Solvent effect for oxidative addition of hydrogen in solvents from toluene to water: reaction of H_2 with *trans*-$[Ir(CO)Cl\{PPh_2(C_6H_4SO_3K\text{-}m)\}_2]$

David P. Paterniti, Paul J. Roman, Jr. and Jim D. Atwood*

Department of Chemistry, University at Buffalo, State University of New York, Buffalo, NY 14260-3000, USA

A significant enhancement in the rate of oxidative addition of H_2 to square-planar iridium(I) complexes in water is observed; kinetic studies of the addition of H_2 to *trans*-$[Ir(CO)Cl(PPh_3)_2]$ in toluene and of H_2 to *trans*-$[Ir(CO)Cl\{PPh_2(C_6H_4SO_3K\text{-}m)\}_2]$ in water show a factor of 45 increase in rate constant in water; this solvent effect is shown to be general for the solvents toluene, chlorobenzene, *N,N*-dimethylformamide, dimethyl sulfoxide and water, and has important ramifications for catalysis in water.

Research aimed at catalysis in water, or at a water/organic solvent interface, has greatly expanded in recent years.[1–5] The impetus derives from reducing the role of organic solvents and from easier separation of products. Industrial production of butanal using rhodium catalysts with a water-soluble phosphine $[P(C_6H_4SO_3Na)_3$ = tppts] in a hydroformylation reaction provides an example.[4,6] A number of other catalytic reactions have also been described; the most numerous studies of catalytic reactions by organometallic complexes in aqueous solution involve the use of water-soluble phosphine ligands.[1–4,7,8] In most examples the catalytic reactions in water are similar to reactions in organic solvents, although somewhat different isomer ratios were observed in hydroformylation.[6,8] The studies of catalytic reactions, in general, have not been accompanied by stoichiometric reactions examining the differences provided by aqueous solution. Here, we report a study of the solvent effect for reaction of H_2 with *trans*-$[Ir(CO)Cl(tppms)_2]$ [tppms = $PPh_2(C_6H_4SO_3K\text{-}m)$] as a comparison to the reaction of H_2 with *trans*-$[Ir(CO)Cl(PPh_3)_2]$.

The ligand, tppms, was prepared as previously described.[9] The complex *trans*-$[Ir(CO)Cl(tppms)_2]$ was prepared by ligand exchange with *trans*-$[Ir(CO)Cl(PPh_3)_2]$ in thf, from which the product precipitated [eqn. (1)].†

$$trans\text{-}[Ir(CO)Cl(PPh_3)_2] + tppms \xrightarrow{thf} trans\text{-}[Ir(CO)Cl(tppms)_2](\downarrow) \quad (1)$$

The characterization data are all consistent with a square-planar, iridium(I) complex. The complex *trans*-$[Ir(CO)Cl(tppms)_2]$ reacts with H_2 in H_2O or Me_2SO to give $[Ir(CO)Cl(H)_2(tppms)_2]$‡ [eqn. (2)], similar to the reaction of *trans*-$[Ir(CO)Cl(PPh_3)_2]$ with H_2 in toluene.[10]

$$trans\text{-}[Ir(CO)Cl(tppms)_2] + H_2 \longrightarrow [Ir(CO)Cl(H)_2(tppms)_2] \quad (2)$$

The similarity of the complexes *trans*-$[Ir(CO)Cl(tppms)_2]$ and *trans*-$[Ir(CO)Cl(PPh_3)_2]$ and their reactions with H_2 offers an excellent opportunity to examine kinetically the effect of solvent on oxidative addition of H_2. The kinetics of H_2 addition to *trans*-$[Ir(CO)Cl(PPh_3)_2]$ were previously examined in toluene by gas uptake experiments showing an overall second-order reaction, first order in iridium complex and first order in H_2 [eqn. (3)]:

$$\text{rate} = k_{\text{toluene}}[trans\text{-}Ir(CO)Cl(PPh_3)_2][H_2] \quad (3)$$

