The $Ru^{II}(OH_2)$–$Ru^{IV}(O)$ Couple in a Ruthenium Complex of 2-(Phenylazo)pyridine: Homogeneous Catalysis of the Oxidation of Water to Dioxygen

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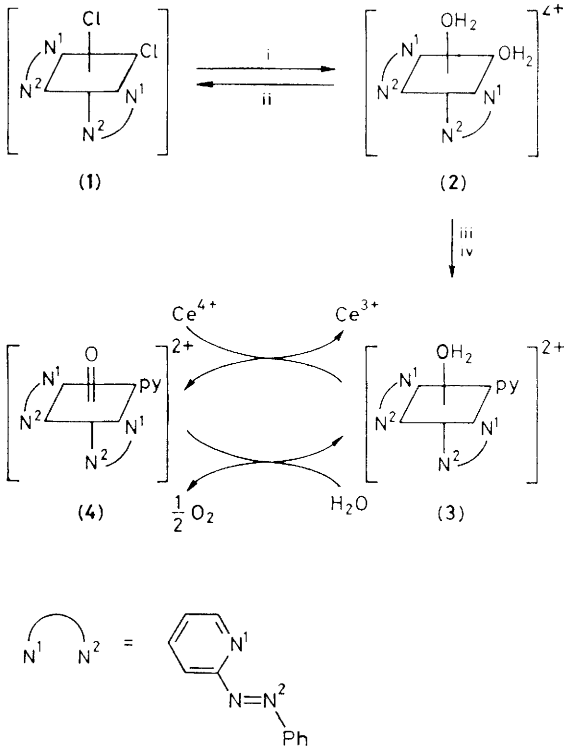
In acidic solution $[Ru^{II}(OH_2)(py)L_2]^{2+}$ can be oxidised to $[Ru^{IV}(O)(py)L_2]^{2+}$ in a single reversible step (E°_{298} = 1.20 V) and the oxidised complex catalyses the dehydrogenation of water to dioxygen in the presence of Ce^{4+} [py = pyridine; L = 2-(phenylazo)pyridine].

The role of aquo- and oxo-complexes of ruthenium as catalysts in oxidation reactions is of current interest.[1] We report herein some reactions of the new complexes (**3**) and (**4**) (Scheme 1) isolated as diperchlorates. The structures of the precursor complexes (**1**)[2] and (**2**)[3] are known.

In acidic aqueous solution (pH 1—4) complex (**3**) displays a cyclic voltammetric response (platinum electrode) near 1 V *vs.* S.C.E. (saturated calomel electrode). This response is characterised by: (a) both anodic and cathodic peak currents indicating a two-electron transfer, (b) a peak-to-peak separation (ΔE_p) of 30 ± 5 mV, and (c) a shift of peak potentials with pH at the rate of about 60 mV per unit change of pH (Figure 1). Clearly the reversible single-step $2e^- + 2H^+$ electrode process (1) is involved. The formal potential (E°_{298}) of the process calculated from equation[4] (2) is 1.20 V *vs.* S.C.E. (E_{pa} and E_{pc} are anodic and cathodic peak potentials respectively). The couple (1) is the first example of its type in ruthenium chemistry. The conversion of (**3**) into (**4**) is conveniently achieved chemically using Ce^{4+} in 1.0 mol dm^{-3} $HClO_4$ or H_2SO_4.

$$(\mathbf{4}) + 2e^- + 2H^+ \rightleftharpoons (\mathbf{3}) \qquad (1)$$

$$E^\circ_{298} = 0.5\,(E_{pa} + E_{pc}) + 0.059\ \text{pH} \qquad (2)$$



Scheme 1. i, Ag^+; ii, Cl^-; iii, pyridine (py); iv, H^+ (all in aqueous solution).

In solution the brown complex (**4**) is reconverted into (**3**). The net reaction is represented by equation (3). The progress of this reaction can be conveniently followed using the intense (ϵ = 11 200 $dm^3\,mol^{-1}\,cm^{-1}$) band of (**3**) at 530 nm; (**4**) has no absorption at this wavelength. The pseudo-first-order rate constant in 1.0 mol dm^{-3} $HClO_4$ at 298 K is $2.5 \times 10^{-3}\,s^{-1}$. When excess of Ce^{4+} is present, the catalytic cycle shown in Scheme 1 becomes operative and virtually all the ruthenium reappears as complex (**3**). On addition of more Ce^{4+} the cycle repeats itself. The progressive accumulation of dioxygen in such solutions is established with the help of the characteristic reduction peak ($O_2 \rightarrow O_2^-$) at −0.3 V. Whether dioxygen is formed directly ($\frac{1}{2}O_2 + 2e^- + 2H^+ \rightleftharpoons H_2O$) or *via* the intermediacy of hydrogen peroxide ($\frac{1}{2}H_2O_2 + e^- + H^+ \rightleftharpoons H_2O$; $\frac{1}{2}O_2 + e^- + H^+ \rightleftharpoons \frac{1}{2}H_2O_2$) is under

$$(\mathbf{4}) + H_2O \rightarrow (\mathbf{3}) + \tfrac{1}{2}O_2 \qquad (3)$$

$[Ru^{II}(OH_2)(py)(bipy)_2]^{2+}$ $[Ru^{IV}(O)(py)(bipy)_2]^{2+}$
(**5**) (**6**)

bipy = 2,2′-bipyridine

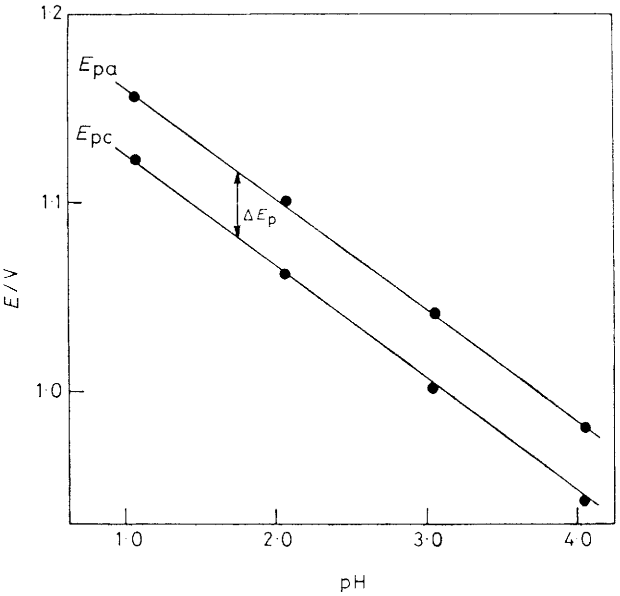


Figure 1. Variation of cyclic voltammetric peak potentials with pH.

investigation. Cerium(IV) is known to oxidise hydrogen peroxide.

A comparison of complexes (**3**) and (**4**) with complexes (**5**) and (**6**) is in order. Complex (**5**) (pK = 10.26)[1] is a weaker acid than (**3**) (pK = 6.8 ± 0.05 at 298 K). The conversion (**5**) → (**6**) occurs[1] in two discrete one-electron transfer steps. The couple (**6**)/(**5**) *fails* to mediate the *catalytic* oxidation of water to dioxygen by Ce^{4+}. The high potential of the couple (1) and its single-step character are believed to be crucial for the facile interfacing of the couple (1) and the water oxidation couple into reaction (3): a prerequisite for the observed catalytic process. The relatively low pK of (**3**) is no doubt a contributing factor in causing the transfer of $2e^- + 2H^+$ to occur in a single step [couple (1)].

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