Ruthenium Dioxide Hydrate: Is it a Hydrogen Catalyst?

Andrew Mills* and Geraint Williams

Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP, Wales, U.K.

$RuO_2 \cdot xH_2O$ needs to be reduced quite substantially before it can function as a hydrogen catalyst; without reduction, $RuO_2 \cdot xH_2O$ is a strong oxidant, capable of oxidising $MV^{+\cdot}$, I^-, Br^-, Cl^-, $Ru(bpy)_3^{2+}$, and $Fe(phen)_3^{2+}$ (bpy = 2,2′-bipyridine and phen = 1,10-phenanthroline).

A great deal of research into solar to chemical energy conversion has been directed towards the development of a photochemical system capable of splitting water into hydrogen and oxygen.[1] In any such system a strong reducing agent (R^-) and oxidising agent (S^+) must be photogenerated and then used to reduce water to hydrogen, *i.e.* equation (1) and oxidise water to oxygen, *i.e.* equation (2) respectively.

$$2R^- + 2H^+ \longrightarrow 2R + H_2 \qquad (1)$$

$$4S^+ + 2H_2O \longrightarrow 4S + 4H^+ + O_2 \qquad (2)$$

Both reactions (1) and (2) require a catalyst which, ideally, is stable and specific.[1] The most commonly used H_2 catalyst, *i.e.* catalyst for reaction (1), is platinum which is often employed in a colloidal form.[1] Unfortunately, platinum is also an excellent hydrogenation catalyst[2—4] and, thus, its use as a H_2 catalyst in photochemical systems for water reduction can lead to low H_2 formation rates and yields if one or more of the components of the photochemical system are readily hydrogenated, as is often the case.[2—4] Recent work by Amouyal and his co-workers[5,6] on the sacrificial photochemical system $Ru(bpy)_3^{2+}/MV^{2+}$/EDTA (MV^{2+} = methylviologen; EDTA = ethylenediaminetetra-acetic acid), appeared to establish that ruthenium dioxide hydrate ($RuO_2 \cdot xH_2O$), like Pt, is capable of mediating efficiently the reduction of water by the photogenerated reduced methylviologen radical ($MV^{+\cdot}$). However, in contrast to Pt, it was also noted by these workers that the $RuO_2 \cdot xH_2O$ does not catalyse the hydrogenation of MV^{2+}. It is worth noting at this point that $MV^{+\cdot}$ is not particularly stable even in the absence of a H_2 catalyst owing to radical-initiated side reactions.[6] Here we describe the results of a series of experiments which lead us to question whether $RuO_2 \cdot xH_2O$, rather than a markedly reduced form, is a H_2 catalyst.

A series of irradiations were carried out using the $Ru(bpy)_3^{2+}/MV^{2+}$/EDTA photochemical system under similar reaction conditions to those employed by Amouyal *et al.*[5,6] Three different materials were used as the H_2 catalyst: two were samples of $RuO_2 \cdot xH_2O$ from different commercial sources (Johnson Matthey and Alfa-Ventron) and the third was a sample of platinised SiO_2. The concentration of dissolved H_2 was monitored as a function of time using a hydrogen membrane polarographic detector (H_2–MPD) set in the base of the irradiation cell, a detailed description of which is given elsewhere.[7]

Curves (A)—(C) in Figure 1 illustrate the observed dissolved hydrogen *vs.* time profiles upon irradiation of the $Ru(bpy)_3^{2+}/MV^{2+}$/EDTA photosystem in the presence of each of the three different 'H_2 catalysts.' From Figure 1 it appears that only with the SiO_2/Pt H_2 catalyst [curve (A)] is the photogeneration of hydrogen prompt. Other work carried out using the same photosystem has shown that hydrogen evolution is also prompt if colloidal Pt is used as a H_2 catalyst.[8]

