The Photochemical Water-gas Shift Reaction Catalysed by Bis(2,2′-bipyridyl)(carbonyl)chlororuthenium(II) Chloride †

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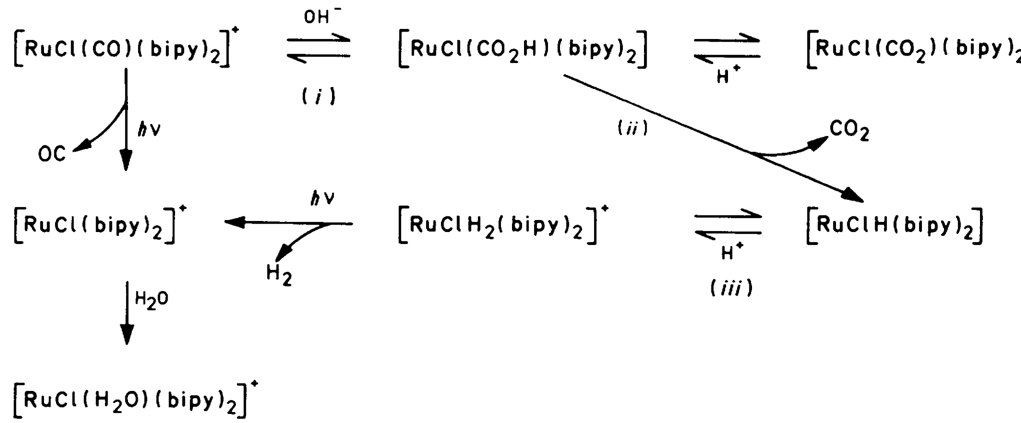
$[RuCl(CO)(N\text{-}N)_2]Cl$ [N–N = 2,2′-bipyridyl (bipy) or 1,10-phenantholine] are shown to be active catalytic species for the water-gas shift reaction under mild conditions (1—3 atm CO, 100—160 °C) and under illumination with white light. Turnover numbers of up to 20 h^{-1} are observed. Stoicheiometric reactions, including labelling studies, show that CO_2 is produced thermally, whilst H_2 is produced in a photochemical step. Mechanistic and kinetic data are presented for the catalytic reaction and they show that the reaction has a mechanism similar to those previously reported for the water-gas shift reaction and it does not involve formate decomposition. The rate-determining step at all pH is photochemical loss of H_2 from $[RuClH_2(bipy)_2]^+$ and different activation energies at high and low pH are attributed to different contributions from pre-equilibria involving attack of OH^- on co-ordinated CO (dominant at low pH) or protonation of $[RuClH(bipy)_2]$ (dominant at high pH). Experiments at high conversion show that at 140 °C CO can be completely converted to products. Attempts to catalyse related reactions using unsaturated substrates are also described.

A number of recent studies has appeared [1–3] in which metal complexes have been shown to catalyse the water-gas shift reaction under mild conditions in homogeneous media. These studies have shown that two conflicting criteria must be balanced in the choice of a suitable metal catalyst. In general, the reaction appears to involve nucleophilic attack of hydroxide ion on a metal carbonyl, which requires an electrophilic metal complex and, in a subsequent step, protonation of an hydrido-intermediate which leads to the transfer of two electrons from the metal to the proton. Subsequent reductive elimination leads to the formation of hydrogen. For this hydrogen-producing series of reactions to occur, the metal centre must be nucleophilic and it is perhaps this dichotomy that has led to relative few reports of catalytically active complexes.

We now report that complexes which are apparently quite electron poor are capable of catalysing the homogeneous water-gas shift reaction, provided that light is used to assist the hydrogen-producing step. A preliminary communication of our results has appeared [4] and examples of the photo-assisted water-gas shift reaction have been reported,[5,6] using heterogeneous TiO_2.



Scheme 1. Proposed mechanism for the stoicheiometric reaction between $[RuCl(CO)(bipy)_2]^+$ and water under illumination (all complexes have *cis* stereochemistry)

Results and Discussion

Stoicheiometric Reactions.—Our preliminary investigations concentrated on stoicheiometric reactions between water and $[RuCl(CO)(bipy)_2]Cl$ (bipy = 2,2′-bipyridyl), prepared [4,7] from prolonged reaction of $RuCl_3$ with bipy in refluxing dimethylformamide (dmf).

These studies showed that thermolysis of dilute solutions of $[RuCl(CO)(bipy)_2]Cl$ in water gives carbon dioxide and a pale yellow solution containing a complex which we have been unable to isolate, but which we believe to be an hydrido-ruthenium complex. In more concentrated solution, CO_2 is again formed, but only partial conversion to products occurs. This reaction presumably involves nucleophilic attack of hydroxide ion on co-ordinated carbon monoxide followed by β-hydrogen abstraction to give CO_2 and the metal hydride [reactions (*i*)—(*iii*), Scheme 1]. The observation that only

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† *Non-S.I. units employed*: 1 atm = 101 325 Pa.

partial reaction occurs at higher ruthenium concentration can be attributed to the fact that both the presence of CO_2 as a product and the participation of hydroxide ion in the reaction lead to a drop in pH, and hence a depletion of OH^-, and lowering of the rate of reaction. This is confirmed by carrying out the reaction in buffered solution, in which case complete reaction occurs with more concentrated solutions. Carbon monoxide does not appear to be a product of these thermolyses, although it is produced [8] on irradiation of $[RuCl(CO)(bipy)_2]Cl$.

Photolysis of the product of thermolysis of $[RuCl(CO)(bipy)_2]Cl$ produces hydrogen and $[RuCl(H_2O)(bipy)_2]Cl$ identified by its visible spectrum (Scheme 1).

Predictably, therefore, the products of combined thermolysis and photolysis of $[RuCl(CO)(bipy)_2]Cl$ are CO, CO_2, and H_2.

For the combined thermal and photochemical reactions, labelling studies show that the β-elimination step is much slower than nucleophilic attack of OH^- on co-ordinated CO since in $H_2{}^{18}O$, both the CO and the CO_2 produced contain ^{18}O, and some CO_2 has both oxygens labelled. Further support for the idea that hydrogen transfer from co-ordinated CO_2H is rate determining is provided by the observation that almost no CO_2 or D_2 is produced when $[RuCl(CO)(bipy)_2]Cl$ is photolysed at 100 °C in D_2O. This suggests a dramatic isotope effect which makes the photochemical loss of CO considerably more rapid than formation of CO_2. It is possible to produce both D_2 and CO_2 by first thermolysis and then photolysis of $[RuCl(CO)(bipy)_2]Cl$, but under these conditions, the ratio of HD : D_2 produced is 1 : 1.2, compared with 1 : 7 on reaction of the same batch of D_2O with lithium. This suggests a kinetic isotope effect of *ca.* 6, which can only be rationalized if the rate-determining step involves hydrogen transfer.

Under CO, we have been able to show that the reaction is catalytic and, by systematic variation of a number of parameters, we can provide some information about the mechanism of the reaction.

Catalytic Reactions.—Both $[RuCl(CO)(bipy)_2]Cl$ and $[RuCl(CO)(phen)_2]Cl$ (phen = 1,10-phenanthroline) catalyse the photochemical water-gas shift reaction at temperatures between 80 and 160 °C and low pressures (1—3 atm). At higher temperatures, catalyst decomposition appears to occur, as evidenced by the appearance of a dark solid in what is otherwise a pale yellow homogeneous solution. The efficiency of $[RuCl(CO)(phen)_2]Cl$ as a catalyst is less than that of its bipy analogue under the same conditions (see Table) so a full analysis of the effects of varying various reaction parameters has only been carried out for the bipy complex.

