Available online at www.sciencedirect.com
ScienceDirect
Journal of Molecular Catalysis A: Chemical 267 (2007) 218–223
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Transition metal catalyzed D_2/H_2O exchange: Distinguishing between the single and double exchange pathways

Jennifer L. Carriker [a], Paul S. Wagenknecht [a,*], Mitra A. Hosseini [b], Patrick E. Fleming [b]

[a] *Department of Chemistry, Furman University, Greenville, SC 29613, United States*
[b] *Department of Chemistry, San Jose State University, San Jose, CA 95192, United States*

Received 21 September 2006; received in revised form 20 November 2006; accepted 21 November 2006
Available online 26 November 2006

Abstract

Isotopic exchange between D_2 (g) and H_2O (l) is catalyzed by the water soluble complexes $Rh(TPPTS)_3Cl$ and $Rh(TPPMS)_3Cl$ (where TPPTS = tris(3-sulfonatophenyl)phosphine, trisodium salt and TPPMS = 3-sulfonatophenyldiphenylphosphine, sodium salt). This isotope exchange has been monitored by gas chromatographic analysis of the gaseous headspace over the aqueous catalyst solution. Upon binding to the catalyst, the hydrogen isotopologues can either exchange one or both atoms with solvent. Kinetic schemes have been developed for both situations. Analysis of exchange data demonstrates that for both catalysts at pH ≥ 8 the D_2 molecule only undergoes one exchange event per visit to the active site. At lower pH values this changes. $Rh(TPPMS)_3Cl$ shows evidence of double exchange at pH 7 and below. $Rh(TPPTS)_3Cl$ shows evidence of double exchange at pH 6 and below. Rate constants for both single and double exchange can be determined and have been analyzed in the pH range from 3 to 12. Mechanistic implications of the rate constants are discussed.

Keywords: H/D exchange; Hydrogenase enzymes; Dihydrogen complex acidity; Kinetics; Water soluble phosphines; H_2/D_2O exchange

1. Introduction

Transition metal catalyzed H_2/D^+ and D_2/H^+ exchange reactions, where the H^+ and D^+ originate from water or alcohols, have been of significant interest because of the relevance of these processes to the study of the hydrogenase enzymes [1–11], transition metal dihydrogen complexes [7–13], and catalytic hydrogenations [14–17]. For example, the D_2/H_2O exchange catalyzed by the hydrogenase enzymes has been instrumental in monitoring the activity and studying the mechanism of this important class of enzymes [1–4,18–26]. Consequently, this exchange process has often been a primary screening tool for functional models of the hydrogenase enzymes [5–11]. Such functional models usually invoke heterolytic cleavage of dihydrogen through the intermediacy of a transition metal dihydrogen complex [7–13]. Recent interest in performing hydrogenations in aqueous solution has also kindled an interest in the ability of water soluble hydrogenation catalysts to catalyze this type of H/D exchange [15–17].

Exchange studies involving the hydrogenase enzymes often employ a mass spectroscopic measurement of the gaseous products in the headspace over a solution of the enzyme [1,3,4,18–26]. Such studies can distinguish between single exchange (Eq. (1)) and double exchange (Eq. (2)).

$$D_2 + H_2O \rightarrow HD + HDO \quad (1)$$

$$D_2 + 2H_2O \rightarrow H_2 + 2HDO \quad (2)$$

The distinction here is whether only one nucleus of D_2 exchanges or both nuclei exchange during one visit to the active site. The observation of more H_2 than HD in the headspace at early reaction times indicates that double exchange predominates. However, it is worth noting that the observation of initial H_2/HD ratios greater than one in the headspace could also result from reaction of HD with a second enzyme molecule before escaping from the aqueous phase into the gas phase. If this were the case, increasing the concentration of the enzyme would increase the observed H_2/HD ratio. This test has commonly been employed in studies of hydrogenase enzymes in order to distinguish between true double exchange and the more trivial concentration dependent case [18–21]. Different hydrogenase enzymes differ in both

* Corresponding author. Tel.: +1 864 294 2905; fax: +1 864 294 3559.
E-mail address: paul.wagenknecht@furman.edu (P.S. Wagenknecht).

1381-1169/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2006.11.037

their capacity to facilitate double exchange [3,18–25] and in their overall exchange activity as a function of pH [3,18–26].