In contrast to SiO_2/Pt, when $RuO_2 \cdot xH_2O$ is used as a 'H_2 catalyst,' there is always an induction period before hydrogen evolution occurs, regardless of the source of the $RuO_2 \cdot xH_2O$. In addition, it appears that when hydrogen evolution does eventually occur its rate of generation is much lower than that found with the SiO_2/Pt catalyst, *cf.* Figure 1, curves (B) and (C). From the $[H_2]$ *vs.* time profiles illustrated in Figure 1 and other work it appears that the length of the induction period depends directly upon the amount of $RuO_2 \cdot xH_2O$ added and upon the source of the $RuO_2 \cdot xH_2O$. Interestingly, in the course of their studies using $RuO_2 \cdot xH_2O$ as a H_2 catalyst in the $Ru(bpy)_3^{2+}/MV^{2+}$/EDTA photosystem, Amouyal and his co-workers also noted[5] that hydrogen evolved only 'after long induction periods (up to 2 h).' We have found that once a sample of $RuO_2 \cdot xH_2O$ has been used successfully to catalyse the reduction of water to H_2 by photogenerated $MV^{+\cdot}$ radicals, H_2 evolution is then prompt in any subsequent irradiations of the same system, although the rates and yields of hydrogen evolution are always much lower than those for SiO_2/Pt or colloidal Pt.

In a separate set of experiments using reduced MV^{2+} (*i.e.* $MV^{+\cdot}$) in 10^{-2} mol dm^{-3} acetate buffer (pH 4.7) we were able to show that a certain 'threshold' amount of $MV^{+\cdot}$ had to be added before hydrogen evolution occurred. As with the

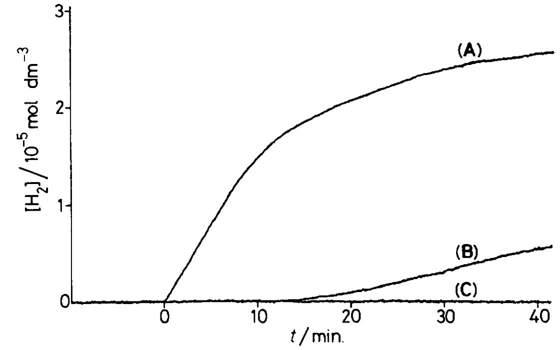

Figure 1. Plot of dissolved hydrogen concentration *vs.* time, upon irradiation, at $t = 0$, of 36 cm^3 of a N$_2$-purged solution containing: Ru(bpy)$_3^{2+}$ (2×10^{-4} mol dm^{-3}), MV^{2+} (10^{-3} mol dm^{-3}), EDTA (0.1 mol dm^{-3}), and the H$_2$ catalyst under test (0.1 g dm^{-3}). The three 'H$_2$ catalysts' used were: (A) SiO$_2$/Pt (0.1% Pt), (B) $RuO_2{\cdot}xH_2O$ (Alfa Inorganics), and (C) $RuO_2{\cdot}xH_2O$ (Johnson Matthey). The irradiation source was a 100 W quartz–iodide lamp coupled with a 330 nm cut-off filter.

Table 1. Number of oxidising equivalents as determined by the 'tri-iodide' system for different samples of $RuO_2{\cdot}xH_2O$ and RuO$_2$.

Sample	% Water content	$10^3 N_{ox}$ per g of sample[a]	N_{ox} per mole of sample[a]
(1) $RuO_2{\cdot}xH_2O$ (Johnson Matthey)	25	2.0	0.35
(2) $RuO_2{\cdot}yH_2O^*$ (thermally activated)[b]	12	3.3	0.50
(3) $RuO_2{\cdot}xH_2O$ (Alfa Inorganics)[c]	19	3.0	0.49
(4) $RuO_2{\cdot}xH_2O$[d]	24	1.0	0.18
(5) Commercial RuO$_2$ (Johnson Matthey)	0	0	0
(6) RuO$_2$[e]	0	0	0