Since $[RuCl(CO)(bipy)_2]Cl$ can be prepared [7] from $[RuCl_2(bipy)_2]$ and CO, we have used $[RuCl_2(bipy)_2]$ as catalyst precursor. Although reaction to form the active species is slow in refluxing methanol, it is considerably more rapid in water at 100 °C, and complete conversion *via* $[RuCl(H_2O)(bipy)_2]Cl$ occurs in under an hour. At low pH and low p_{CO}, however, this is not the case (see below) but it is interesting to note that the rate of formation of $[RuCl(CO)(bipy)_2]Cl$ from $[RuCl(H_2O)(bipy)_2]Cl$ is enhanced by irradiation, suggesting that substitution of H_2O by CO, which occurs slowly in the dark, can be light-assisted. Such light-assisted substitutions have previously been reported.[9]

Table. Effect of various additives and procedures on the rate of hydrogen production in the water-gas shift reaction

Catalyst precursor	Additive	Volume of H_2 produced [a]	Conditions
$[RuCl_2(bipy)_2]$		0.51	*b*
$[RuCl_2(phen)_2]$		2.41	*b*
$[RuCl_2(bipy)_2]$		8.30	*c*
$[RuCl_2(bipy)_2]$	Na_2SO_4 (0.5 mol dm^{-3})	8.90	*c*
$[RuCl_2(bipy)_2]$	$S(NH_4)_2$	0	*c*
$[RuCl_2(bipy)_2]$		13.4	*d*
$[RuCl_2(bipy)_2]$	NaCl (1 mol dm^{-3})	6.7	*d*
$[RuCl_2(bipy)_2]$	D_2O	2.6	*e*
$[RuCl_2(bipy)_2]$	1 h preheating in dark	0.19	*f*
$[RuCl_2(bipy)_2]$	2 h preheating in dark	0.33	*f*
$[RuCl_2(bipy)_2]$		74.6	*g*

[a] In cm^3 at 295 K. [b] As general procedure but T = 120 °C, p_{CO} = 3 atm, t = 20 h, in pure water. [c] As *b* but T = 140 °C. [d] As general procedure but T = 140 °C, p_{CO} = 3 atm, t = 2 h, in pH 8.9 buffer. [e] As *d* but pH = 9.2. [f] As general procedure but T = 140 °C, p_{CO} = 1 atm, t = 2 h, in pH 6.1 buffer. [g] As *b* but T = 158 °C, t = 64 h; volume of CO_2 produced = 68.3 cm^3.

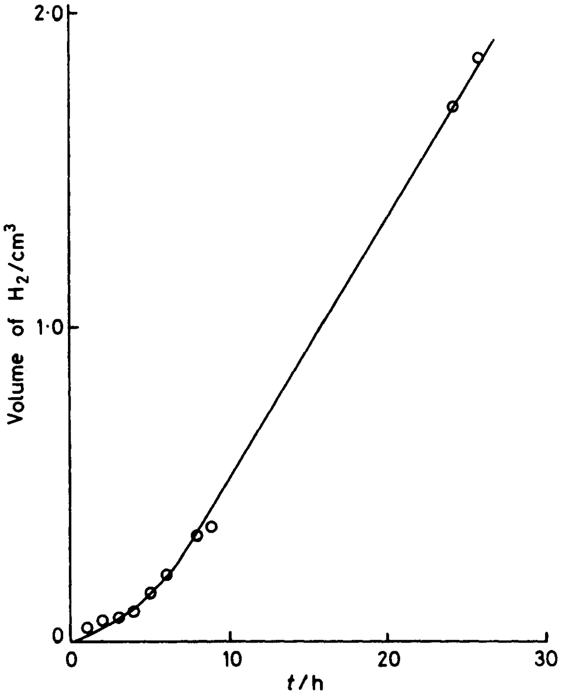

Figure 1. Plot of volume of hydrogen evolved at 1 atm and 295 K against time: p_{CO} = 3 atm, 110 °C; no induction period, pure water

Reaction Stoicheiometry, Nature of the Active Species, and the Effect of Catalyst Concentration on the Reaction Rate.—Figure 1 shows the amounts of hydrogen produced from a catalytic reaction carried out in pure water at 110 °C under 3 atm CO plotted as a function of time (t). This shows that the reaction is catalytic over a long period of time. Other reactions (see Table) show that the amount of CO_2 produced is, within experimental error, the same as the amount of hydrogen produced, and hence that no side reactions occur during the water-gas shift reaction. In view of this, reactions were, in general, followed by monitoring the hydrogen produced.

In a preliminary communication, we suggested [4] that the active CO-containing species in the catalytic cycle was $[Ru(CO)(H_2O)(bipy)_2]^{2+}$, on the basis of the findings of Kelly and co-workers [8] that $[RuCl(CO)(bipy)_2]^+$ loses halide ion on heating in the presence of donor ligands. Subsequently, we

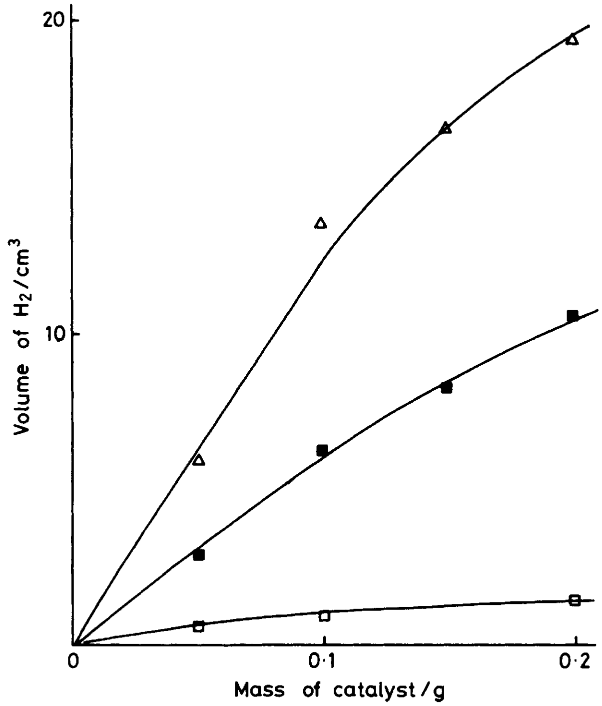

Figure 2. Plot of rate of hydrogen production (cm^3 in 2 h at 295 K) against catalyst concentration (g in 5 cm^3 solution): p_{CO} = 3 atm, 140 °C; (□) pure water, (■) pH 6.88, (△) pH 8.9

have reported [7] the synthesis of $[Ru(CO)_2(bipy)_2]^{2+}$ from $[RuCl_2(bipy)_2]$, CO, and $Ag[SbF_6]$. Accordingly, either of these two species or $[RuCl(CO)(bipy)_2]^+$ could be the active CO-containing species in the catalytic cycle.

In order to investigate which of these species is present in solution under reaction conditions, we have heated a concentrated solution of $[RuCl(CO)(bipy)_2]Cl$ in unbuffered water under 3 atm CO. Under these conditions, as noted above, not all the active species undergoes nucleophilic attack on CO but chloride solvolysis or dicarbonyl formation should occur if it occurs during the catalytic reaction.