Most studies with transition metal complexes, on the other hand, have been performed by ^{1}H NMR studies of H_2/D_2O exchange. Here the total isotopic exchange is monitored by measuring the increase in the HDO signal with time. Thus, no distinction can be made between single exchange and double exchange. Even if H_2O were formed in a double exchange it would result in HDO due to rapid isotope exchange. We have been particularly intrigued with reports by Kovács et al. concerning H_2/D_2O exchange catalyzed by ruthenium and rhodium complexes with water soluble phosphines such as TPPTS (tris(3-sulfonatophenyl)phosphine, trisodium salt) and TPPMS (3-sulfonatophenyldiphenylphosphine, sodium salt) [15–17]. These reports demonstrate that the pH profile of the turnover frequency (TOF) is asymmetric. At high pH (∼11–12), no exchange is observed, whereas the TOF approaches a constant value at low pH. We have been curious to determine if there is any difference in single versus double exchange for these systems as a function of pH and to use such information to gain a better mechanistic understanding of these processes. Adding to our interest in the $Rh(TPPTS)_3Cl$ and $Rh(TPPMS)_3Cl$ complexes is that complexes of this type have been shown to be catalysts for the reduction of $NAD(P)^+$ to NAD(P)H using hydrogen gas [27]. Herein, we report the measurement of D_2/H_2O exchange with $Rh(TPPTS)_3Cl$ and $Rh(TPPMS)_3Cl$ as a function of pH using a gas chromatographic method that distinguishes between single and double exchange. These studies demonstrate that under basic conditions a single exchange mechanism predominates, whereas under acidic conditions there is a significant component of double exchange. Mechanistic implications of this discovery will be discussed.

2. Experimental

2.1. Materials and methods

$Rh(TPPMS)_3Cl$ [28] and $[RhCl(\eta^2\text{-}C_2H_4)_2]_2$ [29] were prepared according to the literature procedures. $Rh(TPPTS)_3Cl$ was prepared by a slight modification of Method C by Herrmann and Kohlpaintner [30] where $[RhCl(\eta^2\text{-}C_2H_4)_2]_2$ was used in place of $[RhCl(\eta^4\text{-}C_8H_{12})]_2$. Buffer solutions (0.1 M) were prepared and checked using a Fisher Scientific Accumet Model 25 pH meter. The composition of each buffer solution was as follows: pH 3, 4, 5 – phthalate buffer; pH 6, 7, 8, 12 – phosphate buffer; pH 9 – borate buffer; and pH 10 – bicarbonate buffer [31]. Separation and quantification of H_2, HD, and D_2 was performed by gas chromatography on a Hewlett Packard 5890 A gas chromatograph at 77 K using an Al_2O_3 column as described in the literature [33].

2.2. Isotopic exchange methods

In a typical experiment, buffer solutions were degassed on an Ar Schlenk line. Solutions of $Rh(TPPTS)_3Cl$ and $Rh(TPPMS)_3Cl$ (2.2 mM) in 1 mL buffer solutions were prepared in a glove bag under argon gas. The 1 mL solutions were placed in a 5 mL gas-tight vial with a stir bar. The gas-tight vial was a Kontes reaction vial fitted with a valved cap that enables gas sampling by syringe. The vial was removed from the glovebag, and D_2 (g) was bubbled through the solution for approximately one minute by inserting the needle through the valve and slightly loosening the cap. The cap was tightened, the needle was removed, and the solution was stirred at 25 °C on a temperature-controlled stir plate. At regular intervals, using a gas-tight syringe, 25 μL headspace samples were removed through the valve and injected onto the GC column.

2.3. Kinetic modelling

D_2, HD and H_2 concentrations were expressed as percentages of the total hydrogen concentration in the headspace of the reaction vessel. Thus, the constraint

$$[D_2] + [HD] + [H_2] = 100\% \quad (3)$$

holds at all times during the reaction, with each concentration calculated as the percentage of total area under the curves for D_2, HD and H_2 peaks in the gas chromatogram. It is assumed that the concentration of each isotopologue in solution is proportional to the partial pressure of the species in the head space, according to what is predicted by Henry's Law.

