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PHOTOCATALYTIC DEHYDROGENATION OF PROPAN-2-OL USING RHODIUM BASED CATALYSTS

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Summary

We have discovered that efficient photogeneration of hydrogen, from propan-2-ol can be achieved with a number of preformed Rh^I complexes, as well as $RhCl_3$ in the presence of Ph_3PO or Ph_3P, after exposure to air. The catalyst turnovers, for the Rh^I species are in the range of 2000–6000 mmol H_2 h^{-1} mmol Rh^{-1}, which are much higher than those previously claimed for such photolytic systems. The $RhCl_3$ based systems are however of lower activity (~ 1000 turnovers). Overall the systems appear to be catalytic even over long irradiation periods, where no reduction of gas evolution has been observed.

Introduction

The photogeneration of catalytically active organometallic species in homogeneous organic reactions has become of interest in a large number of areas [1]. Particular interest has recently been devoted to the photolytic dehydrogenation of propan-2-ol as a possible energy storage system [2,3]. This reaction is attractive since the reaction shown in eq. 1 is endoergic, with $\Delta G^{\ominus}$ 32 kJ mol^{-1}, resulting in spontaneous separation of hydrogen into the gas phase above the reaction liquid.

$$(CH_3)_2CHOH \rightarrow (CH_3)_2CO + H_2 \qquad (1)$$

Recent studies [2,3] has shown that catalytic systems, based on rhodium species, can dehydrogenate propan-2-ol although low catalyst efficiencies have been observed. Sugi [4] however in his investigation on replace with dehydrogenation of propan-2-ol, using $RhCl(PPh_3)_3$ as catalyst, has found that efficient hydrogen evolution can be obtained after exposure to air and particularly oxygen.

We have investigated the photolysis of $RhCl(PPh_3)_3$ in propan-2-ol, after exposure to air, and report here some preliminary results on this and other rhodium-based dehydrogenations of propan-2-ol.

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Experimental

All photolyses were carried out at 21°C using a water cooled 125 W medium pressure lamp, with an immersion well reactor. Gas evolutions were measured by a thermostatted gas burette connected to the immersion well reactor. $RhCl(PPh_3)_3$, $RhCl[P(OPh)_3]_3$ and Ph_3PO were prepared by, or with slight modifications to, the literature methods [5–7], and stored under nitrogen in the absence of light prior to use. Propan-2-ol (Fisons $\geqslant 99\%$ by GLC) and "$RhCl_3 \cdot 3H_2O$" (Johnson-Matthey) were used as received.

A typical photolysis was as follows: a known weight of rhodium compound ($\sim$ 10–15 mg) was added to propan-2-ol (150 ml) in the immersion well reactor. The mixture was then stirred, in direct contact with air, for 30–40 min [4]. After this time the system was closed to the air (by addition of the lamp housing), the photolysis begun with stirring (600 rpm) and gas evolution monitored over a set period.

Photocatalytic hydrogen evolution from propan-2-ol using $RhCl(PPh_3)_3$

Although exact experimental duplication of Sugi's work was not possible e.g. reactor size, photon source, initial experiments showed that the rate of hydrogen evolution was dependent on reactor mixing characteristics. In particular the stirring speed was found to affect the gas evolution up to 600 rpm (as measured by a tachometer). Above 600 rpm the effect was constant, consequently all experiments were carried out at this speed, using 150 ml of solvent.

Generally the overall features observed by Sugi were duplicated e.g. induction periods before gas evolution, restarting of gas evolution after restarting the photolysis [4]. However the catalyst turnovers observed in our work, measured in mmol H_2 h^{-1} mmol Rh^{-1}, have been found to be twice those calculated from Sugi's work, as shown in Table 1. The induction period observed before gas evolution was also found to be shorter i.e. 30 min compared to 45 min.

From a series of control experiments it was found that:

(i) The reaction was strongly wavelength dependent, with hydrogen evolution being produced with light $\lambda \leqslant 300$ nm. All attempts to use light of longer wavelength to liberate H_2 were unsuccessful e.g. 150 W solar light $\geqslant 400$ nm.

(ii) Preconditioning solutions, prior to photolysis, by stirring in contact with air could be achieved by gently bubbling air through a prospective photolysis solution for 5 min.