Precipitation of the solution obtained by this treatment with KPF_6 precipitates * only $[RuCl(CO)(bipy)_2][PF_6]$, identical to that which we have prepared [7] by treatment of $[RuCl(CO)(bipy)_2]Cl$ with KPF_6 in cold methanol. Since both $[Ru(CO)_2(bipy)_2]^{2+}$ and $[Ru(CO)(H_2O)(bipy)_2]^{2+}$, being dications,[7] should have $\nu(C{\equiv}O)$ above 2 000 cm^{-1}, we conclude that if they are present it is only in trace amounts and hence that $[RuCl(CO)(bipy)_2]^+$ is probably the active catalytic species.

Further support for this contention comes from the observation that the reaction is only slightly inhibited by the presence of excess chloride ion (1.0 mol dm^{-3} NaCl approximately halves the rate of reaction, see Table).

Figure 2 shows reaction rate plotted against catalyst concentration under a number of different reaction conditions. In cases where buffer solutions are employed, the reaction is approximately first order in [catalyst], although slight deviations from linearity are observed at high concentrations of catalyst. These deviations arise because under these conditions significant conversion to products occurs, hence p_{CO} is reduced and lower reaction rates than expected for first-order kinetics are observed. This is particularly the case for the results obtained in pH 6.88 buffer since the reaction time was 20 h and up to 100 cm^3 of CO (equivalent to p_{CO} = 1 atm) was consumed. These results, as well as those obtained in pure water (reaction time = 20 h), have been divided by 10 to obtain a more direct comparison with the results at pH 8.9 (reaction time = 2 h).

In pure water, more significant deviations from linearity are observed, particularly at high catalyst concentrations, despite the lower conversions. In this case, we believe the explanation derives from the pH dependence of the reaction (see below). Thus, since the catalyst reacts with OH^- to give CO_2, the greater the catalyst concentration, the lower will be the pH of the solution and hence the lower will be the rate of the reaction. In buffer, the pH of the solution is independent of catalyst concentration and hence first-order dependence on [catalyst] is observed.

Another important result illustrated in Figure 1 is that the rate of reaction in buffered water (pH 6.88) is *ca.* 10 times the rate in pure water. This clearly is not an effect of ionic strength since Na_2SO_4 (1 mol dm^{-3}) does not affect the reaction rate (Table), but it can again be attributed to the low pH of the active solution in pure water.

In view of these findings, further reactions were generally carried out in chloride-free buffer solution and we concentrate on these results in the following discussion of the reaction mechanism based upon a study of the effect on the reaction rate of changing various parameters.

Mechanism.—In order to simplify the subsequent discussion, it is pertinent to consider possible mechanisms for the water-gas shift reaction at this stage.

Two types of mechanism have been proposed to explain the various kinetic results obtained with different catalyst systems. Thus, in most cases, the reaction is thought [1,2] to proceed *via* a series of reactions involving attack of OH^- (or water) on co-ordinated CO, loss of CO_2 to give a metal hydride, protonation, loss of hydrogen, and finally co-ordination of CO.

An alternative mechanism, which has been shown [3] to operate for $[M(CO)_6]$ (M = Cr, Mo, or W) catalysed reactions in basic solution, involves reaction of CO with base to give formate ion followed by the catalytic decomposition of formate ion.

Certain pieces of evidence lead us to conclude that the mechanism of our photochemical water-gas shift reaction does not involve formate decomposition. (*i*) Pressures of CO used in our studies are considerably lower than those used [3] in studies where formate ion decomposition is implicated, so that, except at very high pH, little or no formate ion would be expected to be formed. (*ii*) The reaction proceeds even in moderately acid solution (pH 5.5) where formation of formate ion would not be favoured. (*iii*) Although for formate ion decomposition a plot of reaction rate against base concentration shows [3] a slight negative deviation from linearity at high pH which has been attributed to the ionic strength of the medium, it would not be expected that the rate would actually fall at high pH (high $[HCO_2^-]$) as it does in our system (see below). (*iv*) Our system † proceeds stoicheiometrically in the absence of added CO and under conditions where CO dissociation does not occur (*i.e.* sequential thermal and photochemical steps, see above). (*v*) The effect of light on formate ion decomposition is to accelerate [10] the reaction by forming the active species $[M(CO)_5]$ by CO dissociation, whereas in our system the role of the light is clearly to release hydrogen from some species in the system.

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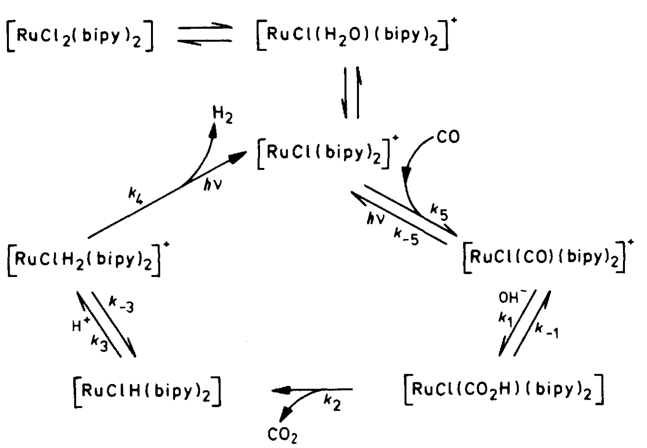
* Interestingly, when $[RuCl_2(phen)_2]$ is employed in this reaction, small amounts of $[Ru(CO)_2(phen)_2][PF_6]_2$ are precipitated along with $[RuCl(CO)(phen)_2][PF_6]$.

† The exact significance of this result is not certain as some catalyst precipitation occurs at high pH.



Scheme 2. Proposed mechanism for catalysis of the water-gas shift reaction under illumination using $[RuCl_2(bipy)_2]$ as catalyst precursor (all complexes have *cis* stereochemistry)

On the basis of these results, we conclude that a mechanism involving attack of OH^- on co-ordinated carbon monoxide operates for the photochemical water-gas shift reaction catalysed by $[RuCl(CO)(bipy)_2]Cl$. A plausible mechanism is shown in Scheme 2.

Support for some of these steps has already been offered. Thus, stoicheiometric studies (see above) confirm that CO_2 loss is slower than the reversible attack of OH^- on co-ordinated CO and loss of CO from $[RuCl(CO)(bipy)_2]^+$ occurs photochemically but *not* thermally.

We do not include $[RuCl(H_2O)(bipy)_2]^+$ as an intermediate in the cycle since, under the reaction conditions, carbonylation of $[RuCl(bipy)_2]^+$ is likely to be considerably more rapid than aquation. Evidence for this is offered by the observation that, even at $p_{CO} = 1$ atm, photolysis of $[RuCl(H_2O)(bipy)_2]^+$ in water rapidly produces $[RuCl(CO)(bipy)_2]^+$, presumably *via* the intermediacy of $[RuCl(bipy)_2]^+$ (see above).

Assuming this mechanism to be correct, applying steady-state kinetics to *all* of the ruthenium-containing species included in the cycle leads to the rate expression (1) where I is

$$\frac{d(H_2)}{dt} = \frac{k_1k_2k_3k_4k_5K_wI[CO][Ru_{tot.}]}{\Sigma} \qquad (1)$$

intensity of the incident radiation, $[Ru_{tot.}]$ is the total concentration of ruthenium in the system, K_w is the dissociation constant for water, and $\Sigma = k_1k_2k_3k_5K_w[CO] + k_1k_3k_4k_5K_wI[CO] + k_1k_2k_{-3}k_5[OH^-][CO] + k_1k_2k_4k_5I[OH^-][CO] + k_{-1}k_3k_4k_5I[H^+][CO] + k_2k_3k_4k_5I[H^+][CO] + k_1k_2k_3k_4K_wI + k_{-1}k_3k_4k_{-5}I^2[H^+] + k_2k_3k_4k_{-5}I^2[H^+]$.