The measured concentrations were fit to the relationships in Eqs. (8)–(10) as predicted by the effective mechanism shown in Eqs. (5)–(7) (vide infra). Rate constants k_1 and k_2 were chosen using a non-linear least squares fitting procedure so as to minimize χ^2 defined in Eq. (4).

$$\chi^2 = \sum_t ([D_2]_{t,\text{obs.}} - [D_2]_{t,\text{calc.}})^2 + ([HD]_{t,\text{obs.}} - [HD]_{t,\text{calc.}})^2 + ([H_2]_{t,\text{obs.}} - [H_2]_{t,\text{calc.}})^2 \quad (4)$$

It is estimated that the individual rate constants determined by this procedure have an uncertainty of less than 5%. To study variability among duplicate experiments, four replicate measurements were performed for $Rh(TPPMS)_3Cl$ at pH 7. The standard deviation for k_1 was 19% of the mean and for k_2 it was 11% of the mean.

3. Results and discussion

3.1. General exchange results

The progress of D_2/H_2O exchange reactions catalyzed by $Rh(TPPTS)_3Cl$ and $Rh(TPPMS)_3Cl$ has been monitored in buffered aqueous solutions between pH 3 and pH 12 at 25 °C under 1 atm of D_2. The headspace over the stirred aqueous catalyst solution was sampled approximately every 20 min and analyzed for $\%H_2$, HD, and D_2. This is demonstrated in Fig. 1 for $Rh(TPPTS)_3Cl$ at pH 4 and in Fig. 2 for $Rh(TPPTS)_3Cl$ at pH 8. The turnover frequencies (TOF) as a function of pH for both catalysts (calculated from the total moles of H appearing in the headspace over the first 20 min: TOF = mol H/mol Rh·0.33 h) are shown in Figs. 3 and 4.

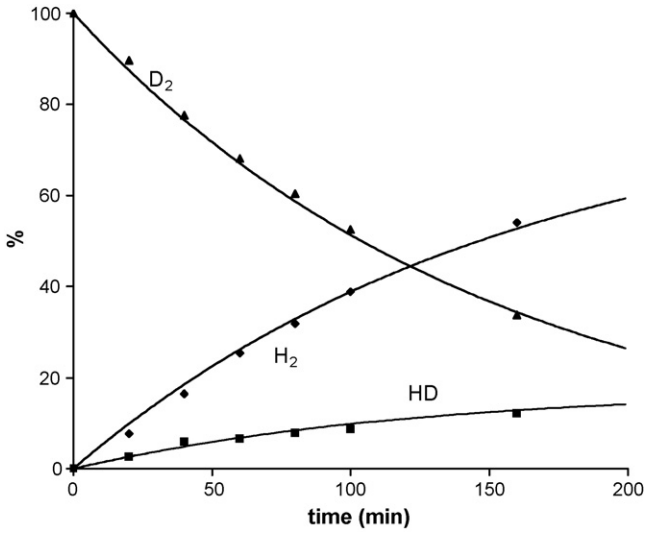

Fig. 1. Percent composition as a function of time for the $Rh(TPPTS)_3Cl$ catalyzed D_2/H_2O exchange reaction at pH 4. $[Rh(TPPTS)_3Cl] = 2.2$ mM, initial $pD_2 = 1$ atm. Lines represent fits to the data. The observation of HD production lagging behind the production of H_2 is an indication of a significant contribution due to double exchange.

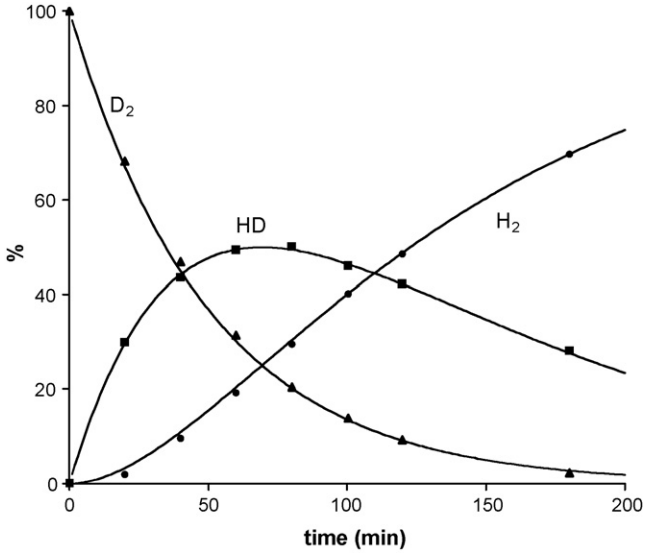

Fig. 2. Percent composition as a function of time for the $Rh(TPPTS)_3Cl$ catalyzed D_2/H_2O exchange reaction at pH 8. $[Rh(TPPTS)_3Cl] = 2.2$ mM, initial $pD_2 = 1$ atm. Lines represent fits to the data.

