Reactions and Catalytic Properties of Ruthenium Dioxide Hydrate with Aqueous Solutions of Cerium(IV)

By **Andrew Mills,** Davy Faraday Research Laboratory, The Royal Institution, 21 Albemarle Street, London W1X 4BS

The redox catalytic properties of ruthenium dioxide hydrate ($RuO_2 \cdot xH_2O$) were studied using a test system of Ce^{4+} in 0.5 mol dm^{-3} H_2SO_4. In powder form $RuO_2 \cdot xH_2O$ appeared a poor redox catalyst unless bound to an inert support, such as titanium dioxide (TiO_2). This was attributed to the production of ruthenium tetraoxide (RuO_4), which was observed with $RuO_2 \cdot xH_2O$ and a $RuO_2 \cdot xH_2O$–TiO_2 mixture but not with a TiO_2-bound RuO_2 catalyst. In the absence of a catalyst, or when TiO_2 or Al_2O_3 were used, no decay of the Ce^{4+} was observed ($t > 200$ h).

FOR many years considerable effort has been directed towards finding chemical processes which are capable of collecting and storing light energy.[1,2] More recently [3-9] work has focused on the photochemical production of H_2 from water, of which one approach is the combination of a photo-redox process, equation (1) (where S represents

$$S + R \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} S^+ + R^- \qquad (1)$$

the photoactive donor and R the electron acceptor), with the catalytic step, equation (2). In many of the systems

$$R^- + H_2O \xrightarrow{\text{catalyst}} \tfrac{1}{2}H_2 + OH^- + R \qquad (2)$$

developed so far [10] the back-conversion of S^+ into S is achieved using a donor which undergoes irreversible oxidation according to equation (3). Due to the irreversibility of equation (4), such systems are often called 'sacrificial.'

$$D + S^+ \longrightarrow D^+ + S \qquad (3)$$

$$D^+ \longrightarrow \text{permanent products} \qquad (4)$$

Ultimately, however, a practical device must use water as the electron donor as in equation (5). For this

$$4S^+ + 2H_2O \xrightarrow{\text{catalyst}} 4S + O_2 + 4H^+ \qquad (5)$$

reason there is a great deal of work and interest surrounding the study of catalysts capable of O_2 production from equation (5). The difficulties lie in finding a catalyst able to operate, without corrosion, under the very oxidising conditions necessary to oxidise water. In addition, the catalyst must be specific to water oxidation, especially as they are often used in the presence of readily oxidisable organic material, such as dye sensitisers. Such problems are not new and a great deal of electrochemical work has gone into finding suitable anode materials for water oxidation. Interestingly, ruthenium dioxide hydrate ($RuO_2 \cdot xH_2O$) has a low overpotential and great stability toward Cl_2 and O_2 evolution when bound to an electrode surface.[11] In the study of suitable catalysts for equation (5), it is mostly the noble metal oxides [11-18] that have been used with any success and, of these $RuO_2 \cdot xH_2O$ has been used most extensively.[13-18] Indeed, whether it is used as a powder,[13] colloid,[14,15] or bound to some inert material, such as titanium dioxide,[17] $RuO_2 \cdot xH_2O$ is now generally recognised as one of the best catalysts capable of mediating O_2 evolution from water *via* equation (5).

In a previous communication [19] we briefly outlined work on $RuO_2 \cdot xH_2O$, both in powder and TiO_2-bound forms, as a mediator in equation (5) using a test system of Ce^{4+} in 0.5 mol dm^{-3} H_2SO_4. Under these conditions the Ce^{4+} ion is stable, although from its redox potential [$E^0(Ce^{4+}/Ce^{3+}) = +1.44$ V] it should spontaneously liberate O_2 from water. This reaction fails due to kinetic factors [20] and a redox catalyst is required. In this paper I describe, in more detail, this and subsequent work which brings into question the redox catalytical properties of $RuO_2 \cdot xH_2O$ in the presence of strong oxidising agents and offers RuO_2 bound to TiO_2 as an alternative catalyst.

EXPERIMENTAL

Materials.—Samples of $RuO_2 \cdot xH_2O$ from both Aldrich Chemicals and Alpha Inorganics were used. Concentrated volumetric solutions of cerium sulphate were purchased (B.D.H.) and diluted with 0.5 mol dm^{-3} H_2SO_4 as required. Ruthenium tetraoxide and titanium dioxide were obtained from Pierce Inorganics and B.D.H. respectively. The RuO_2–TiO_2 'unbound' catalyst was prepared by thoroughly grinding TiO_2 (1 g) with $RuO_2 \cdot xH_2O$ (8 mg). The TiO_2-bound RuO_2 catalyst was prepared as outlined by Grätzel and co-workers,[21] using TiO_2 in place of CdS. Using *ca.* 10 mg of RuO_4 to 1 g of TiO_2, the final product had a ruthenium content of 5.7 mg/g as determined by atomic absorption.