This rate expression assumes that the concentrations of the photochemically active species, $[RuClH_2(bipy)_2]^+$ and $[RuCl(CO)(bipy)_2]^+$, are small so that terms involving the squares of these concentrations may be neglected. This assumption is very likely to be valid at high pH ($k_{-1} \ll k_1$; $k_3 \ll k_{-3}$) but it may well break down at low pH.

Making these assumptions, certain predictions can be made, irrespective of which step is rate-determining. Thus, at constant pH, I, and [CO], the reaction should be first order in $[Ru_{tot.}]$ as is indeed observed (see above).

Furthermore, plots of the inverse of the rate of hydrogen production against the inverse of CO partial pressure, all else being equal, should be straight lines. Figure 3 shows that this is the case at various pH and that, at least qualitatively, the slopes of these lines increase with $[H^+]$. The linear dependence of these slopes on $[H^+]$ is not observed, either because at low pH concentrations of the photochemically active species are not small, or because of the large errors associated with measurements at low pH. These arise because turnover numbers * are often less than 1 under these conditions and because of difficulties associated with catalyst activation. Thus, at pH

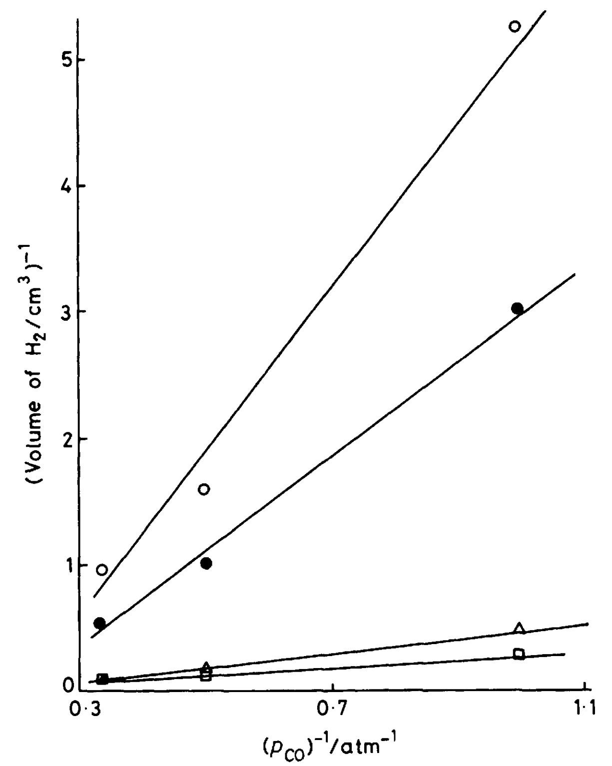


Figure 3. Plot of (rate of hydrogen production cm^3 in 2 h at 295 K)$^{-1}$ against $(p_{CO})^{-1}$: 140 °C; (○) pH 5.5, (●) pH 6.1, (△) pH 8.9 (containing Cl^-), (□) pH 12.2

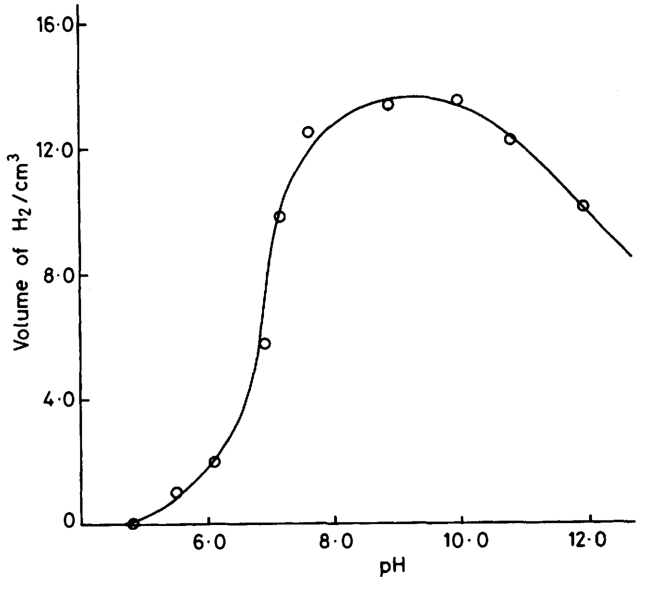


Figure 4. Plot of rate of hydrogen production (cm^3 in 2 h at 295 K) against pH of solution: 140 °C, p_{CO} = 3 atm

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* One catalyst turnover corresponds to the production of 1 mol of H_2 per mol of catalyst per hour; units h^{-1}.

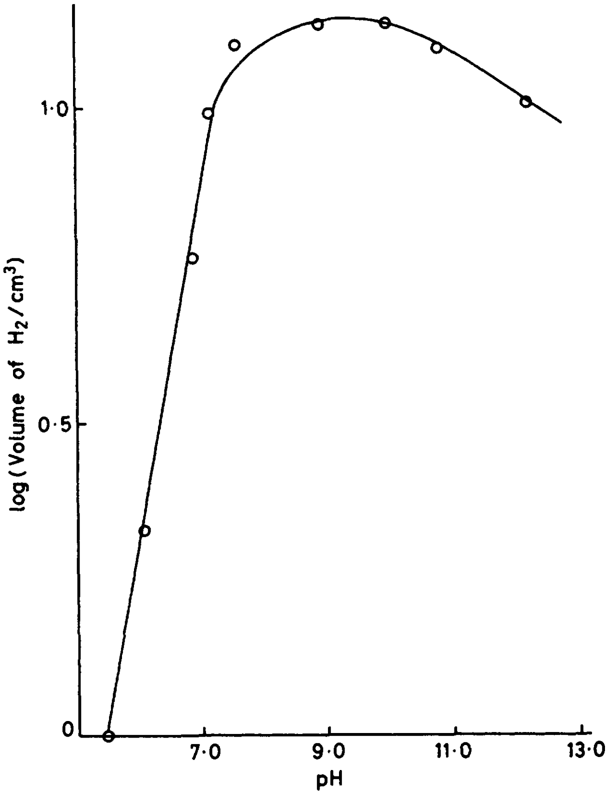


Figure 5. Plot of log (rate of hydrogen production/cm^3 in 2 h) against pH: 140 °C, $p_{CO} = 3$ atm

6.2 and $p_{CO} = 1$ atm, for example, the standard reaction conditions (140 °C, 1 h activation in the dark followed by 2 h irradiation) produce 0.19 cm^3 of H$_2$ and the solution is orange-red after the activation period, although it rapidly becomes yellow on irradiation. A similar experiment, but using an activation period of 2 h, produces 0.33 cm^3 of H$_2$ and the solution is yellow after the activation period.

The pH Dependence of the Reaction.—Since the numerator of the rate expression is devoid of terms in [H$^+$] or [OH$^-$], whereas the denominator contains terms in [H$^+$], [OH$^-$], or K_w, a complex dependence of rate on pH of the reaction solution would be expected and is, indeed, observed (Figure 4). This behaviour can be modelled if it is assumed that $k_1 \ll k_{-1}$ and $k_{-3} \ll k_3$ at low pH, whereas at high pH the reverse is true.