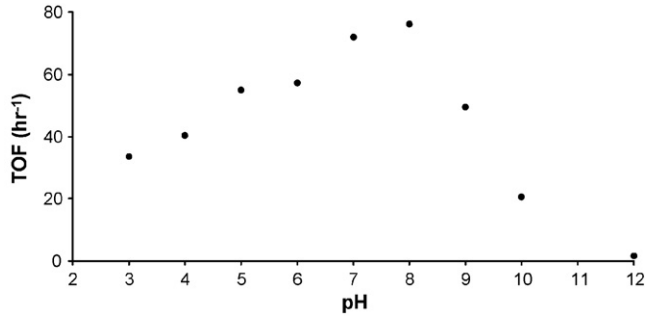

Fig. 3. Turnover frequency for the $Rh(TPPTS)_3Cl$ catalyzed D_2/H_2O exchange reaction as a function of pH. $[Rh(TPPTS)_3Cl] = 2.2$ mM, initial $pD_2 = 1$ atm.

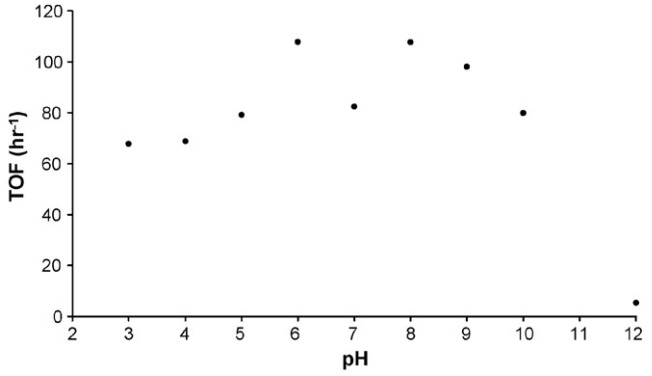

Fig. 4. Turnover frequency for the $Rh(TPPMS)_3Cl$ catalyzed D_2/H_2O exchange reaction as a function of pH. $[Rh(TPPMS)_3Cl] = 2.2$ mM, initial $pD_2 = 1$ atm.

Other than the method of analysis, there are four key differences in how we performed these experiments versus previously published exchange reactions with these catalysts [15,16]. First, the solutions in this report are buffered. Second, these studies were performed at 1 atm instead of 20 atm. Third, we have performed D_2/H_2O exchange instead of H_2/D_2O exchange in order to simplify buffer preparation. Fourth, we have not used a three-fold excess of the phosphine ligands. With regard to these differences: (1) Buffered solutions in this report are used only as a precaution. (2) Lower pressures were necessitated by our experimental set up. However, Kovács et al. stated that for one of the systems they fully analyzed, the rate was linear with pressure at least down to atmospheric pressure of hydrogen. Furthermore they described that higher than atmospheric pressures were only necessary to maintain sufficient H_2 in the small headspace above the solution in the NMR tube. (3) Kovács et al. reported a negligible isotope effect (~10%) for H_2/D_2O versus D_2/H_2O exchange catalyzed by $Rh(TPPMS)_3Cl$ [16], and we also have not observed significant isotope effects for these exchange reactions. (4) We tested the effect of excess ligand on the $Rh(TPPTS)_3Cl$ catalyzed exchange and found no dependence of the TOF on added ligand (0–10 equiv.). Thus, none of these differences are expected to drastically affect the pH profiles. Optimal turnover frequencies in our experiments are in reasonable agreement with those reported by Kovács et al. [16] when differences in pressure are accounted for. In addition, the pH profiles exhibit similar overall shapes to those reported, even showing a slight dip in rate near neutral pH for the $Rh(TPPMS)_3Cl$ catalyzed exchange.