Methods.—Absorption spectra were recorded on a Perkin-Elmer–Hitachi 200 spectrophotometer. Dissolved oxygen measurements were made on a Clark membrane oxygen electrode purchased from Rank Brothers (Cambridge). A detailed description of the experimental arrangement, sensitivity, and calibration of this instrument is given elsewhere.[22] The Ce^{4+} concentrations were determined by absorption spectroscopy ($\lambda_{max.} = 320$ nm; $\varepsilon_{320} = 5\,580$ dm^3 mol^{-1} cm^{-1}) [23] after filtration through a 0.2 μm disposable filter holder (Schleicher and Schüll) coupled with a 1 cm^3 syringe to remove any powder. This allowed samples (1 cm^3) to be taken free from catalyst, diluted with 0.5 mol dm^{-3} H_2SO_4, and the optical density at 320 nm determined in a 1 cm quartz cell. Analysis of the RuO_2 bound to TiO_2 powder for Ru, using atomic absorption, was performed by Butterworths Ltd. (Teddington). Electron micrographs were recorded at Westfield College, University of London on a AEI 801 transmission electron microscope, with the help of C. Walker.

RESULTS AND DISCUSSION

Previous work by Kiwi and Grätzel [13,14] established $RuO_2{\cdot}xH_2O$ as a suitable redox catalyst to mediate O_2 production from water using the test system of Ce^{4+} in 0.5 mol dm^{-3} H_2SO_4. They reported [14] a rate constant of 0.3 h^{-1} for equation (5), where S^+ represents Ce^{4+}. Unfortunately I have been unable to reproduce these results. Indeed, small amounts of $RuO_2{\cdot}xH_2O$, well dispersed in 0.5 mol dm^{-3} H_2SO_4, on addition to a Ce^{4+} solution appeared to dissolve completely with no concomitant rapid Ce^{4+} decay, the solution remaining stable over several weeks. In an attempt to resolve this situation a more rigorous study was undertaken.

If a sonicated $RuO_2{\cdot}xH_2O$ suspension (5 cm^3) (1 mg cm^{-3} in 0.5 mol dm^{-3} H_2SO_4) is added to 250 cm^3 of a 3.5×10^{-3} mol dm^{-3} Ce^{4+} solution, the black dioxide ' catalyst ' appears to dissolve. Minutes later, any organic material introduced above the solution is rapidly blackened. Further work with starch-iodide paper indicated that a strong oxidant was released into the gas phase upon addition of the oxide to the Ce^{4+} solution. Using a 10 cm quartz cell, the change in optical density of the gas phase above a $RuO_2{\cdot}xH_2O$–Ce^{4+} solution mixture was recorded, at intervals, over a period of 5 h. The results showed conclusively that a substance was indeed released into the gas phase on addition of $RuO_2{\cdot}xH_2O$ to the Ce^{4+} solution and, in addition, the absorption spectrum of this substance could be identified as that of RuO_4 vapour,[24] a very strong oxidant. The vapour could also be condensed onto a cold-finger and the resultant absorption spectrum of the collected solution identified as that of an aqueous RuO_4 solution.[24] Using chlorine as an oxidant, instead of Ce^{4+}, it was found that this too would oxidise $RuO_2{\cdot}xH_2O$ to RuO_4. In contrast, neither Ce^{4+} nor chlorine appeared to oxidise anhydrous RuO_2. The reasons for this are not known.

Further work showed that RuO_4 in 0.5 mol dm^{-3} H_2SO_4 appears to decay slowly in the dark back to the +4 state; not to $RuO_2{\cdot}xH_2O$ but instead to a red-brown water-soluble species, identified from its absorption spectrum ($\lambda_{max.} = 500$ nm) [25] as RuO^{2+}. This cationic species appeared readily oxidisable, using Cl_2 or Ce^{4+}, to RuO_4. Addition of alkali to a RuO^{2+} solution resulted in precipitation of a fine dark brown-green solid which, in contrast with $RuO_2{\cdot}xH_2O$, was soluble on reacidification. The identity of this precipitate is unclear but, if allowed to age, it appears to take on some of the characteristics of $RuO_2{\cdot}xH_2O$ (*e.g.* colour, acid insolubility *etc.*).