Making these assumptions, the rate expression at high pH simplifies to equation (2).

$$\frac{d(H_2)}{dt} = \frac{k_3k_4k_5K_wI[CO][Ru_{tot.}]}{k_5k_{-3}[CO][OH^-] + k_3k_4K_wI} \quad (2)$$

This clearly implies a positive order in [H$^+$], which tends to 1 at very high [OH$^-$], as is observed (Figure 5). This expression further predicts that at very high hydroxide ion concentration or high CO pressure the orders in [CO], [H$^+$], and light intensity should be 0, 1, and 1 respectively, whereas at high light intensity they should tend to 1, 0, and 0. This clearly explains the slight deviation from linearity of the plots of rate against light intensity (Figure 6) and of rate against p_{CO} (Figure 7) at high pH.

Using the assumptions stated above and remembering that $k_2 \ll k_{-1}$ (from stoicheiometric reactions) the rate expression at low pH simplifies to equation (3). This expression implies

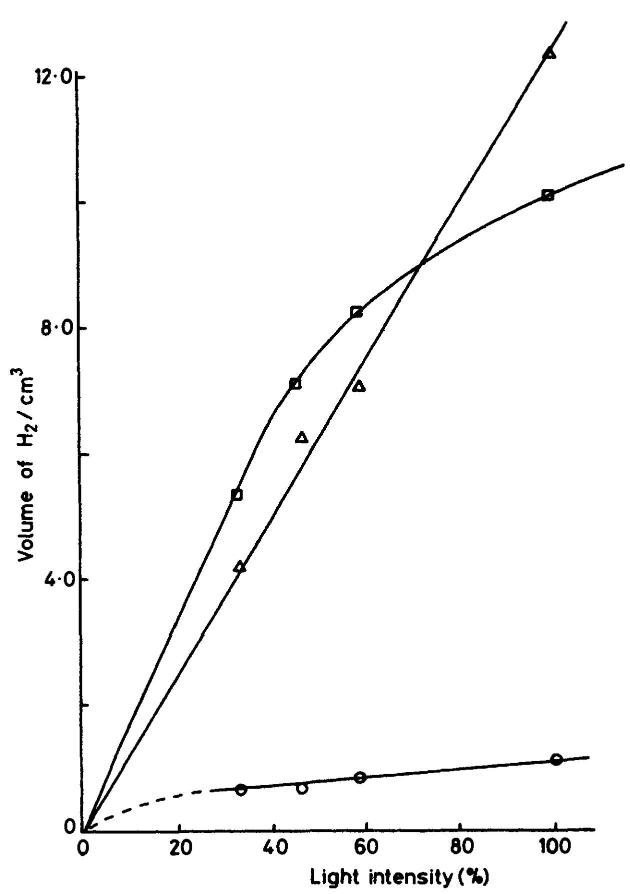


Figure 6. Plot of rate of hydrogen production (cm^3 in 2 h at 295 K) against light intensity (100% = full illumination): 140 °C, $p_{CO} = 3$ atm; (○) pH 5.5, (△) pH 8.9 (containing Cl$^-$), (□) pH 12.2

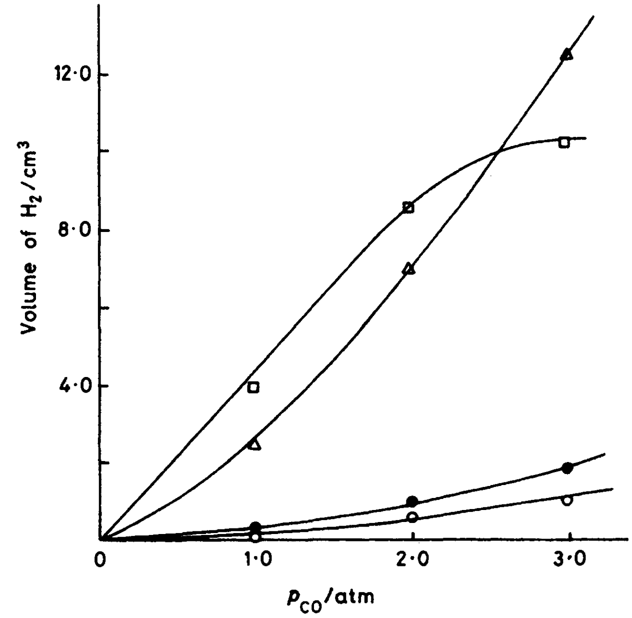


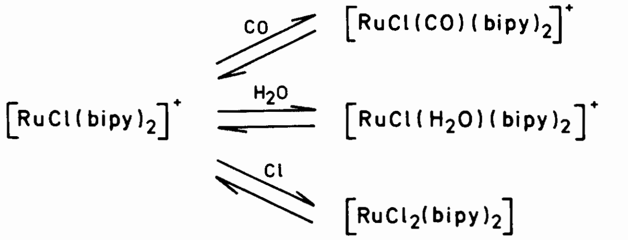
Figure 7. Plot of rate of hydrogen production (cm^3 in 2 h at 295 K) against p_{CO}: 140 °C; (○) pH 5.5, (●) pH 6.2, (△) pH 8.9 (containing Cl$^-$), (□) pH 12.2

$$\frac{d(H_2)}{dt} = \frac{k_1k_2k_4k_5K_wI[CO][Ru_{tot.}]}{k_1k_2k_5K_w[CO] + k_{-1}k_4k_5I[H^+][CO] + k_1k_2k_4K_wI + k_{-1}k_4k_{-5}I^2[H^+]} \quad (3)$$

positive order in $[OH^-]$, tending to 1 at very high $[H^+]$. Other inferences that can be drawn suggest that at very high $[H^+]$, orders in $[OH^-]$, [CO], and I are 1, <1, and <0 whereas at high p_{CO} these are <1, 0, and <1. Finally, at very high light intensity, the orders should tend to 1, 1, and -1 respectively.

Once again, these orders are qualitatively borne out (Figures 4—7), the near-zero (slightly positive) order in light intensity suggesting that the term in I^2 does not dominate under the maximum illumination conditions that we have employed.

The positive deviation from linearity of the graph of rate of H_2 production against p_{CO} at low pH is more difficult to explain but it may be an artifact arising from incomplete catalyst activation at lower partial pressures of CO, or it may arise because at low p_{CO} and low pH, chlorination and/or aquation of $[RuCl(bipy)_2]^+$ compete with carbonylation (Scheme 3).



Scheme 3. Possible competition between carbonylation, aquation, and chlorination of $[RuCl(bipy)_2]^+$, which is proposed to occur at low pressures of CO or in the presence of excess Cl^-

Some support for the idea that chloride ion suppresses the reaction at low p_{CO} comes from the plot of rate against p_{CO} at pH 8.9. These measurements were carried out in buffer containing chloride ion and the graph also shows a positive deviation from linearity.

The Nature of the Rate-determining Step.—Although our observed results are well explained by the reaction shown in Scheme 2, we have said nothing about the rate-determining step of the reaction. Possible slow steps are the photochemical loss of hydrogen from $[RuClH_2(bipy)_2]^+$ and the loss of CO_2 from $[RuCl(CO_2H)(bipy)_2]$. It is also possible that addition of CO to $[RuCl(bipy)_2]^+$ is slow since formation of $[RuCl(CO)(bipy)_2]^+$ from $[RuCl(S)(bipy)_2]^+$ (S = H_2O or MeOH) is known [7] to be slow, although it is considerably faster if light is employed to generate $[RuCl(bipy)_2]^+$, see above.