Of particular interest is the shape of the plot of TOF versus pH, that is, the rather steep descent from the maximum TOF at pH > 7 but the flattening out of the TOF to a relatively constant value under acidic conditions. Assuming the exchange mechanism involves deprotonation and reprotonation of a dihydrogen complex intermediate as Kovács et al. suggest [16], one would expect a maximum exchange rate at or near the pK_a of the dihydrogen complex intermediate with a relatively symmetric decrease in exchange rate at higher and lower pH values. Interestingly, the D_2/H_2O exchange processes catalyzed by the hydrogenase enzymes often go through a maximum near physiological pH and the rate typically falls off reasonably

symmetrically at higher and lower pH values [3,18,19,21,22]. Thus, a closer examination of the details of the exchange rate versus pH is necessary in order to understand the asymmetry of the exchange activity for these catalysts.

3.2. Theoretical analysis of single versus double exchange

As mentioned above, hydrogenase enzymes from different organisms differ in their capacity to effect single versus double exchange [3,18–25]. For the case of D_2/H_2O exchange, if H_2 is observed before the appearance of HD, it is assumed that double exchange is occurring. It is instructive, however, to attempt to better quantify single versus double exchange. Eqs. (5) through (7) are generalized equations intended only to distinguish between single exchange (Eqs. (5) and (6)) and double exchange (Eq. (7)). Within the context of this article these processes are assumed to be catalyzed by the rhodium catalysts and thus require binding of dihydrogen to the rhodium complex.

$$D_2 + H_2O \xrightarrow{k_1} HD + HDO \quad (5)$$

$$HD + H_2O \xrightarrow{(1/2)k_1} H_2 + HDO \quad (6)$$

$$D_2 + 2H_2O \xrightarrow{k_2} H_2 + 2HDO \quad (7)$$

For the case of pure single exchange, the only way to obtain H_2 is for HD that was formed in Eq. (5) to return to the active site and undergo another exchange event (Eq. (6)). The rate constant for this exchange event, ignoring any isotope effects, would be $(1/2)k_1$ due to a statistical factor that takes into account that one-half of these exchange events are non-productive. These equations also assume a large excess of H_2O so that the reverse processes are negligible. If both single and double exchange are operable, then Eqs. (5)–(7) must be considered simultaneously. The resulting integrated rate expressions are given in Eqs. (8)–(10), the derivations of which can be found in Appendix A.

$$[D_2]_t = [D_2]_0 e^{-(k_1+k_2)t} \quad (8)$$

$$[HD]t = [D_2]_0 \left\{ \frac{k_1}{k_2 + (1/2)k_1} (e^{-(1/2)k_1 t} - e^{-(k_1+k_2)t}) \right\} \quad (9)$$

$$[H_2]_t = [D_2]_0 - ([D_2]_t + [HD]_t) \quad (10)$$

If only single exchange is occurring, i.e., k_2 is negligibly small, the isotopic compositions as a function of time simplify to Eqs. (11)–(13).

$$[D_2]t = [D_2]_0 e^{-k_1 t} \quad (11)$$

$$[HD]_t = [D_2]_0 (2e^{-(1/2)k_1 t} - 2e^{-k_1 t}) \quad (12)$$

$$[H_2]_t = [D_2]_0 - ([D_2]_t + [HD]_t) \quad (13)$$

Theoretical isotopic composition curves for the single exchange case are shown in Fig. 5. The shapes of the isotopic composition curves when both single and double exchange are operable depend on the relative values of k_1 and k_2. By fitting data obtained from catalyzed D_2/H_2O exchange reactions to the above equations, a determination of the relative importance of single versus double exchange for a given set of conditions should be possible.

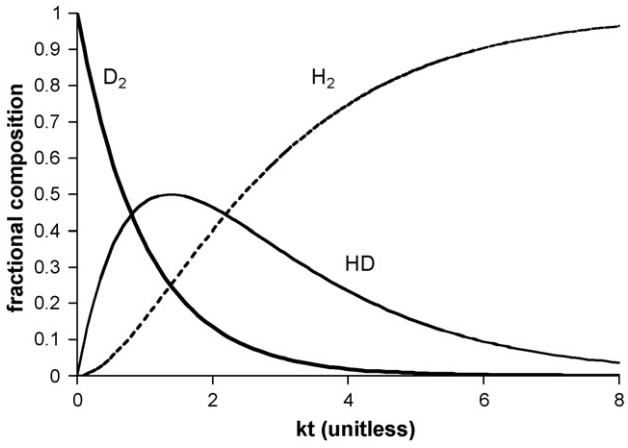

Fig. 5. Predicted fractional composition of the headspace during D_2/H_2O exchange in the presence of a large excess of H_2O and assuming no isotope effects and no double exchange. Note that if only single exchange is important, H_2 production necessarily lags behind HD production at early reaction times.