with a rate constant, $k_{\text{toluene}} = 0.34\ \text{M}^{-1}\ \text{s}^{-1}$ at 20 °C.[11,12] We have repeated these studies using UV–VIS spectra§ and obtained a value of $k_{\text{toluene}} = 0.26 \pm 0.07\ \text{M}^{-1}\ \text{s}^{-1}$ at 21 °C, in satisfactory agreement with the earlier study. Reaction of *trans*-$[Ir(CO)Cl(tppms)_2]$ with H_2 in water occurs more rapidly, also with a rate law [eqn. (4)]:

$$\text{rate} = k_{\text{water}}[trans\text{-}Ir(CO)Cl(tppms)_2][H_2] \quad (4)$$

first order in iridium complex and in $[H_2]$.¶ The kinetic studies were run under pseudo-first-order conditions with H_2 in excess; plots of k_{obs} *vs.* $[H_2]$ are shown in Fig. 1 for several reactions. The k_{water} value was $12 \pm 3\ \text{M}^{-1}\ \text{s}^{-1}$ at 95% confidence limits.

To directly compare the rates of H_2 addition for the complexes *trans*-$[Ir(CO)Cl(PPh_3)_2]$ and *trans*-$[Ir(CO)Cl(tppms)_2]$, Me_2SO is an appropriate solvent. The rate constants determined for H_2 addition to Ir^I complexes in various solvents are shown in Table 1.§ The rate constants for *trans*-$[Ir(CO)Cl(PPh_3)_2]$ and *trans*-$[Ir(CO)Cl(tppms)]$ in Me_2SO are identical within experimental error, indicating that sulfonation of the phosphine ligand has no effect on the rate of H_2 addition. The similarity of these two complexes allows the solvent effect for H_2 addition to be considerably expanded. Previously reported values for *trans*-$[Ir(CO)Cl(PPh_3)_2]$ in toluene, chloro-

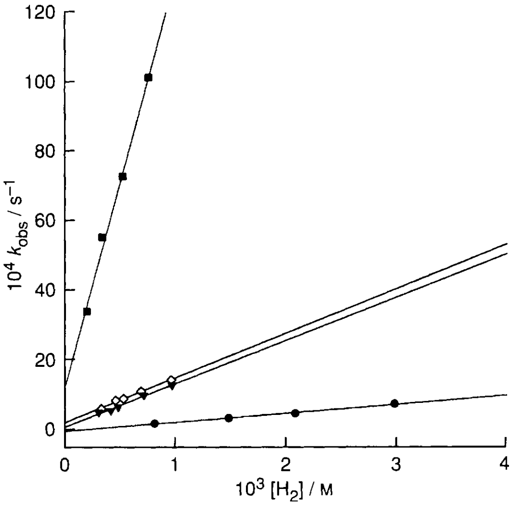

Fig. 1 Plots of k_{obs} *vs.* $[H_2]$ M for reaction of H_2 with square-planar iridium(I) complexes at 21 °C: (●) *trans*-$[Ir(CO)Cl(PPh_3)_2]$ in toluene; (▼) *trans*-$[Ir(CO)Cl(PPh_3)_2]$ in Me_2SO; (◇) *trans*-$[Ir(CO)Cl(tppms)_2]$ in Me_2SO and (■) *trans*-$[Ir(CO)Cl(tppms)_2]$ in H_2O. For each of the plots the *y* intercept includes zero within the error limits.

Table 1 Second-order rate constants for reactions of iridium complexes with H_2 and D_2 in various solvents at 21 °C

Reaction	10^5 [M]/M	$k^a/\text{M}^{-1}\ \text{s}^{-1}$	Solvent
trans-$[Ir(CO)Cl(PPh_3)_2]$ + H_2	6.8	0.26 ± 0.07	Toluene
trans-$[Ir(CO)Cl(PPh_3)_2]$ + H_2	1.9	1.2 ± 0.2	Me_2SO
trans-$[Ir(CO)Cl(tppms)_2]$ + H_2	1.38	1.3 ± 0.2	Me_2SO
trans-$[Ir(CO)Cl(tppms)_2]$ + H_2	1.54	12 ± 3	Water
trans-$[Ir(CO)Cl(tppms)_2]$ + D_2	1.36	11 ± 2	Water