[a] N_{ox} = Number of oxidising equivalents. [b] Prepared by annealing a highly hydrated sample of $RuO_2{\cdot}xH_2O$ (*e.g.* from Johnson Matthey) at 140 °C for 5 h in air. [c] Purchased from the same company as the original $RuO_2{\cdot}xH_2O$ used by Amouyal and his co-workers. [d] Prepared by the alkaline hydrolysis of $RuCl_3{\cdot}nH_2O$. [e] Prepared by annealing $RuCl_3{\cdot}nH_2O$ at 400 °C for 5 h in air and similar to the RuO$_2$ 'H$_2$ catalyst' used by Kleijn and her co-workers.[10,11]

Table 2. Number of oxidising equivalents for $RuO_2{\cdot}yH_2O^*$ determined using different electron acceptors.

Oxidation reaction (reaction medium)	E^0 [a]	$10^3 N_{ox}$[b]	M_{ox}[c]
$2Cl^- - 2e^- \longrightarrow Cl_2$ (2 mol dm^{-3} KCl in 0.5 mol dm^{-3} H$_2$SO$_4$)	1.36	2.4	0.36
$3Br^- - 2e^- \longrightarrow Br_3^-$ (glacial AcOH/MeOH/conc. HCl/KBr)	1.05	2.7	0.41
$3I^- - 2e^- \longrightarrow I_3^-$ (KI/NaOH/potassium hydrogen phthalate)	0.54	3.3	0.50
$Ru(bpy)_3^{2+} - e^- \longrightarrow Ru(bpy)_3^{3+}$ (0.5 mol dm^{-3} H$_2$SO$_4$)	1.29	0.016	0.002
$Fe(phen)_3^{2+} - e^- \longrightarrow Fe(phen)_3^{3+}$ (0.5 mol dm^{-3} H$_2$SO$_4$)	1.06	0.52	0.079
$MV^{+\cdot} - e^- \longrightarrow MV^{2+}$ (acetate buffer)	0.45	>0.6[d]	>0.091[d]

[a] E = Standard redox potential [V *vs.* Normal Hydrogen Electrode (NHE)]. [b] N_{ox} = number of oxidising equivalents per g of $RuO_2{\cdot}yH_2O^*$. [c] M_{ox} = number of oxidising equivalents per mol of $RuO_2{\cdot}yH_2O^*$. [d] Determined for $RuO_2{\cdot}xH_2O$ (not $RuO_2{\cdot}yH_2O^*$).

induction period observed in the photochemical irradiations, this 'threshold' amount of MV$^{+\cdot}$ ($N_{MV^{+\cdot}}$) varied from sample to sample of $RuO_2{\cdot}xH_2O$, *e.g.* $N_{MV^{+\cdot}}$ = *ca.* 6×10^{-4} moles of MV$^{+\cdot}$ per g of $RuO_2{\cdot}xH_2O$ from Johnson Matthey. After this 'threshold' amount of MV$^{+\cdot}$ had been added, hydrogen evolution was then always prompt following any subsequent additions of MV$^{+\cdot}$ although usually much less than stoicheiometric (*ca.* 2—10%). A gradual increase in the stoicheiometry, typically up to 20%, was achieved through repeated injection of additional amounts of MV$^{+\cdot}$. It was also found that, for any sample of $RuO_2{\cdot}xH_2O$, $N_{MV^{+\cdot}}$ could be reduced to zero by bubbling hydrogen through the dispersion for *ca.* 1 h, prior to its use as a hydrogen catalyst. When MV$^{+\cdot}$ was added to commercial anhydrous RuO$_2$ hydrogen evolution was prompt, but slow, *i.e.* $N_{MV^{+\cdot}}$ = 0 mol g^{-1}. When MV$^{+\cdot}$ was added to a dispersion of SiO$_2$/Pt or colloidal Pt hydrogen evolution was not only prompt but also very nearly stoicheiometric.

