Light-induced Hydrogen Generation from Water catalysed by Ruthenium Dioxide

By EDMOND AMOUYAL,*[a] PATRICK KELLER,[b] and ALEC MORADPOUR[b]
([a]*Laboratoire des Processus Photophysiques et Photochimiques, Bat 350 and* [b] *Laboratoire de Physique des Solides, Université Paris-Sud,* 91405 *Orsay, France*)

Summary Ruthenium dioxide, which is known to be a catalyst for the oxidation of water to oxygen, has been observed to mediate hydrogen formation from water in a model system containing Ru(2,2′-bipyridyl)$_3^{2+}$, methyl viologen, and ethylenediaminetetra-acetic acid with higher efficiency above pH = 5 than that previously observed with colloidal platinum as catalyst

THERE is an increasing interest in the development of highly active redox catalysts required as components of a photochemical water-splitting system Several heterogeneous catalysts mediating light-induced hydrogen formation (PtO_2,[1–3] colloidal Pt,[4,5] Ru, Pd and IrO_2[6]) as well as oxygen generation (mainly RuO_2,[6–8] and also other oxides such as IrO_2,[9,10] and MnO_2[10]) from water have been recently proposed These were tested in 'sacrificial' model systems, since in these processes hydrogen and oxygen were respectively produced at the expense of irreversible oxidations of external electron-releasing compounds (*i e* ethylenediaminetetra-acetic acid, EDTA), or irreversible reductions of added electron-accepting species {*i e* $[Co(NH_3)_5Cl]^{2+}$} However, subsequent efforts to achieve cyclic, non-sacrificial cleavage of water require further studies involving new catalytic species, beyond the tempting procedure of simply mixing two of the above catalysts † Thus, the possibility of promoting both hydrogen and oxygen formation on the same catalytic surface, after the reaction sites had been created thereon, is a very attractive prospect Investigations on the specificity of the presently available catalysts for these two reactions‡ are therefore of major interest, and may offer guidelines in this direction

We report here, for the first time, that RuO_2, used until now exclusively to catalyse water oxidation to oxygen,[6–8] also catalyses, with a high efficiency, hydrogen formation from water This new catalytic activity of RuO_2 was tested in the now well-known Ru(bipy)$_3^{2+}$–methyl viologen (MV^{2+})–EDTA model system (bipy = 2,2′-bipyridyl) [5] The amounts of H_2 evolved upon visible light irradiation (λ 400—600 nm) after long induction periods (up to 2 h) were measured as previously described [5] Hydrogen formation was not observed if any one of the components was omitted, and the rates and yields (Table) varied markedly as a function of pH (entries 1—6) maximum values were observed at pH = 5 (as with Pt),[5] but nearly the same values were obtained at pH = 6 It should be noted that, under similar conditions, the previously mentioned colloidal Pt-catalysed photosystem behaved quite differently hydrogen formation efficiencies at pH = 6 were over one order of magnitude lower (compare entries 3 and 12) than that presently obtained with RuO_2 Moreover, hydrogen formation is now observed up to pH = 8, whereas using Pt gas formation was limited to pH ⩽ 7 [5] Hydrogen generation at this pH value (water reduction potential −0·47 V) is probably not related to the electron-relay MV^{2+} [$E°$ ($MV^{2+}/MV^{+\bullet}$) = −0·44 V, pH-independent], and the possibility of water reduction by a separate yet unidentified route cannot be presently excluded Finally, the dependence of hydrogen production efficiency on the added amounts of RuO_2 was

TABLE Rates and yields of hydrogen formation from aqueous solutions of Ru(bipy)$_3^{2+}$–MV^{2+}–EDTA irradiated with visible light[a] and catalysed by RuO_2[b] as compared with colloidal Pt [5]

Entry	pH[c]	Added amounts of catalyst/μmol (A = RuO_2, B = Pt)	Hydrogen-formation[d] rates/ml h^{-1}	Hydrogen yields[d]/mmol
1	4	A 30	1·1	0·56
2	5	A 30	2·7	1·00
3	6	A 30	2·3	0·91
4	7	A 30	1·0	0·32
5	8	A 30	0·3	0·26
6	9	A 30	0·0	0·00
7	5	A 7·5	1·7	0·54
8	5	A 15	2 0	0·67
9	5	A 60	2·7	1·12
10	5	A 120	2·6	1·12
11	5	B 0·7	4·5	1·35
12	6	B 0·4	0·2	0·04

[a] 30 ml aqueous solutions were argon-purged and irradiated by a 250 W halogen slide projector lamp as previously reported [5] [b] Ru(bipy)$_3^{2+}$ (6 × 10^{-6} mol), MV^{2+} (1·5 × 10^{-5} mol), EDTA (6 × 10^{-3} mol) and RuO_2 (Ventron, soluble form) as specified, other samples, commercially available or prepared from $RuCl_3$, were also active but have not yet been investigated at length [c] Buffers acetate, pH = 4 and 5, phosphate, pH = 6, 7, and 8, and borate pH = 9 [d] Measured to within ±10% as already described [5]

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† K Kalyanasundaram and M Gratzel, *Angew Chem , Int Ed Engl* , 1979, **18**, 701, using aqueous mixtures of RuO_2 and Pt catalysts containing $Ru(bipy)_3{}^{2+}$ as a light absorbing species, and methyl viologen as electron relay, a cyclic cleavage of water has been claimed but this result has been questioned [5]

‡ Absence of specificity for some of the tested catalysts (*i e* IrO_2 [6,10]) does exist, though the efficiencies are very low for one or both reactions

examined and found to reach, after the reactions had spontaneously stopped, plateau values when the amount of the catalyst was increased (entries 7—10 and 2) Using Pt, sharp decreases of hydrogen formation rates and yields have been observed[5,11] as increased amounts of catalyst were used, and attributed to an MV^{2+} hydrogenation side-reaction We believe that the results obtained so far with RuO_2 reflect the lower ability of this catalyst, as compared to Pt, to mediate the undesired hydrogenation of MV^{2+}, which limits hydrogen production [5] In fact, when solutions containing only RuO_2 and MV^{2+} ($pH = 5$) are kept under hydrogen (1 atm, room temperature) the hydrogenation of MV^{2+} is noticeable, on the photochemical experiments time-scale, after only extremely long induction periods, as is usual with RuO_2-based hydrogenation catalysts [12]

In summary, we have shown that RuO_2, already used to catalyse the oxidation of water, may also mediate hydrogen formation from water with very high efficiencies Though several aspects of the reaction mechanism remain to be clarified, in particular the formation and nature of the catalytic sites involved, the isolation and further use of such modified catalysts is highly desirable and is now in progress

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[12] See for example 'Catalytic Hydrogenation', R L Augustine, M Dekker, New York, 1965, p 39