Photocatalysis of the Homogeneous Water-gas Shift Reaction

By David J. Cole-Hamilton

(*Department of Inorganic, Physical and Industrial Chemistry, University of Liverpool, Liverpool* L69 3BX)

Summary The complex [RuCl(CO)(bipy)$_2$]Cl, a product of the long term reaction of $RuCl_3.3H_2O$ with 2 mol of bipyridyl (bipy) in refluxing dimethylformamide, produces H_2, CO, and CO_2 on photolysis in water; under CO the photochemical water-gas shift reaction is catalytic.

IN 1976 Whitten and his co-workers published[1] the first example of the photochemical cleavage of water into hydrogen and oxygen using complex transition-metal catalysts Subsequent study by these[2] and other workers[3,4] showed that, using purified samples of the surfactant analogues of $[Ru(bipy)_3]^{2+}$ (bipy = bipyridyl) as catalyst, no hydrogen or oxygen was produced on irradiation in water It is, thus, assumed that some impurity in the original preparation was responsible for the photocatalytic reaction, probably *via* a co-operative effect

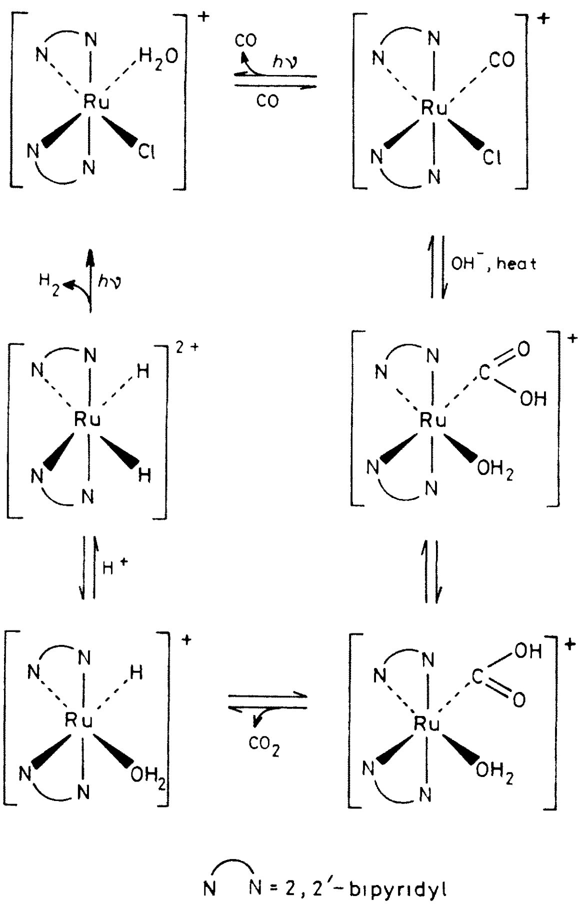
We have recently suggested[5] that an impurity present in $RuCl_2(bipy)_2$ prepared by the method of Whitten and co-workers[1] might have been carried through to the surfactant monolayers and might have been responsible for the observed hydrogen production The presence of a peak at *ca* 1970 cm^{-1} in the i r spectrum of this impurity was tentatively assigned to ν Ru–H We report herein further studies on this complex and show that it does indeed produce hydrogen on irradiation with visible light in aqueous solution, but that it is $[RuCl(CO)(bipy)_2]Cl$, a conclusion which has independently been reached[6] by other workers during the course of this study

When $RuCl_3$ $3H_2O$ and 2 mol of bipy were refluxed in dimethylformamide (DMF) for several days, the colour of the solution changed from purple [predominantly $RuCl_2(bipy)_2$] to red-brown Evaporation of this red-brown solution to low volume and then slow evaporation to dryness afforded large crystals of $[RuCl(CO)(bipy)_2]Cl$[6,7] (ν CO 1965 and ν Ru–Cl 322 cm^{-1}) contaminated with small amounts of $[Ru(bipy)_3]Cl_2$ which were readily separated by crystal picking

Irradiation of aqueous solutions of $[RuCl(CO)(bipy)_2]Cl$ with visible light at 100 °C† in the presence or absence of air produces hydrogen, but no oxygen Since CO and CO_2 are also products, this is clearly a photochemical water–gas shift reaction, rather than a straightforward photodissociation of water The final ruthenium product is $[RuCl(H_2O)(bipy)_2]^+$, as previously reported [6]