Further evidence that CO co-ordination is not rate-determing comes from the following observations. (*i*) At low pH, CO, CO_2, and H_2 are produced on photolysis of $[RuCl(CO)(bipy)_2]^+$ at 100 °C. This suggests either that photochemical loss of CO from $[RuCl(CO)(bipy)_2]^+$ has a rate comparable to that of H_2 loss, and CO co-ordination is slow, or that CO loss and co-ordination are both fast and comparable in rate to one another. We prefer the latter explanation since it is difficult to explain the observed dependence of the rate of the catalytic reaction on light intensity at high pH.* (*ii*) The rate of D_2 production from D_2O buffered to pH 9.2 is *ca.* one fifth the rate of H_2 production. This gives an isotope effect of *ca.* 5, which can only be explained if cleavage of O–H or Ru–H bonds is involved in the rate-determining step.

We conclude, therefore, that either loss of CO_2 or photochemical loss of H_2 is rate-determining in the catalytic reaction.

At high pH, the near-first-order dependence on light intensity strongly suggests that the photochemical loss of hydrogen is rate-determining. Support for this view comes from the temperature dependence of the reaction.

Previously observed activation energies for the thermal water-gas shift reaction show [11–13] that, where hydrogen loss is rate-determining, activation energies are in the range 80—110 kJ mol^{-1}, regardless of the type of catalyst employed. In contrast, in the only system where CO_2 is thought [13] to be rate-determining $\{[RhI_2(CO)_2]^-$ at high temperature, high $[H^+]$, or high $[I^-]\}$ an activation energy of only 38 kJ mol^{-1} is observed. Formate ion decomposition has [3] a higher activation energy (*ca.* 140 kJ mol^{-1}).

Arrhenius plots for the photochemical water-gas shift reaction at three different pH's are shown in Figure 8. These give activation energies of 35.3, 35.3, and 52.5 kJ mol^{-1}, at pH 12.0, 8.9, and 5.5 respectively. Clearly, at high pH the values observed could be explained by CO_2 loss being rate-determining. However, since this does not explain the dependence on light intensity, we believe that the observed activation energy simply reflects the temperature dependence of the dominant pre-equilibrium which at this pH will be protonation of

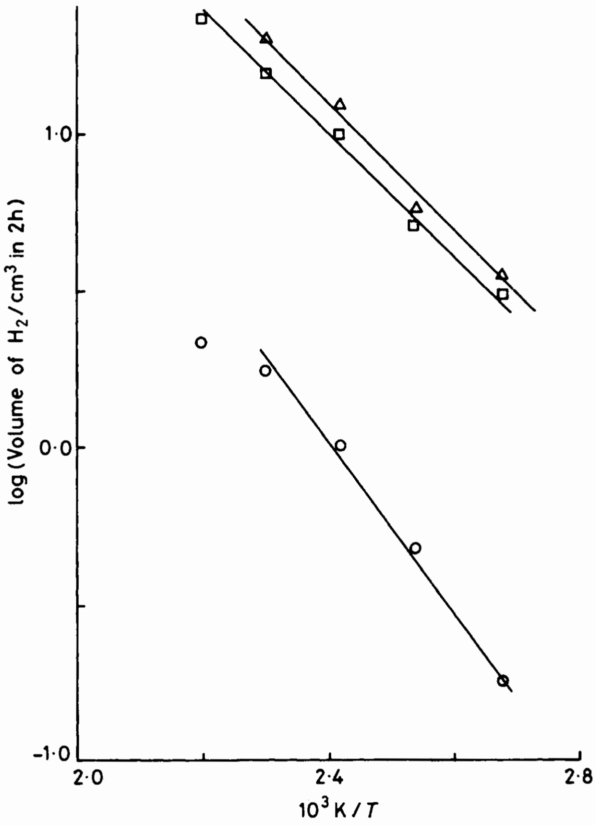


Figure 8. Arrhenius plots for the water-gas shift reaction: p_{CO} = 3 atm; (○) pH 5.5, (△) pH 8.9, (□) pH 12.2

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* It should be noted, however, that the partial pressure of CO generated in the stoicheiometric reaction would be very low.

[RuClH(bipy)$_2$].* The observed activation energy is of the same order of magnitude as that found in the only other reported photochemical water-gas shift reaction using platinized TiO_2 as a catalyst (31.5 kJ mol^{-1}),[6] in which the photochemical step was proposed to be rate-determining.

At low pH, the activation energy is considerably higher than at high pH and there seem to be two possible explanations for this observation. Either there is a change in the rate-determining step, or the change in activation energy may simply reflect the fact that the dominant pre-equilibrium at low pH will be attack of hydroxide ion on [RuCl(CO)(bipy)$_2$]$^+$ whereas at high pH it will be protonation of [RuClH(bipy)$_2$]. Since the temperature dependences of these two equilibria may well be different, different activation energies would be expected at high and low pH.

Were CO_2 loss rate-determining at low pH, the pre-equilibrium involving photochemical loss of CO from [RuCl(CO)(bipy)$_2$]$^+$ should lead to a negative order in light intensity. Since this is not the case (a slight positive order is observed), we favour the view that the photochemical loss of H_2 from [RuClH$_2$(bipy)$_2$]$^+$ is rate-determining at all values of pH.

Experiment at High Conversion.—Since one of the main reasons for carrying out the homogeneous water-gas shift reactions is that the milder conditions required favour the hydrogen side of the reaction, we have carried out a reaction to see whether complete conversion to products may be obtained in the light-driven reaction. The reaction was carried out in a manner similar to those described above, except that the gas phase consisted of 1 atm CO_2 and 2 atm H_2. Carbon monoxide (1 cm^3) was injected into the reactor. After 16 h photolysis at 140 °C, no CO was detectable in the gas phase; this indicates that <0.05 cm^3 of CO remained and hence that essentially complete conversion to products can be obtained under these conditions. (This corresponds to $<0.02\%$ of CO in the product gases.)

Comparison with Other Systems.—The maximum rate for the water-gas shift reaction (pH 8.9, 3 atm CO, 160 °C, full illumination) that we have observed corresponds to *ca.* 20 catalyst turnovers per hour. Although this reaction rate could be improved by increasing the intensity of the incident radiation (a near-first-order dependence being observed) it already compares favourably with most other systems that promote the reaction under such mild conditions. A comparison of turnover numbers of various systems has been made previously[14] and the only systems with faster rates (100—400 h^{-1})[14-16] than those reported here are ones in which much higher pressures (10—40 atm) have been employed. More recently, Otsuka and co-workers[2] have reported that turnover numbers as high as 35 h^{-1} can be obtained using [RhH$_2$(O$_2$COH)(PPr$^i_3$)$_2$] but once again, high pressures are involved.

Unfortunately, the present reaction is totally inhibited by the presence of excess sulphide ion (see Table).

Reactions involving Other Substrates.—(*i*) *Methanol.* Attempts to carry out a reaction analogous to the water-gas shift reaction using methanol in place of water, which should lead to formation of methane and CO_2 or of acetic acid, proved unsuccessful, no reaction being observed. Addition of water to this system simply resulted in water-gas shift chemistry, the reaction rate showing first-order dependence on [H_2O] (see Figure 9).