3.3. Analysis of exchange reactions catalyzed by $Rh(TPPTS)_3Cl$ and $Rh(TPPMS)_3Cl$

For both catalysts in aqueous solutions at pH ≥ 8, the D_2/H_2O exchange data shows no significant evidence of double exchange, i.e., the data can be satisfactorily fit to a single rate constant, k_1, using Eqs. (11)–(13) as demonstrated in Fig. 2. One implication of this good fit is that the assumption of a negligible isotope effect holds for these systems, as had been inferred by Kovács et al. [16]. Both single and double exchange must be considered for the TPPTS complex at pH ≤ 6 and for the TPPMS complex at pH ≤ 7. These data sets can be satisfactorily fit using Eqs. (8)–(10) as demonstrated in Fig. 1 and this results in rate constants for both single exchange, k_1, and double exchange, k_2. A graphical analysis of the rate constants for single and double exchange for the TPPTS and TPPMS complexes are shown in Figs. 6 and 7, respectively. Figs. 6 and 7 clearly demonstrate that double exchange predominates at lower pH. The rate constants for single exchange proceed through

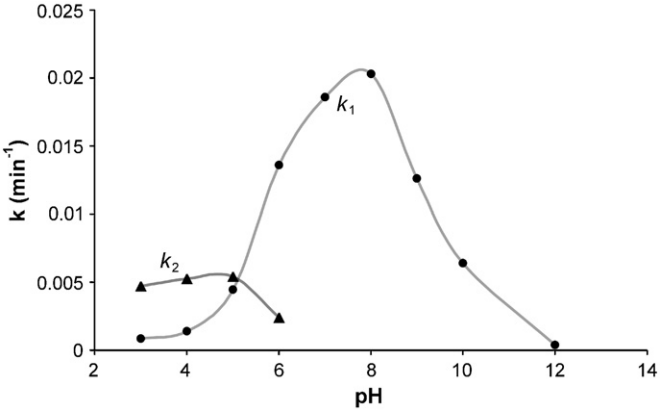

Fig. 6. pH profile for D_2/H_2O exchange with $Rh(TPPTS)_3Cl$ catalyst.

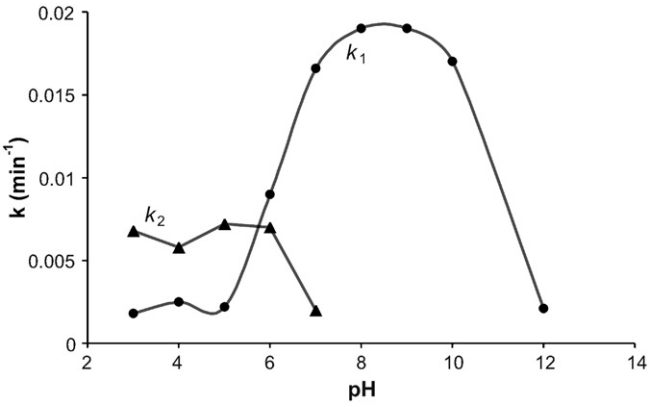

Fig. 7. pH profile for D_2/H_2O exchange with $Rh(TPPMS)_3Cl$ catalyst.

a reasonably sharp maximum as expected (vide supra). These plots also demonstrate that the reason the turnover frequencies shown in Figs. 3 and 4 level out at lower pH values is due to the increase of a double exchange mechanism.

This double exchange also appears to be due to multiple exchanges during one visit to the active site due to the fact that it only appears at the lower pH values where total exchange rates are slower. If the double exchange were of the type requiring release from the transition metal followed by recoordination, one would expect the double exchange to be more evident when the net exchange rates were the highest. This is not observed. In addition, for both catalysts at pH 6, where both single and double exchange are significant, no increase in double exchange was observed at higher catalyst concentrations.

