 6.67×10^{-2} mol dm^{-3} (●)] on the early stage pseudo-first-order rate constant, $k_{obs.}$, for the oxidation of $[Pt(en)(py)_2]^{2+}$ (3.00×10^{-4} mol dm^{-3}) by $IrCl_6^{2-}$ at 20 °C in water (I = 1.0 mol dm^{-3}, pH 3.0). The data were handled in accord with equation (6)

A series of kinetic runs on the oxidation of $[Pt(en)(py)_2]^{2+}$, carried out at 20 °C using chloride-ion concentrations up to 6.67×10^{-1} mol dm^{-3}, showed a rate term of higher order in $[Cl^-]$ when relatively high chloride-ion concentrations are used. Under these conditions the kinetic results are consistent with an early stage $k_{obs.}$ expressed by equation (4), with k_c =

$$k_{obs.} = 2\,(k_a + k_b[Cl^-] + k_c[Cl^-]^2)[Pt(en)L_2^{2+}] \quad (4)$$

58 ± 4 dm^9 mol^{-3} s^{-1}. Data obtained at 20 °C for very fast reactions of $[Pt(en)_2]^{2+}$ ($[Cl^-] = 5.00 \times 10^{-2}$—$4.00 \times 10^{-1}$ mol dm^{-3}), though less accurate, appear to be also consistent with equation (4) with $k_c = 2.4 \times 10^5$ (±20%) dm^9 mol^{-3} s^{-1}

Oxidation Reactions of $[Pt(en)(py)_2]^{2+}$ *carried out in the Presence of Added* $IrCl_6^{3-}$.—Series of kinetic runs for the oxidation of $[Pt(en)(py)_2]^{2+}$ have been carried out in the presence of added $IrCl_6^{3-}$, using various concentrations of either chloride or hexachloroiridate(IV) ions. It has been found that the addition of $IrCl_6^{3-}$ causes a decrease in rates, whose importance increases at lower starting iridium(IV) concentrations (Figure 1). A kinetic investigation at 20 °C in the range of $[Cl^-] = 6.67 \times 10^{-3}$—$6.67 \times 10^{-2}$ mol dm^{-3}, where the k_b rate term predominates, showed that equation (5) accounts for the dependence of the rate on the concentrations of the single chemical species. The early stage pseudo-first-order rate constant for equation (5) can be rearranged in the form (6), which satisfies the experimental results (Figure 2), with $k_d = (6.5 \pm 0.7) \times 10^{-4}$ mol dm^{-3}.

$$-\frac{d[IrCl_6^{2-}]}{dt} = k_{obs.}[IrCl_6^{2-}] = \frac{2k_b[IrCl_6^{2-}]^2[Pt(en)(py)_2^{2+}][Cl^-]^2}{k_d[IrCl_6^{3-}] + [IrCl_6^{2-}][Cl^-]} \quad (5)$$

$$\frac{2k_b[Pt(en)(py)_2^{2+}][Cl^-]}{k_{obs.}} = 1 + k_d \cdot \frac{[IrCl_6^{3-}]}{[IrCl_6^{2-}][Cl^-]} \quad (6)$$

Discussion

Rate law (5) for the oxidation of $[Pt(en)(py)_2]^{2+}$ is consistent with mechanism (7a)—(7d), with $k_b = k_1K_1$ and $k_d = k_{-1}/k_2K_1'$ [*cf.* rate laws (5) and (8)]. Such a reaction mechanism accounts

$$[Pt(en)L_2]^{2+} + Cl^- \underset{}{\overset{K_1}{\rightleftharpoons}} [PtCl(en)L_2]^+ \quad (7a)$$

$$[PtCl(en)L_2]^+ + IrCl_6^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [PtCl(en)L_2]^{2+} + IrCl_6^{3-} \quad (7b)$$

$$[PtCl(en)L_2]^{2+} + Cl^- \overset{K_1'}{\rightleftharpoons} [PtCl_2(en)L_2]^+ \quad (7c)$$

$$[PtCl_2(en)L_2]^+ + IrCl_6^{2-} \xrightarrow{k_2} [PtCl_2(en)L_2]^{2+} + IrCl_6^{3-} \quad (7d)$$