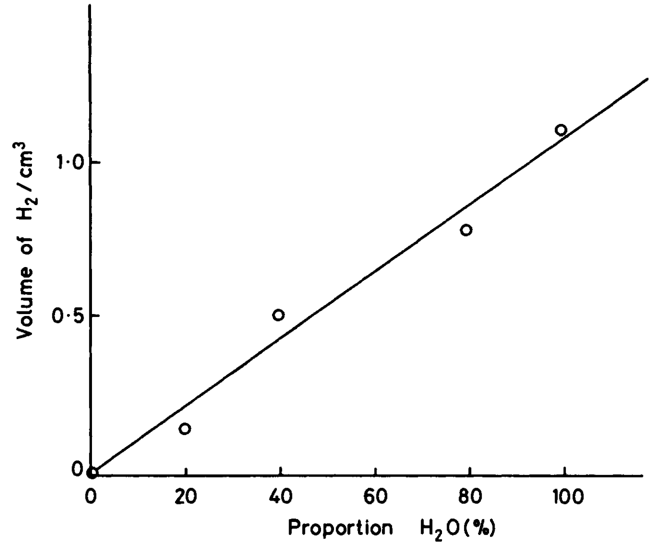

Figure 9. Plot of rate of hydrogen production (cm^3 in 2 h) against percentage of H_2O (v/v): as general procedure for buffer solutions but no buffer; p_{CO} = 3 atm, 140 °C, in methanol

(*ii*) *Unsaturated substrates.* In our preliminary communication,[4] we suggested that hydrogen production, observed[17] irreproducibly on irradiation of monolayers of analogues of [Ru(bipy)$_3$]$^{2+}$ containing surfactant side chains, might arise from chemistry similar to that involved in the photochemical water-gas shift reaction; specifically, that [RuCl(CO)(bipy)$_2$]$^+$ impurity might catalyse the formation of hydrogen from water, with unsaturated groups in the surfactant chains acting as oxygen acceptors. In order to test this, as well as in the hope of promoting reactions such as that shown in the equation below in which hydrogen and a useful oxidised product

$$C_2H_4 + H_2O \xrightarrow{h\nu} CH_3CHO + H_2$$

(CH_3CHO) are formed from water and a relatively cheap and abundant starting material, we have studied the photochemical reactions of water and ethene, allyl alcohol, or diethyl maleate in the presence of [RuCl(CO)(bipy)$_2$]Cl.

Although small amounts of hydrogen were produced from reactions of ethene and allyl alcohol, the reactions were very slow and terminated after <1 cycle. We have not therefore pursued these reactions and now feel that this type of reaction probably does not explain the hydrogen production observed by Whitten and co-workers.[17] For diethyl maleate, formation of large quantities of CO_2 probably arises from hydrolysis of the ester followed by thermal decarboxylation.

Experimental

I.r. spectra were measured on a Perkin-Elmer PE 577 grating spectrophotometer in Nujol mulls between caesium iodide plates, visible spectra on a Pye Unicam SP8-100 spectrophotometer, and mass spectra on a V.G. Micromass 12 spectrometer. Gas-liquid chromatography (g.l.c.) was carried out on Pye-Unicam series 104 or 204 gas chromatographs using molecular sieve (H_2 and CO) or Chromosorb 102 (CO_2) columns with N_2 (H_2 and CO_2) or He (CO) as carrier gas. Water was distilled and degassed before use.

A. Stoicheiometric Reactions.—1. (*a*) *Thermal reaction of* [RuCl(CO)(bipy)$_2$]Cl *with water.* [RuCl(CO)(bipy)$_2$]Cl (*ca.*

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* The activation energy of the photochemical step would be expected to be *ca.* 0 kJ mol^{-1}.

0.004 g) was dissolved in H_2O (3 cm^3) in a quartz u.v. cell stoppered with a serum cap. After heating at 80 °C for 16 h, the gases were analysed by g.l.c. and mass spectroscopy and shown only to contain CO_2. The visible spectrum of the product showed only a shoulder at *ca.* 390 cm^{-1} and we assign it to $[RuClH_2(bipy)_2]^+$. (The visible spectrum is similar[7] to that of $[RuCl(CO)(bipy)_2]Cl$ except that the peak at 342 cm^{-1} is absent and the shoulder near 400 cm^{-1} is more pronounced.)

Using more concentrated solutions (0.05 g in 3 cm^3), CO_2 was again produced but the u.v. spectrum of the yellow-orange solution showed that unreacted $[RuCl(CO)(bipy)_2]^+$ remained and did not disappear on further thermolysis.

(*b*) *Thermal reaction of* $[RuCl(CO)(bipy)_2]Cl$ *in* $H_2{}^{18}O$ *(20% enriched)*. The procedure was as above but using $H_2{}^{18}O$ (20% enriched). Mass spectroscopy of the gases revealed no H_2 or $C^{18}O$ but showed a statistical mixture of labelled CO_2 ($C^{16}O_2 : C^{16}O^{18}O : C^{18}O_2$ 73.5 : 22.6 : 3.9).

(*c*) *Thermal reaction of* $[RuCl(CO)(bipy)_2]Cl$ *in* D_2O. The procedure was as above but using D_2O. Mass spectroscopy of the gases showed that CO_2 was produced but no D_2, HD, or H_2.

2. (*a*) *Photochemical reaction of* $[RuClH_2(bipy)_2]^+$. The solution produced in 1(*a*) was photolysed for 16 h with light from a 500 W tungsten filament lamp focused through a large glass lens to a 1 cm × 1 cm image. Analysis of the gases by g.l.c. and mass spectroscopy showed hydrogen to be the only new product. The visible spectrum of the orange solution was identical to that of $[RuCl(H_2O)(bipy)_2]Cl$.

(*b*) *Photolysis of* $[RuClD_2(bipy)_2]^+$. As 2(*a*) above but using the solution produced in 1(*c*). Mass spectroscopy of the gases showed H_2 : HD : D_2 21.6 : 35.1 : 43.3 (*cf.* 1.2 : 12.5 : 86.4 for the gases obtained by treating the same batch of D_2O with lithium metal).

3. *Photochemical reactions of* $[RuCl(CO)(bipy)_2]Cl$. (*a*) *At room temperature*. A solution of $[RuCl(CO)(bipy)_2]Cl$ prepared as in 1(*a*) above was photolysed in a Schlenk tube attached to a gas-phase i.r. cell for 16 h. I.r. spectroscopy showed that only CO and not CO_2 was formed. Visible spectroscopy identified the orange product solution as containing $[RuCl(H_2O)(bipy)_2]Cl$.

(*b*) *At* 100 °C. A solution of $[RuCl(CO)(bipy)_2]Cl$ prepared as in 1(*a*) above was photolysed in a quartz u.v. cell stoppered with a serum cap at 100 °C. Analysis of the gases showed that both CO_2 (mass spectrum) and hydrogen (g.l.c. and mass spectrum) were formed.

In an identical experiment carried out in the apparatus described in 3(*a*) above, i.r. spectroscopy showed that both CO and CO_2 were present as products.

(*c*) *At* 100 °C *in* $H_2{}^{18}O$ *(20% enriched)*. The procedure was as in 3(*b*) above but using $H_2{}^{18}O$ (20% enriched). Mass spectroscopic analysis of the gases showed the presence of H_2, $C^{18}O$, and a statistical mixture of labelled CO_2 ($C^{16}O_2 : C^{16}O^{18}O : C^{18}O_2$ 69.5 : 27.2 : 4.6).