[a] Error limits reported at the 95% confidence level.

benzene and dmf[12] can now be extended to Me_2SO and, using *trans*-[Ir(CO)Cl(tppms)$_2$], to water. The acceleration in rate of H_2 addition in polar solvents[12] continues with the rate constant in Me_2SO a factor of five greater than toluene and the rate constant in H_2O a factor of 40 greater. A number of solvent effect parameters have been used and a summary indicates good correlations between them;[15] the most comprehensive data are available for E_T parameters which is the charge-transfer transition energy for a pyridinium salt.[15] Fig. 2 shows a plot of the data for oxidative addition of H_2 to *trans*-[Ir(CO)Cl(PPh$_3$)$_2$] and *trans*-[Ir(CO)Cl(tppms)$_2$] correlated with the E_T values. The good correlation for solvents ranging from toluene to water indicates a common mechanism.

As observed for addition of H_2 or D_2 to *trans*-[Ir(CO)Cl(PPh$_3$)$_2$] in toluene (k_H/k_D = 1.1)[16] the deuterium isotope effect for H_2 or D_2 addition to *trans*-[Ir(CO)Cl(tppms)$_2$] in water is small (1.1). The presence of excess Cl^- (added as KCl)[||] or excess tppms had no significant effect on the rate of H_2 oxidative addition in H_2O. Thus the mechanism must involve direct addition of H_2 to the square-planar iridium complex with an early transition state involving very little H–H bond breaking. There is no evidence in our studies to distinguish a transition state with molecular hydrogen bound from a transition state with only a small amount of H–H bond breaking.

The good correlation of log *k vs.* E_T for solvents ranging from toluene to water (Fig. 2) and a constant, small deuterium isotope effect indicates no change in mechanism with solvent for H_2 oxidative addition to *trans*-[Ir(CO)(Cl)L$_2$]. In an earlier study, the solvent effect was suggested to arise from a more polar six-coordinate transition state than reactants, and dipole moment studies of *trans*-[Ir(CO)Cl(PPh$_3$)$_2$] and [Ir(CO)Cl(H)$_2$(PPh$_3$)$_2$] were used to support this explanation.[12] Since the transition state is very early, [Ir(CO)Cl(H)$_2$(PPh$_3$)$_2$] is a poor model. The pseudo-five-coordinate, molecular hydrogen complex would be a more appropriate model for the transition state. In molecular hydrogen complexes, the initial interaction is donation of the H–H σ-bond density to the metal.[17] Such an interaction creates positive charge on the hydrogen atoms and would lead to a more polar transition state.[17]

A general solvent effect for H_2 addition to *trans*-[Ir(CO)ClL$_2$] for solvents from toluene to water gives nearly a factor of 50 increase in rate for the more polar solvent. This observation has important ramifications for extension of non-aqueous catalytic processes to aqueous solution. Acceleration of hydrogenation in polar solvents has been observed in systems for copper(II) salts,[18] [Co(CN)$_5$H]$^{3-}$,[19] [RhCl(PPh$_3$)$_3$],[20] and now [Ir(CO)ClL$_2$]. A general interpretation may be possible.