In neutral solution, RuO_4 appears to decay over a period of days to a green, water-soluble species (possibly a Ru^{VI} complex) which, on further standing, decays to a fine black solid (probably $RuO_2{\cdot}xH_2O$). In alkaline solution, RuO_4 is reduced (at a rate which is dependent upon OH^- concentration and impurities present) to the perruthenate ion (RuO_4^-). This anionic species ($\lambda_{max.} =$ 385 and 310 nm) [26] is unstable [27] and decomposes to O_2 and the orange ($\lambda_{max.} = 465$ nm) [26] ruthenate ion (RuO_4^{2-}). Both species were identified by absorption spectroscopy. The literature [26,28] is divided on the stability of the RuO_4^{2-} species, but I have found that solutions could be kept for long periods of time ($t > 6$ months) with no decomposition. Here, as with the +7 and +8 oxidation states, the reduction of ruthenium appears to be very sensitive to minute traces of impurities.[26]

In agreement with work by Gortsema and Cobble,[29] the Ce^{4+} concentration dropped rapidly on addition of the oxide powder and this fall in concentration corresponded to more than (up to two times) the number of equivalents necessary to oxidise the $RuO_2{\cdot}xH_2O$ to RuO_4. These extra equivalents are believed to oxidise water bound to the oxide.[29] From this work I propose the qualitative scheme shown in equations (6)—(11).

$$RuO_2{\cdot}xH_2O \xrightarrow[\text{Ce}^{4+}\ (0.5\ \text{mol dm}^{-3}\ \text{H}_2\text{SO}_4)]{\text{fast}} RuO_4 + nO_2\uparrow \quad (6)$$

$$RuO_2{\cdot}xH_2O \xrightarrow[\text{Cl}_2]{\text{fast}} RuO_4 \quad (7)$$

$$RuO_4 \xrightarrow[0.5\ \text{mol dm}^{-3}\ \text{H}_2\text{SO}_4]{\text{slow}} RuO^{2+} + H_2O + O_2 \quad (8)$$

$$RuO_4 \xrightarrow[\text{neutral}]{\text{slow}} \underset{(\text{Ru}^{\text{VI}}\ \text{complex ?})^{27}}{\text{green intermediate}} \xrightarrow{\text{slow}} RuO_2{\cdot}xH_2O \quad (9)$$

$$\begin{tikzcd} RuO_4 \arrow[r, "OH^-"'] & \underset{\text{unstable}}{RuO_4^-} \arrow[r] & RuO_4^{2-} \arrow[d, "\text{if trace impurities present}"] \\ & & RuO_2{\cdot}xH_2O \end{tikzcd} \quad (10)$$

$$RuO_2^{2+} \xrightarrow[\text{Ce}^{4+}\ (0.5\ \text{mol dm}^{-3}\ \text{H}_2\text{SO}_4)\ \text{or Cl}_2]{\text{fast}} RuO_4 \quad (11)$$

The rapid nature of reaction (6) is illustrated in Figure 1 from which we can see that on addition of the dispersed oxide, the Ce^{4+} concentration drops ' instantaneously ' (*i.e.*, within the time taken for the measurement) to an approximately constant value (this variation in Ce^{4+} concentration is repeated when further amounts of oxide are added). If no more oxide is added, the Ce^{4+} con-

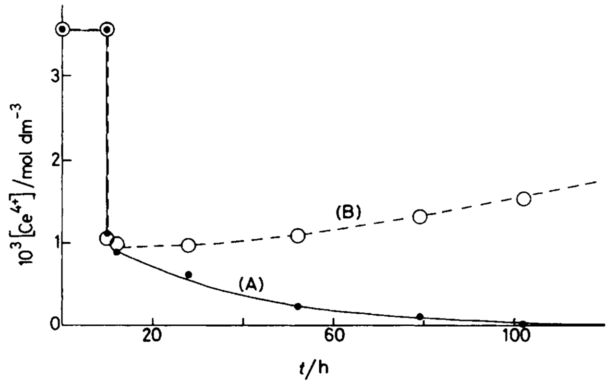

FIGURE 1 Ce^{4+} concentration *versus* time profiles for $RuO_2{\cdot}xH_2O$ (15 mg), dispersed in 0.5 mol dm^{-3} H_2SO_4 (15 cm^3), added (at t = 10 h) to a Ce^{4+} solution (100 cm^3). Curve (A) represents no N_2 purging and (B) represents continuous N_2 purging (causing a slow increase in Ce^{4+} concentration due to solvent evaporation) centration remains constant over 1—2 h but over a period of days the Ce^{4+}–RuO_2 solution mixture decays to Ce^{3+} and RuO^{2+} [Figure 1, curve (A)] owing to the cyclic nature of equations (8) and (11).