A measure of the number of oxidising equivalents available from any sample of $RuO_2{\cdot}xH_2O$ was readily obtained by adding 10 mg of the $RuO_2{\cdot}xH_2O$ sample under test to 100 cm^3 of a solution containing KI (0.36 mol dm^{-3}), NaOH (0.025 mol dm^{-3}), and potassium hydrogen phthalate (0.049 mol dm^{-3}). The oxidation of the I$^-$ in the solution to tri-iodide (I$_3^-$) by any sample of $RuO_2{\cdot}xH_2O$ appeared to be complete within 20 min; the concentration of any I$_3^-$ generated was determined spectrophotometrically.[9]

Table 1 lists the number of oxidising equivalents per g and per mole of oxide sample for RuO$_2$ and a series of different samples of $RuO_2{\cdot}xH_2O$, determined using the 'tri-iodide' system described above. Separate experiments using the 'tri-iodide' system showed that the amount of I$_3^-$ generated was proportional to the number of moles of $RuO_2{\cdot}xH_2O$ added. The results in Table 1 suggest that $RuO_2{\cdot}xH_2O$ is able to oxidise I$^-$ to I$_3^-$, regardless of source. In addition the number of oxidising equivalents per mole of $RuO_2{\cdot}xH_2O$ is appreciable, *i.e.* typically > 18%. Previous work carried out by our group on the corrosion of $RuO_2{\cdot}xH_2O$ by Ce^{IV} ions[12] and a separate ESCA study of its surface oxidation states has provided strong evidence that the ruthenium atoms are in the (IV) oxidation state and little evidence of the presence of higher or lower oxidation states of ruthenium.

In a previous paper we established that partial dehydration of $RuO_2{\cdot}xH_2O$ converts the oxide from a poor to a good oxygen catalyst.[13] From the results in Table 1 it appears that this dehydration process also brings about an increase in the number of available oxidising equivalents per mole of oxide. However, this increase in available oxidising equivalents with increasing degree of dehydration peaks between 200 and 300 °C with the result that commercial anhydrous RuO$_2$ does not appear to have any oxidising equivalents available (see Table 1, sample No. 5). This latter finding is in agreement with our previous observation of prompt H$_2$ evolution when RuO$_2$ is added to MV$^{+\cdot}$. Unfortunately RuO$_2$ is also a recognised hydrogenation catalyst.[14]

Other oxidation reactions were attempted using, as the oxidant, the most oxidising of the $RuO_2{\cdot}xH_2O$ samples in Table 1, namely, thermally activated $RuO_2{\cdot}xH_2O$ (*i.e.* $RuO_2{\cdot}yH_2O^*$). The results of this work are summarised in Table 2 along with the redox potentials for the different electron acceptors. In all cases the number of oxidising equivalents was found to depend directly upon the amount of $RuO_2{\cdot}yH_2O^*$ added.

The observed oxidation of $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{3+}$ is of particular interest since $Ru(bpy)_3^{2+}$ is one of the most popular[1] sensitisers used in photochemical systems for water splitting [reactions (1) and (2)] and has often been used in this role in conjunction with $RuO_2{\cdot}xH_2O$, which was initially believed to be a good O_2 catalyst.[15] At the pH chosen for the reaction *i.e.* pH 0, neither $Ru(bpy)_3^{3+}$ or $Fe(phen)_3^{3+}$ are able to oxidise water and, therefore, once formed are stable species. From the results in Table 2 it appears that $RuO_2{\cdot}yH_2O^*$ is able to oxidise Cl^- more efficiently than $Ru(bpy)_3^{2+}$ and $Fe(phen)_3^{2+}$. This surprising result may be because the Cl_2 generated was swept out of the reaction vessel and collected in a tri-iodide trap, whereas with $Ru(bpy)_3^{2+}$ and $Fe(phen)_3^{2+}$, their oxidised forms were allowed to accumulate in the reaction solution.