(iii) Addition of Ph_3P (1–10 equiv. per rhodium atom) increased the induction

TABLE 1

HYDROGEN EVOLUTION BY PHOTOLYSIS OF PROPAN-2-OL (125 W Hg LAMP) WITH $RhCl(PPh_3)_3$ AT 21°C

Induction period (min)	Rhodium added (μmol)	H_2 evolved		Catalyst turnovers [a]
		(ml h^{-1})	(mmol h^{-1})	
30	1.2	156	6.50	5415
45	1.1	70	2.92	2655 [b]

[a] Measured in mmol H_2 h^{-1} mmol Rh^{-1} and obtained 2 h after the induction period. [b] Reference 4.

period observed before gas evolution, which was initially slower than observed with no added PPh_3. However continued photolysis (> 6 h) affords gas evolutions, and hence catalyst turnovers, approaching those seen without Ph_3P present.

The reason for the enhanced gas evolution observed in our experiments is not clear, particularly as our catalyst concentration, 7.5 μM, is below the optimum observed by Sugi i.e., 10–40 μM. The difference in gas evolution we believe is due to increased diffusion effects in our photolysis apparatus. This effectively aids hydrogen outgassing at the experimental determined, optimal stirring speed. The wavelength dependence of the reaction is very similar to that observed in the photolytic dehydrogenation of propan-2-ol using rhodium-tin complexes [2].

Photocatalytic hydrogen evolution from propan-2-ol with Rh^I complexes other than $RhCl(PPh_3)_3$

Catalyst systems based on Rh^I systems, other than $RhCl(PPh_3)_3$, have been investigated for the photogeneration of hydrogen from propan-2-ol. Preliminary experiments have initially centred on Rh^I complexes containing potentially photolabile ligands; with this in mind $[RhCl(CO)_2]_2$, $[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) and $RhCl[P(OPh)_3]_3$ were photolysed typically using $\sim 1 \times 10^{-2}$ mmol of catalyst in 150 ml of propan-2-ol. Hydrogen evolution was obtained in all the above cases, as well as when Ph_3P was added to the above compounds, as shown in Table 2.

With $[RhCl(CO)_2]_2$ and $RhCl[P(OPh)_3]_3$ the gas evolutions observed were higher than that for $RhCl(PPh_3)_3$; $[RhCl(COD)]_2$ was found to be ~ 10% as active as $RhCl(PPh_3)_3$. However addition of 1 equiv. of Ph_3P to $[RhCl(COD)]_2$ caused a dramatic increase in gas evolution i.e. 23 to 203 ml h^{-1} at 21°C, with a 50% reduction in the induction period. With $[RhCl(CO)_2]_2$ addition of 1 equiv. of Ph_3P resulted in a drop in gas evolution and a two fold increase in the induction period. While the highest gas evolution is observed with $[RhCl(COD)_2]_2$ with 1 equiv. of added Ph_3P, the most efficient catalyst in terms of turnovers observed is $RhCl[P(OPh)_3]_3$ at ~ 6400 mmol H_2 h^{-1} mmol Rh^{-1}. The catalytic activity displayed by $RhCl[P(OPh)_3]_3$ exceeds that seen for $RhCl(PPh_3)_3$ in our studies by

TABLE 2

HYDROGEN EVOLUTION BY PHOTOLYSIS OF PROPAN-2-OL (125 W Hg LAMP) IN THE PRESENCE OF $\sim 1 \times 10^{-2}$ mmol Rh^I SPECIES AT 21° C

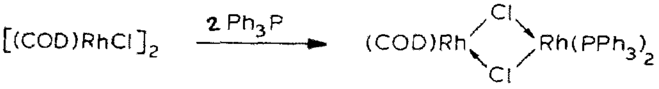
Catalyst	Induction period (min)	Rhodium added (μmol)	H_2 evolved		Catalyst turnover rates [a]
			(ml h^{-1})	(mmol h^{-1})	
$RhCl(PPh_3)_3$	30	2.3	156	6.50	5370
$RhCl[P(OPh)_3]_3$	30	1.3	200	8.33	6410
$[RhCl(COD)]_2$	50	2.4	23	0.95	395
$[RhCl(CO)_2]_2$	20	2.7	193	8.04	2980
$[RhCl(COD)]_2$ + 1 equiv. PPh_3	25	2.1	203	8.46	4030
$[RhCl(CO)_2]_2$ + 1 equiv. PPh_3	40	3.3	174	7.25	2200

[a] Measured in mmol H_2 h^{-1} mmol Rh^{-1} and obtained > 2 h after the induction period.

~ 20%, and is also 500 times that observed for photolytic dehydrogenation of propan-2-ol at reflux, using homogeneous rhodium-tin complexes [2].