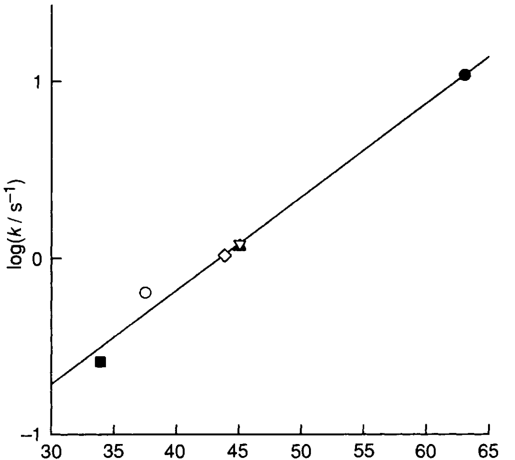

Fig. 2 Correlation of log *k* with solvent parameter E_T [the transition energy for the longest wavelength absorption band for 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate].[15] (■) *trans*-[Ir(CO)Cl(PPh$_3$)$_2$] in toluene; (○) *trans*-[Ir(CO)Cl(PPh$_3$)$_2$] in chlorobenzene; (◇) *trans*-[Ir(CO)Cl(PPh$_3$)$_2$] in dmf; (▲) *trans*-[Ir(CO)Cl(PPh$_3$)$_2$] in Me_2SO; (▽) *trans*-[Ir(CO)Cl(tppms)$_2$] in Me_2SO and (●) *trans*-[Ir(CO)Cl(tppms)$_2$] in H_2O.

Footnotes

† In an inert atmosphere glovebox, a 125 ml Ehrlenmeyer flask equipped with a magnetic stir bar was charged with 0.530 g of tppms (1.3×10^{-3} mol) and 0.500 g *trans*-[Ir(CO)Cl(PPh$_3$)$_2$] (6.4×10^{-4} mol). 50 ml of thf were added (diethyl ether was also used as a solvent) and the reaction mixture stirred overnight in the glove box. The yellow precipitate was filtered from the reaction mixture using a fine sintered glass frit and washed with *ca.* 75 ml of benzene to remove any unreacted starting complex or free triphenylphosphine. After drying overnight in the glovebox 0.42 g of yellow powder remained. This corresponds to a 60% yield based on starting iridium complex. IR(KBr): 1962 cm^{-1}. ^{31}P NMR [(CD$_3$)$_2$SO], δ 25.6. Anal. Calc. for {Ir(CO)Cl{PPh$_2$(C$_6$H$_4$SO$_3$K·H$_2$O)}$_2$]: C, 42.2; H, 3.1; P, 5.9, S, 6.1; K, 7.4). Found: C, 42.6; H, 3.4; P, 5.8; S, 5.7; K, 7.1%.

‡ Characterization of [Ir(CO)Cl(H)$_2$(tppms)$_2$]: ^{1}H NMR [(CD$_3$)$_2$SO], δ −8.3 (td, J_{PH} 17.6, J_{HH} 4.8 Hz), −20.4 (td, J_{PH} 14.0, J_{HH} 4.8 Hz); ^{31}P NMR, δ 11.6; IR (Me_2SO), ν_{CO} = 1990, ν_{IrH} 2093 s, 2204 w, cm^{-1}.

§ For *trans*-[Ir(CO)Cl(PPh$_3$)$_2$] in toluene the 388 nm absorption was monitored as a function of time with various concentrations of H_2. The k_{obs} values were plotted *vs.* [H_2] to give the $k_{toluene}$ value. Similarly, *trans*-[Ir(CO)Cl(tppms)$_2$] was monitored at 374 nm to give the k_{water} value. Error limits in rate constants are 95% confidence limits.

¶ [H_2] in each solvent is calculated from the mole fraction solubility assuming that Henry's law applies for pressures < 1 atm. In general, the solubility of H_2 is about 10 times lower in H_2O than toluene.[13] The values[13,14] used in data for Fig. 1 are in terms of [H_2]/M. In a typical experiment in H_2O, [*trans*-Ir(CO)Cl(tppms)$_2$] = 1.5×10^{-5} M and [H_2] is in the range 2–8 × 10^{-4} M.

|| Stock solutions containing [Ir(CO)Cl(tppms)$_2$] and KCl (1.74×10^{-5} or 17.4×10^{-5} M) in H_2O were treated with H_2 and the rates determined at 21 °C. With no added KCl, $k_{obs} = 9.7 \pm 0.8 \times 10^{-3}$ s^{-1}; with added KCl the rate constants were $k_{obs} = 8.3 \pm 0.7 \times 10^{-3}$ s^{-1} and $= 8.8 \pm 0.8 \times 10^{-3}$ s^{-1} for 1.74×10^{-5} and 17.4×10^{-5} M KCl, respectively. Error limits are quoted as 95% confidence limits.

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