Some confirmation of the above hypothesis was obtained by passing a continuous stream of N_2 through the solution. Owing to the volatile nature (b.p. 40 °C)[27] of RuO_4, the N_2 should sweep it out, preventing the cyclic equations (8) and (11). The Ce^{4+} concentration *versus* time profile [Figure 1, curve (B)] was compared with that of an identical system, with no N_2 purging [Figure 1, curve (A)]. Although, in both cases, the Ce^{4+} concentration dropped instantaneously on addition of the oxide, only the non-N_2 purged solution decayed further over the following hours. In contrast there was no subsequent slow decay of the Ce^{4+} concentration in the continuously N_2 purged solution. Further work on RuO_4, using an oxygen-detecting membrane electrode, indicated that equation (8) was light catalysed. For example, a dilute solution of RuO_4 (10^{-4} mol dm^{-3}) in the dark gave a rate of oxygen production of 2×10^{-8} mol dm^{-3} min^{-1} and, upon illumination with a 900 W xenon lamp, the rate increased to 1.6×10^{-7} mol dm^{-3} min^{-1}.

These findings bring into question the suitability of $RuO_2{\cdot}xH_2O$ as a redox catalyst to mediate water oxidation from strong oxidants, such as Ce^{4+}. Also, these results, in particular the loss of RuO_4 to the gas phase, may help to explain the irreproducibility found by other workers using powdered $RuO_2{\cdot}xH_2O$ as a redox catalyst.[30-32] Ruthenium dioxide hydrate appears to act more as a catalyst when bound to TiO_2 (*ca.* 9.5 mg $RuO_2{\cdot}xH_2O$: 1 g TiO_2). In contrast, if approximately the same amount of $RuO_2{\cdot}xH_2O$, as that on the TiO_2-bound RuO_2 catalyst, is added to an identical Ce^{4+} solution, only a slow Ce^{4+} decay is observed. In addition, there is evidence for RuO_4 in both vapour and liquid phases, whereas with the TiO_2-bound RuO_2 catalyst no such evidence for RuO_4 formation is found. The role of TiO_2 in the TiO_2-bound RuO_2 catalyst appears not to be one of simply absorbing the unstable RuO_4. Evidence for this comes from a study of the catalytic properties of an unbound RuO_2 powder. In the presence of Ce^{4+} this unbound catalyst shows many of the features of $RuO_2{\cdot}xH_2O$ alone (see above) and none of those associated with the bound form.

There was no appreciable decrease in Ce^{4+} concentration in the absence of catalyst or when TiO_2 or Al_2O_3 were used. In contrast, the TiO_2-bound RuO_2 powder was found to catalyse the Ce^{4+} to Ce^{3+} decay on the addition of not only one but several further aliquots of Ce^{4+} (Figure 2), although the rate of Ce^{4+} decay appears slower with each addition (this might partly result from the loss of available overpotential for O_2 evolution due to the accumulation of Ce^{3+}). Initial transmission electron micrographs show the TiO_2-bound RuO_2 powder to consist of particles *ca.* 50—100 nm which, in a dispersed solution, form aggregates of *ca.* 600—700 nm. A more detailed study of these particles, using electron microscopy coupled with *X*-ray analysis, is in progress.

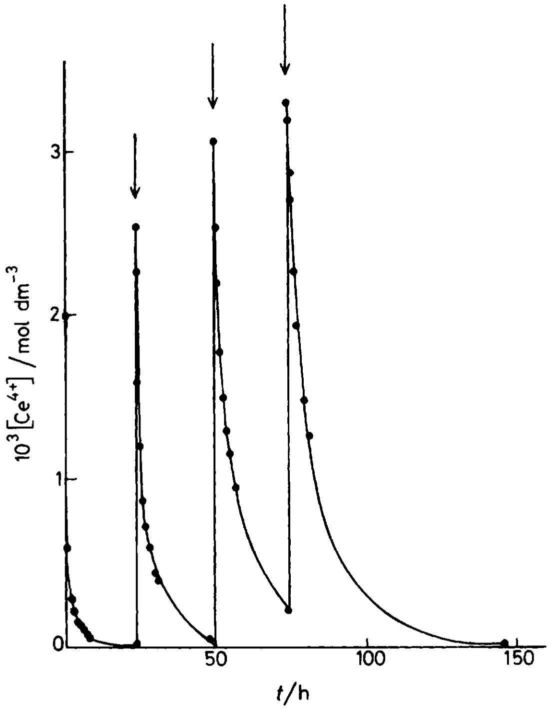

FIGURE 2 Ce^{4+} concentration *versus* time profile on addition (at $t = 0$) of a TiO_2-bound RuO_2 powder (100 mg), dispersed in 0.5 mol dm^{-3} H_2SO_4 (20 cm^3), to a Ce^{4+} solution (80 cm^3). The vertical arrows indicate further additions of Ce^{4+}

Until this and further studies are completed an explanation as to how the TiO_2-bound RuO_2 catalyst works cannot be attempted.

I thank the S.R.C., the E.E.C., and G.E. (Schenectady) for financial support, M. L. Zeeman for her assistance, C. Walker and Westfield College for the electron microscopy, and Professor Sir George Porter, Dr. A. Harriman, and the members of the Davy Faraday Research Laboratory for their help and advice.

[1/1778 *Received, 16th November*, 1981]

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