For the halides Cl^-, Br^-, and I^-, it appears from the results in Table 2 that the higher the oxidation potential of the halide the lower the number of oxidising equivalents available from $RuO_2{\cdot}yH_2O^*$, a trend which is expected from the thermodynamics. Given this trend it is surprising to note from Table 2 that $MV^{+\cdot}$ which is a much better reducing agent than any of the halides, has a low value for N_{ox}. However, the value of N_{ox} for $MV^{+\cdot}$ given in Table 2 is the 'threshold' value and, therefore, very likely to be much less than the true value. This is because, although H_2 evolution occurs once this 'threshold' amount of $MV^{+\cdot}$ has been added, the reaction is very non-stoicheiometric, indicating that further reduction of the $RuO_2{\cdot}xH_2O$ occurs.

In conclusion, there is clear evidence that in aqueous solution $RuO_2{\cdot}xH_2O$ can act as a strong oxidising agent, capable of oxidising $MV^{+\cdot}$ I^-, Br^-, Cl^-, $Ru(bpy)_3^{2+}$, and $Fe(phen)_3^{2+}$. In order to convert it to a good H_2 catalyst a substantial number of moles of reducing equivalents must be added; usually $\geqslant 18\%$ of the number of moles of $RuO_2{\cdot}xH_2O$ present. From these initial results it appears that the $RuO_2{\cdot}xH_2O$ itself is not a H_2 catalyst, but that after some reduction it can be converted into a material with some H_2 catalytic sites. At the present time it is not clear what the nature of the hydrogen catalytic site is on the reduced $RuO_2{\cdot}xH_2O$ and further work is in progress in this direction. From the results of Amouyal and his co-workers[5,6] it would appear that extensive reduction of $RuO_2{\cdot}xH_2O$ eventually produces a catalyst of comparable efficiency to that of Pt, but with the added advantage of a much lower efficiency as a hydrogenation catalyst.

We thank the S.E.R.C. for supporting this work.

Received, 26th August 1988; Com. 8/03470B

References

1 'Energy Resources through Photochemistry and Catalysis', ed. M. Grätzel, Academic Press, New York, 1983.
2 P. Keller, A. Moradpour, E. Amouyal, and H. B. Kagan, *Nouv. J. Chim.* 1980, **4**, 337.
3 O. Johansen, A. Launikonis, J. W. Loder, A. W. H. Mau, W. H. F. Sasse, J. D. Swift, and D. Wells, *Aust. J. Chem.*, 1981, **34**, 981.
4 A. Harriman and G. Porter, *J. Chem. Soc., Faraday Trans. 2,* 1982, **78**, 1937.
5 E. Amouyal, P. Keller, and A. Moradpour, *J. Chem. Soc., Chem. Commun.*, 1980, 1019.
6 E. Amouyal, P. Keller, and A. Moradpour, *J. Chem. Soc., Faraday Trans. 1,* 1982, **78**, 3331.
7 A. Mills, A. Harriman, and G. Porter, *Anal. Chem.*, 1981, **53**, 1254.
8 A. Mills and A. Harriman, *J. Chem. Soc., Faraday Trans. 2,* 1981, **77**, 2111.
9 A. Mills and A. Cook, *Analyst (London)*, 1987, **112**, 1289.
10 M. Kleijn and J. Lyklema, *Colloid Polym. Sci.*, 1987, **265**, 1105.
11 M. Kleijn, E. Rouwendal, H. P. Van Leeuwen, and J. Lyklema, *J. Photochem. Photobiol.*, 1988, **44**, 29.
12 A. Mills, S. Giddings, I. Patel, and C. Lawrence, *J. Chem. Soc., Faraday Trans. 1,* 1987, **83**, 2331.
13 A. Mills, S. Giddings, and I. Patel, *J. Chem. Soc., Faraday Trans. 1,* 1987, **83**, 2317.
14 Y. Tagaki, *Sci. Pap. Inst. Phys. Chem. Res. (Jpn.)*, 1963, **57**, 210.
15 J. Kiwi, K. Kalyanasundaram, and M. Grätzel, *Chimia*, 1979, **33**, 289.