

Ruthenium Dioxide Hydrate, is it a Redox Catalyst?

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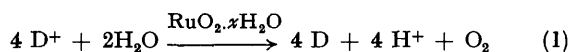
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Summary Ruthenium dioxide hydrate is shown to be a poor redox catalyst for O_2 evolution from Ce^{4+} , unless it is bound to an inert support such as titanium dioxide; this is attributed to the release of RuO_4 into the gas phase which was observed when ruthenium dioxide

hydrate alone was used but not when it was bound to titanium dioxide.

In recent years ruthenium dioxide hydrate ($RuO_2 \cdot xH_2O$) has been used extensively as a redox catalyst to mediate

oxygen production from water.¹ Whether used as a powder^{1a} or colloid^{1b} or bound to some inert material^{1d} such as titanium dioxide (TiO₂), RuO₂.xH₂O is now generally recognised as one of the best catalysts² capable of mediating O₂ evolution from water *via* reaction (1) where



D⁺/D stands for a redox couple whose standard redox potential is more positive than E° (O₂/2H₂O). A major reason for the extensive use of RuO₂.xH₂O lies in its low overpotential and great stability toward Cl₂ and O₂ evolution, when bound to an electrode surface.² A particular importance of such redox catalysts lies in their current use in photochemical systems to split water as one approach to convert and store solar radiation in the form of chemical energy.³ As a cautionary note we describe our work using RuO₂.xH₂O in powder and TiO₂-bound forms as a mediator in reaction (1), using a test system of Ce⁴⁺ in 1N H₂SO₄.

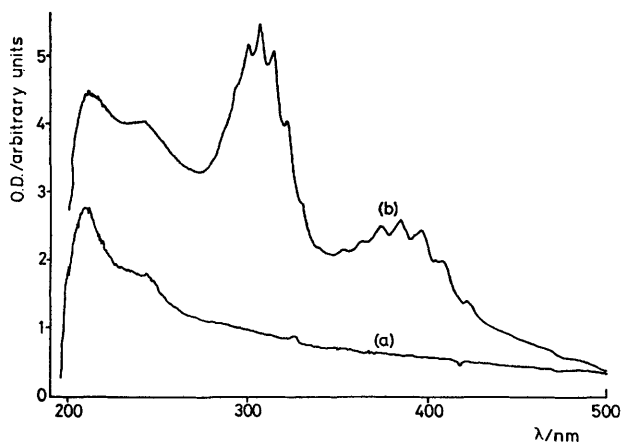
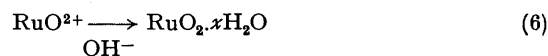
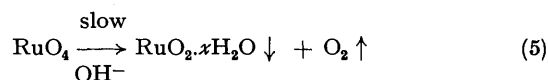
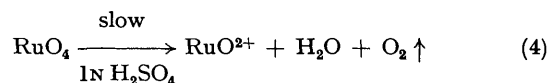
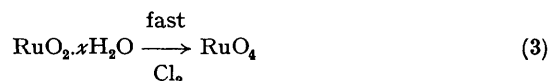
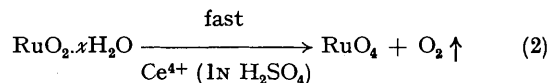


FIGURE. Absorption spectra of the gas phase above a 5 ml solution containing Ce⁴⁺ (1.8 × 10⁻² M) and RuO₂.xH₂O powder (20 mg), (a) immediately after addition of oxide powder, (b) 22 h after addition of oxide powder.

If 5 ml of a sonicated RuO₂.xH₂O (Alpha Inorganics or Aldrich Chemicals) solution (1 mg/ml of 1N H₂SO₄) are added to 250 ml of a 3.5 × 10⁻³ M Ce⁴⁺ solution, the black dioxide 'catalyst' appears to dissolve. Minutes later any organic material introduced above the solution is rapidly blackened. Starch-iodide paper indicated that a strong oxidant was released into the gas phase on addition of the oxide to the Ce⁴⁺ solution. Using a 10 cm quartz cell, the absorption spectrum of this gas phase oxidant was determined (Figure) and found to agree very closely with that of RuO₄.⁴ In addition, RuO₂.xH₂O was oxidised by Cl₂ to RuO₄. Further work showed that RuO₄ (Pierce Inorganics) in 1N H₂SO₄ appears to decay slowly, in the dark, back to the (+IV) state; not to RuO₂.xH₂O, but instead to a brown water-soluble species, identified from its absorption spectrum (λ_{max} 500 nm) as RuO²⁺.⁵ Addition of alkali to this cation results in precipitation of a fine black solid (possibly RuO₂.xH₂O). In neutral or alkaline solution RuO₄ appears to decay slowly to this fine black solid. As

noted by Gorstsema and Cobble,⁶ the rapid drop in Ce⁴⁺ concentration, on addition of some oxide power, corresponded to *ca.* twice the number of equivalents necessary to oxidise the RuO₂.xH₂O to RuO₄. These extra equivalents are believed to oxidise the water bound to the oxide.⁶ From this work we propose the scheme shown in steps (2)–(6).



Further evidence for this scheme came from the use of an excess of Ce⁴⁺. On addition of the RuO₂.xH₂O dispersed in 1N H₂SO₄, the catalyst 'dissolved' and the Ce⁴⁺ concentration (determined spectrophotometrically; λ_{max} 320 nm, ε₃₈₀ 5580) dropped 'instantaneously' to a value which remained constant over a period of 1–2 h but after a period of days the solution had decayed to Ce³⁺ and RuO²⁺ (λ_{max} 500 nm) owing to the cyclic nature of steps (4) and (7).



Some confirmation of the above hypothesis was obtained by passing a continuous stream of N₂ through the solution. Owing to the volatile nature (b.p. 40 °C)⁷ of RuO₄, N₂ should sweep it out; preventing the cyclic steps (4) and (7). Under these conditions there was an instantaneous drop in Ce⁴⁺ concentration on addition of the oxide [step (1)], with no subsequent slow decay of the Ce⁴⁺ [(4) and (7)], which confirmed our expectations. Further work on RuO₄, using an 'Oxygen Electrode' (Rank Brothers, Cambridge),⁸ indicated that steps (4) and (5) were light-catalysed (λ > 400 nm). These results, in particular the loss of RuO₄ to the gas phase, may go some way to explain the irreproducibility found by other workers⁹ using powdered RuO₂.xH₂O as a redox catalyst.

Ruthenium dioxide hydrate appears to act more as a catalyst when it is bound to TiO₂ [8 mg RuO₂.xH₂O/1 g of TiO₂ (B.D.H.)], prepared as outlined by Gratzel *et al.*, using TiO₂ instead of CdS.¹⁰ Little or no evidence was found for RuO₄ in vapour or liquid phases on addition of a 200 mg (in 40 ml of 1N H₂SO₄) sonicated solution to 250 ml of 3.5 × 10⁻³ M Ce⁴⁺, although the concentration decreased rapidly (t_{1/2} *ca.* 0.5 h) in sharp contrast with RuO₂ (2 mg), TiO₂ (200 mg), or Al₂O₃ (200 mg) where t_{1/2} > 100 h.

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