(*d*) *At* 100 °C *in* D_2O. The procedure was as 3(*b*) above but in D_2O mass spectroscopy showed only traces of H_2, HD, and D_2 (relative ratios 55.5 : 16.7 : 27.8).

B. Catalytic Reactions.—1. *General procedure*. Catalytic reactions were carried out in Fisher-Porter glass bottles of 95 cm^3 capacity closed with a screw-down pressure cap containing an integral tap. These were charged with a weighed quantity of catalyst, usually $[RuCl_2(bipy)_2]$ (0.01 g), and 5 cm^3 of solvent. After evacuation to remove air, the bottles were pressurised to the required reaction pressure. They were then heated to the reaction temperature in the dark for 1 h in an oil bath. At this point the solution was generally pale yellow (at high pH some blue solid was present at this stage) and was illuminated with the apparatus described in 2(*a*) above for 2 h whilst still in the oil bath. Care was taken to ensure that the vessel was against the side of the oil bath nearest to the lamp and that the level of oil was the same as the level of the liquid in the tube. At the end of the reaction the vessel was allowed to cool in the dark and the gases were analysed by sampling with a gas syringe *via* a serum cap placed over the exit of the tap and held in place with copper wire. All gas analyses were performed at least three times to check consistency and many catalytic reactions were carried out in duplicate. Errors were found to be *ca.* ±5%. Samples of gas (0.5 cm^3, at 1 atm) were used for H_2 analysis, whereas for CO_2, the non-linear response of the thermal conductivity detector necessitated the use of only 0.1 cm^3 samples. Calibration was carried out by injecting 1 cm^3 of H_2 (or CO_2) into the reactor containing 1 atm of air and water (5 cm^3). After shaking, the gases were analysed as described above. In H_2 determinations, allowance was made for the H_2 already present in the CO at the start of the reaction (typically 0.05—0.1 cm^3/100 cm^3 of CO). The solubility of CO, CO_2, and H_2 in water was neglected.

For reactions in pure water, as well as for the variation of rate with [catalyst] at pH 6.88, no initiation was carried out but reactions were allowed to run for 20 h.

Reactions involving Variation of pH.—Buffer solutions were prepared as follows. pH 4.8, KH_2PO_4 (0.5 mol dm^{-3}); pH 5.5, KH_2PO_4 (50 cm^3, 0.1 mol dm^{-3}) + NaOH (3.6 cm^3, 0.1 mol dm^{-3}); pH 6.1, KH_2PO_4 (0.375 mol dm^{-3}) + Na_2HPO_4 (0.125 mol dm^{-3}); pH 6.88, KH_2PO_4 (0.25 mol dm^{-3}) + Na_2HPO_4 (0.25 mol dm^{-3}); pH 7.15, KH_2PO_4 (0.375 mol dm^{-3}) + Na_2HPO_4 (0.125 mol dm^{-3}); pH 7.6, KH_2PO_4 (50 cm^3, 0.1 mol dm^{-3}) + NaOH (42.8 cm^3, 0.1 mol dm^{-3}); pH 8.9, Na_2HPO_4 (0.5 mol dm^{-3}) or $Na_2B_4O_7$ (50 cm^3, 0.025 mol dm^{-3}) + HCl (7.1 cm^3, 0.1 mol dm^{-3}) or $Na_2B_4O_7$ (50 cm^3, 0.025 mol dm^{-3}) + H_2SO_4 (7.1 cm^3, 0.05 mol dm^{-3}); pH 10, $Na_2B_4O_7$ (50 cm^3, 0.025 mol dm^{-3}) + NaOH (18.3 cm^3, 0.1 mol dm^{-3}); pH 10.8, $Na_2B_4O_7$ (50 cm^3, 0.025 mol dm^{-3}) + NaOH (24.25 cm^3, 0.1 mol dm^{-3}); pH 12.2, Na_2HPO_4 (50 cm^3, 0.025 mol dm^{-3}) + NaOH (26.9 cm^3, 0.1 mol dm^{-3}).

Reactions involving Variation of Light Intensity.—These were carried out as described above under the general procedure, but gauze filters were placed between the lens and the reactor (close to the reactor). The transmittance of the gauzes was measured on an i.r. spectrometer using rotating sectors of known angle for calibration purposes.

Effect of Activation Time on Rate of Hydrogen Production.—A catalytic reaction was performed using the general procedure described above with pH 6.1 buffer and under 1 atm CO. Gas analysis gave the formation of hydrogen (0.19 cm^3 at 22 °C and 1 atm). The solution was orange after the initiation period, rapidly turning to yellow as illumination was started. An identical reaction but with 2 h preheating in the dark again afforded hydrogen (0.33 cm^3) and the solution was pale yellow after initiation.

Reaction in Deuteriated Buffer.—A buffer solution (pH 9.2) was prepared from $Na_2B_4O_7$ (0.046 g) in D_2O (5 cm^3). This was used for a standard catalytic reaction at 140 °C and p_{CO} = 3 atm; analysis of the gases showed the presence of 2.42 cm^3 of D_2 (g.l.c.).

Identification of the Active Species.—$[RuCl(CO)(bipy)_2]Cl$ (0.095 g) was heated in water (5 cm^3) at 140 °C for 3 h. Addition of KPF_6 to this solution afforded a yellow precipitate which was collected, washed with water, and dried *in vacuo*. The solid had an i.r. spectrum identical to that of [RuCl(CO)(bipy)$_2$][PF$_6$] [ν(C≡O) 1 960 cm^{-1}].[7]

An identical experiment but using [RuCl(CO)(phen)$_2$]Cl (0.2 g) in water (20 cm^3) for 20 h at 100 °C gave a yellow solid which was mostly [RuCl(CO)(phen)$_2$][PF$_6$] [ν(C≡O) 1 967 cm^{-1}][7] but also contained small amounts of *cis*-[Ru(CO)$_2$(phen)$_2$][PF$_6$]$_2$ [ν(C≡O) 2 092 and 2 028 cm^{-1}].[7]

Experiment at High Conversion.—Carbon dioxide was bubbled through a standard catalytic solution at pH 8.9 in a 95 cm^3 pressure bottle. The bottle was quickly closed and pressurised to 3 atm with hydrogen. CO (1 cm^3) was injected into the bottle *via* a serum cap placed over the exit of the valve and thoroughly mixed. The valve was closed and the vessel heated to 140 °C for 16 h. Analysis for CO by g.l.c. showed no detectable peak (minimum detectable amount: 0.05 cm^3).

Attempted Photochemical Reactions of Other Substrates with Water under Pressure.—(*i*) *Ethene.* The procedure was as for the general catalytic reactions, but using ethene (3 atm) for 3 days. Periodic sampling showed small amounts of H$_2$ (0.2 cm^3) to be formed during the early part of the reaction but none later on.

(*ii*) *Allyl alcohol.* [RuCl$_2$(bipy)$_2$] (0.01 g) was heated under irradiation in water (5 cm^3) containing allyl alcohol (0.5 cm^3) for 40 h. Small amounts of hydrogen (0.36 cm^3) were produced but further heating showed no increase in the amount of hydrogen. (One catalyst turnover corresponds to 0.43 cm^3 of hydrogen.)

(*iii*) *Diethyl maleate.* The procedure was as (*ii*) above, but using diethyl maleate (0.5 cm^3) in place of allyl alcohol. No hydrogen was detected as a product, but large amounts of CO$_2$ were formed.

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