$$-\frac{d[IrCl_6^{2-}]}{dt} = -\frac{2\,d[Pt(en)L_2^{2+}]}{dt} = \frac{2k_1K_1[IrCl_6^{2-}]^2[Pt(en)L_2^{2+}][Cl^-]^2}{(k_{-1}/k_2K_1')[IrCl_6^{3-}] + [IrCl_6^{2-}][Cl^-]} \quad (8)$$

also for the k_b rate term found in the oxidation reactions of both $[Pt(en)(py)_2]^{2+}$ and $[Pt(en)_2]^{2+}$, carried out in the absence of added $IrCl_6^{3-}$ [equation (3b)].

Parallel oxidative reaction paths, occurring by a mechanism similar to that proposed above, but involving either $[Pt(en)L_2]^{2+}$ itself or a dichloroplatinum(II) adduct (or an ion pair), can also account for the k_a and k_c rate terms, respectively [equations (3) and (4)].

If the third-order rate terms k_b (which are the more reliable data) for $[Pt(en)(py)_2]^{2+}$ and $[Pt(en)_2]^{2+}$ are compared, one finds that the replacement of one en by two pyridines causes a decrease in the rate by a factor of *ca.* 4.9×10^2. In spite of a more favourable entropy of activation for the reaction of $[Pt(en)(py)_2]^{2+}$, $[Pt(en)_2]^{2+}$ reacts more rapidly owing to a very low enthalpy of activation. A tentative explanation of this behaviour can be made by recalling that pyridine is more able than ethylenediamine to stabilize the oxidation state II than IV, as shown by the values of the standard electrochemical potential in 1 mol dm^{-3} NaCl for the couple $[PtCl_2(en)L_2]^{2+} + 2\,e^- \rightleftharpoons [Pt(en)L_2]^{2+} + 2\,Cl^-$, which is 0.579 V for L = ½ en but 0.74 V for L = py.[11] From these data, the replacement of one en by two py leads to an increase of 31 kJ mol^{-1} in the reaction free energy, *vs.* an increase in the activation free energy of 15 kJ mol^{-1}. Although two data are too few for definite conclusions, the above quantities suggest that a relationship of the type $\Delta G^{\ddagger} = \frac{1}{2}\Delta G^{\circ}$ + constant may operate. Free-energy relationships of this kind, with slopes of ½, are now rather common both in outer- and inner-sphere redox processes.[12—15] An interesting feature is that such a relationship correlates the activation free energy for the first one-electron transfer with the reaction free energy, which refers to the overall transfer of two electrons.

A final remark. The kinetic results obtained imply that, apart from at very low chloride-ion concentrations, the oxidation reactions of both platinum(II) complexes studied in this paper occur mainly by reaction steps (related to k_b and k_c) involving chloride ions. Conversely, Halpern and Pribanič,[5] in studying the oxidation of $[Pt(en)_2]^{2+}$ by $IrCl_6^{2-}$ in the range $[Cl^-]$ = 0.1—1 mol dm^{-3}, obtained rate law (9), which is consistent with reaction mechanism (10). Therefore, it appears that the two sets

$$-\frac{d[IrCl_6^{2-}]}{dt} = -\frac{2\,d[Pt(en)_2^{2+}]}{dt} = \frac{2\,k_1'[IrCl_6^{2-}]^2[Pt(en)_2^{2+}][Cl^-]^2}{(k_{-1}'/k_2'')[IrCl_6^{2-}] + [IrCl_6^{2-}][Cl^-]^2} \quad (9)$$

$$[Pt(en)_2]^{2+} + IrCl_6^{2-} \underset{k_{-1'}}{\overset{k^{-1'}}{\rightleftharpoons}} [Pt(en)_2]^{3+} + IrCl_6^{3-} \quad (10a)$$

$$[Pt(en)_2]^{3+} + IrCl_6^{2-} + 2Cl^- \xrightarrow{k_2''} [PtCl_2(en)_2]^{2+} + IrCl_6^{3-} \quad (10b)$$

of data are not in agreement, at least as far as the rate law for the oxidation of $[Pt(en)_2]^{2+}$ in the absence of added $IrCl_6^{3-}$ and the related mechanism are concerned.

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