Of interest in these alternative Rh^I based systems is the effect of added phosphine to $[RhCl(COD)]_2$, where a dramatic increase in gas evolution was seen. The action of Ph_3P in this reaction may take two possible courses:

(i) "COD" displacement, affording a dimeric species [8] i.e.,



or

(ii) Generation of a four coordinate, monomeric Rh^I species without COD displacement [9] i.e.,

$$[(COD)RhCl]_2 \xrightarrow{2Ph_3P} 2(COD)RhCl(PPh_3)$$

Both options, assuming no initial oxidation to Ph_3PO, are then able to produce coordinatively unsaturated rhodium species under the photolysis conditions e.g. by oxidation of Ph_3P to Ph_3PO followed by Ph_3PO dissociation. Our results to date allow no distinction between either of these options; indeed both mechanisms may be operating, producing a common photocatalyst under the photolytic reaction conditions. The apparently deleterious action of Ph_3P addition to $[RhCl(CO)_2]_2$ may be due to the higher bonding characteristics of the carbonyl ligand, compared to COD, preventing ready photolytic or thermal substitution with Ph_3P.

TABLE 3

HYDROGEN EVOLUTION BY PHOTOLYSIS OF PROPAN-2-OL (125 W Hg LAMP) IN THE PRESENCE OF $RhCl_3$ WITH ADDED PPh_3 or $OPPh_3$, AT 21°C

Catalyst	Induction period (min)	Rhodium added (μmol)	H_2 evolved		Catalyst turnover rates [a]
			(ml h^{-1})	(mmol h^{-1})	
$RhCl_3$	–	4.8	–	–	–
$RhCl_3$ + 1 equiv. PPh_3	100	5.0	51	2.10	420
$RhCl_3$ + 2.2 equiv. PPh_3	60	4.9	54.5	2.27	463
$RhCl_3$ + 3 equiv. PPh_3	25	4.9	56	2.30	500
$RhCl_3$ + 6 equiv. PPh_3	5	5.4	113	4.70	870
$RhCl_3$ + 10 equiv. PPh_3	3	5.4	93	3.90	720
$RhCl_3$ + 1 equiv. $OPPh_3$	30	5.6	143	5.90	1054
$RhCl_3$ + 3 equiv. $OPPh_3$	80	5.4	100	4.15	769
$RhCl_3$ + 6 equiv. $OPPh_3$	80	5.4	100	4.15	769

[a] Measured in mmol H^2 h^{-1} mmol Rh^{-1} and obtained > 2 h after the induction period.

Photocatalytic hydrogen evolution from propan-2-ol with $RhCl_3$ and Ph_3P or Ph_3PO

We have investigated the use of $RhCl_3$, supplied as a "$RhCl_3 \cdot 3H_2O$", as a photocatalyst in the absence and presence of added Ph_3P and Ph_3PO.

Consistent with previous studies [4], photolysis of $RhCl_3$ in propan-2-ol gave no gas evolution, even on prolonged irradiation (> 6 h). However on addition of either Ph_3P (1–10 equiv. per rhodium atom) or Ph_3PO (1–6 equiv. per rhodium atom), prior to irradiation, efficient hydrogen evolution was obtained on photolysis, as shown in Table 3. Addition of Ph_3PO gave a slightly higher turnover rate when 1 equiv. was present i.e. 1054 mmol H_2 h^{-1} mmol Rh^{-1}. The highest turnover for added Ph_3P with $RhCl_3$ was found to be 870 mmol H_2 h^{-1} mmol Rh^{-1} when 6 equiv. of Ph_3P were added. While hydrogen evolution is observed on Ph_3P or Ph_3PO addition—in contrast to no evolution when just $RhCl_3$ is photolysed—the catalyst turnovers are still lower than the majority of preformed Rh^I complexes studied in this work (see Table 2).

From the experiments conducted to date it appears that photolysis of $RhCl_3/PPh_3$ or $RhCl_3/OPPh_3$, in propan-2-ol, does not generate a photocatalyst in situ of comparable catalytic activity to that obtained with $RhCl(PPh_3)_3$ under similar reaction conditions. Triphenylphosphine oxide does appear to play a key role in gas evolution e.g., as a labile ligand towards a coordinatively unsaturated rhodium species, enabling a fully catalytic cycle to proceed. It is of interest to note that addition of Ph_3P to $Rh_2(OAc)_4$ assists the thermal dehydrogenation of propan-2-ol, while $Rh_2(OAc)_4$ alone is inactive in this task [10]. Consequently other systems based on Ir, Ru and Rh hydrogenation catalysts with added phosphines may also be efficient photodehydrogenation catalysts.

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