Under carbon monoxide (1 atmos), the reaction is catalytic and, although slow, appears to proceed without loss of activity for several days We believe this to be the first reported example of a light-assisted water–gas shift reaction and it suggests the possibility that the percentage of hydrogen in water gas may be increased beyond that determined by the thermodynamics of the reaction

The slowness of the reaction enables a mechanistic analysis and we find that CO_2 is produced in a thermal step, whereas formation of hydrogen is photoinitiated Production of CO is also photochemical, but, as observed[6] in other solvents, is not related to the water–gas shift reaction The proposed mechanism of production of these gases is shown in the Scheme and is similar to those suggested for thermal water–gas shift reactions [8,9] The assignment of structures to the ruthenium-containing intermediates is tentative, since they are currently under further investigation, we assume, however, that the Ru–Cl bond is solvolysed under our reaction conditions by analogy with recently reported[6] results on the thermochemistry of $[RuCl(CO)(bipy)_2]ClO_4$ in non-aqueous solvents



SCHEME

Evidence concerning the relative rates of some of these reactions comes from analysis of the gaseous products from the photochemical reaction of $[RuCl(CO)(bipy)_2]Cl$ in $H_2{}^{18}O$ (enrichment *ca* 20%) These products are H_2, $C^{16}O$, $C^{18}O$, $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$, the labelled species being obtained in amounts corresponding to total equilibration of all the oxygen atoms with those of the solvent This confirms that the reversible nucleophilic attack of OH^- on co-ordinated CO and the tautomerism of the CO_2H group are both rapid and that the rate-determining step‡ of the reaction is hydride transfer from $[Ru(CO_2H)(OH_2)(bipy)_2]^+$

This was further confirmed by carrying out the stoicheiometric photochemical reaction in D_2O where only CO and no D_2 is produced § This is presumably because the isotope effect on the hydride transfer from CO_2D to ruthenium makes the production of CO_2, and hence of D_2, compete

---

† The reaction also proceeds at room temperature, but production of CO is favoured and only small amounts of H_2 and CO_2 are detected as products

‡ In the catalytic reaction, the co-ordination of CO is also slow since the colour of the solution is more like that of $[RuCl(H_2O)(bipy)_2]Cl$ than that of $[RuCl(CO)(bipy)_2]Cl$

§ Traces of CO_2 and HD are observed as products.

poorly with the photochemical loss of CO. This marked isotope effect is further emphasised by the observation that the ratios of H_2 and HD to D_2 are substantially higher when they are formed by first heating $[RuCl(CO)(bipy)_2]Cl$ in D_2O in the dark (during which time CO_2, but no H_2, HD, or D_2 is produced) and photolysing the resulting solution, than when the same batch of D_2O is treated with lithium metal.

Although hydrogen is produced photochemically from $[RuCl(CO)(bipy)_2]Cl$ and water, this reaction clearly cannot be responsible for the sustained production of hydrogen in the system studied[1] by Whitten and his coworkers. However, it is possible that in the presence of some other oxygen acceptor, perhaps an unsaturated impurity in the surfactant side-chain, such sustained hydrogen production could be achieved. We are currently investigating this and related possibilities as well as attempting to improve the efficiency of this photochemical water–gas shift reaction.

We thank Johnson-Matthey Ltd. for loans of ruthenium.

(*Received*, 15*th September* 1980; *Com.* 1008.)

---

[1] G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch, and D. G. Whitten, *J. Am. Chem. Soc.*, 1976, **98**, 2337.

[2] G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch, and D. G. Whitten, *J. Am. Chem. Soc.*, 1977, **99**, 4947.

[3] G. L. Gaines and S. Valenty, *J. Am. Chem. Soc.*, 1977, **99**, 1285.

[4] A. Harriman, *J. Chem. Soc., Chem. Commun.*, 1977, 777.

[5] R. F. Jones and D. J. Cole-Hamilton, *Inorg. Chim. Acta*, submitted for publication.

[6] J. M. Clear, J. M. Kelly, C. M. O'Connell, J. G. Vos, C. J. Cardin, S. R. Costa, and A. J. Edwards, *J. Chem. Soc., Chem. Commun.*, 1980, 750.

[7] L. Ruiz-Ramirez and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.*, 1974, 1641.

[8] T. Yoshida, Y. Ueda, and S. Otsuka, *J. Am. Chem. Soc.*, 1978, **100**, 3941.