

The Ru^{II}(OH₂)-Ru^{IV}(O) Couple in a Ruthenium Complex of 2-(Phenylazo)pyridine: Homogeneous Catalysis of the Oxidation of Water to Dioxygen

Sreebrata Goswami, Akhil R. Chakravarty, and Animesh Chakravorty*

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India

In acidic solution [Ru^{II}(OH₂)(py)L₂]²⁺ can be oxidised to [Ru^{IV}(O)(py)L₂]²⁺ in a single reversible step ($E_{298}^{\circ} = 1.20$ V) and the oxidised complex catalyses the dehydrogenation of water to dioxygen in the presence of Ce⁴⁺ [py = pyridine; L = 2-(phenylazo)pyridine].

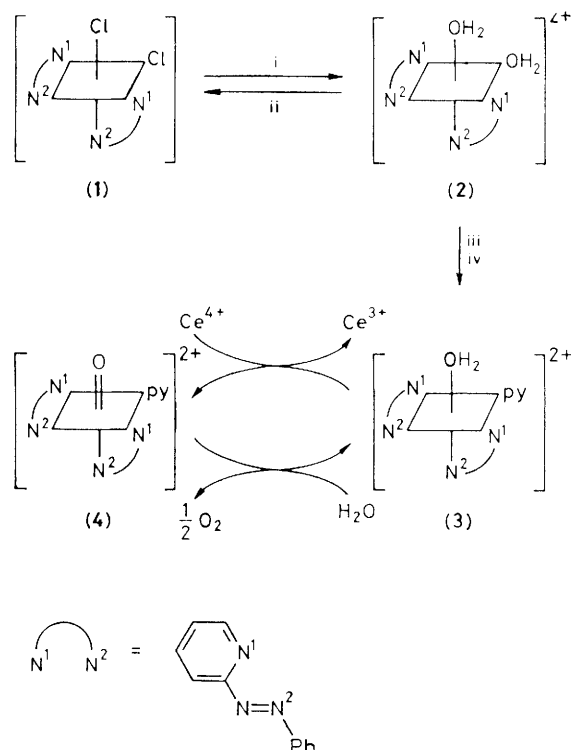
The role of aquo- and oxo-complexes of ruthenium as catalysts in oxidation reactions is of current interest.¹ We report herein some reactions of the new complexes (3) and (4) (Scheme 1) isolated as diperchlorates. The structures of the precursor complexes (1)² and (2)³ are known.

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 equation⁴ (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

$$E_{298}^{\circ} = 0.5(E_{pa} + E_{pc}) + 0.059 \text{ pH} \quad (2)$$



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

in ruthenium chemistry. The conversion of (3) into (4) is conveniently achieved chemically using Ce⁴⁺ in 1.0 mol dm⁻³ HClO₄ or H₂SO₄.

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 ($\epsilon = 11\,200$ dm³ 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 HClO₄ at 298 K is 2.5×10^{-3} s⁻¹. When excess of Ce⁴⁺ is present, the catalytic cycle shown in Scheme 1 becomes operative and virtually all the ruthenium reappears as complex (3). On addition of more Ce⁴⁺ 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

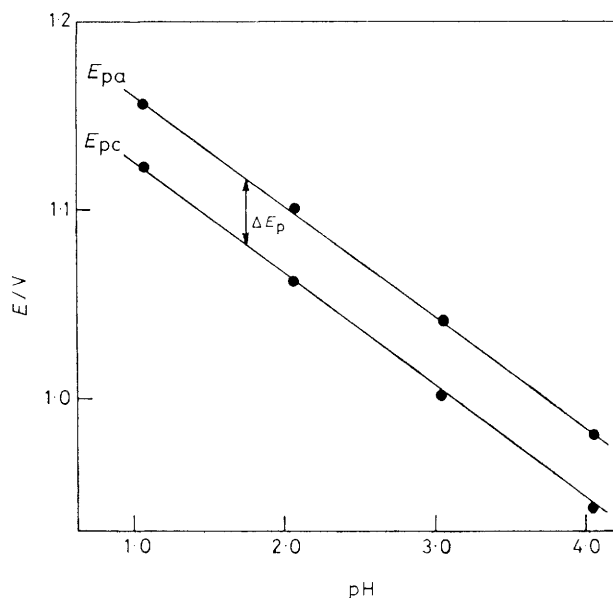


Figure 1. Variation of cyclic voltammetric peak potentials with pH.

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) ($pK = 6.8 \pm 0.05$ at 298 K). The conversion (5) \rightarrow (6) occurs¹ in two discrete one-electron transfer steps. The couple (6)/(5) fails to mediate the catalytic oxidation of water to dioxygen by Ce⁴⁺. 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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