3.4. Mechanistic implications

Kovács et al. [16] have proposed a mechanism for $Rh(TPPMS)_3Cl$ catalyzed D_2/H_2O exchange (Fig. 8). Here the metal catalyst first undergoes oxidative addition of D_2 to make the dideuteride, **I**. The next step is protonation to form a bound HD ligand from one of the deuteride ligands as shown in intermediate **II**. Finally, loss of D^+ to give hydride-deuteride, **III**, is followed by reductive elimination of HD and oxidative addition of D_2 to return to **I**. The idea of single versus double exchange

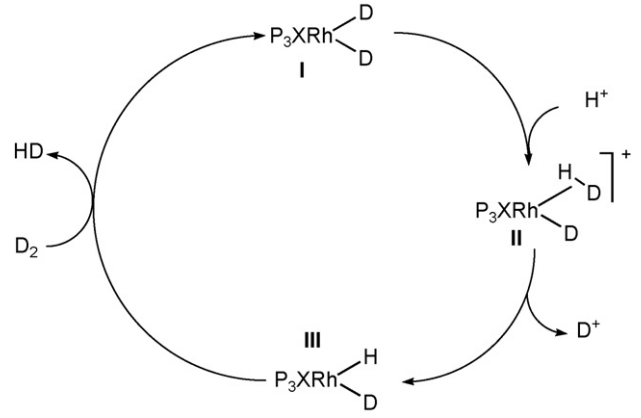

Fig. 8. Proposed mechanism for $Rh(TPPMS)_3Cl$ catalyzed D_2/H_2O exchange.

can thus be described in terms of the lifetime of species **III** versus the "proton" exchange rate. If dihydrogen isotopologue release from species **III** is more rapid than reprotonation of **III** to form an isotopologue of **II**, single exchange should predominate. If reprotonation of **III** is faster, then double exchange predominates. For the catalysts cited herein, this competition is controlled by pH (with double exchange predominating at low pH).

Note that the mechanism in Fig. 8 involves protonation of **I**, followed by deprotonation and reductive elimination. Another mechanism that seemed equally likely to us was *deprotonation* of **I** followed by protonation and reductive elimination. However, the increase in the significance of double exchange at lower pH values is entirely consistent with the proposed mechanism of protonation occurring first. That is, double exchange requires that protonation of **III** is fast relative to reductive elimination so that multiple "proton" exchange reactions occur before release of hydrogen. Since lower pH would accelerate the protonation step, one would expect a higher likelihood of double exchange at low pH if the mechanism in Fig. 8 is operative. On the other hand, if deprotonation *preceded* protonation, one would expect double exchange at higher pH. Thus, the pH profile supports the proposed mechanism.

Finally, the pH at which each catalyst shows maximum single exchange activity is noteworthy. Though the resolution of the data cannot pinpoint the pH at which the maximum activity obtains, it appears that the maximum is between a pH of 8 and 9 for $Rh(TPPMS)_3Cl$, and between a pH of 7 and 8 for $Rh(TPPTS)_3Cl$. As mentioned earlier, the exchange rate should go through a maximum near the pK_a of the "dihydrogen" complex intermediate, **II**. Then, the pH profiles would suggest that the dihydrogen intermediate for $Rh(TPPTS)_3Cl$ is more acidic than the dihydrogen intermediate for $Rh(TPPMS)_3Cl$. This is intuitively satisfying as one would expect that the addition of electron withdrawing sulfonates (in TPPTS, each phenyl ring of triphenylphosphine is sulfonated, whereas for TPPMS, only one of the phenyl rings is sulfonated) would increase the acidity of the dihydrogen complex intermediate – which is what the data appears to demonstrate. Thus, we believe that the pK_a of the dihydrogen complex intermediate, **II**, of $Rh(TPPTS)_3Cl$ is between 7 and 8 and the pK_a of the analogous dihydrogen intermediate for $Rh(TPPMS)_3Cl$ is between 8 and 9.

4. Conclusions

Herein we have demonstrated that significantly more information can be gained from D_2/H_2O exchange by measuring the hydrogen isotopologues than by monitoring the HDO signal by NMR. Namely, single and double exchange can be distinguished and this distinction may have significant mechanistic implications. In this particular case, the data supports a mechanism where protonation of the initial addition product, **I**, precedes deprotonation. The results obtained are also consistent with the contention that the maximum rate for single exchange should occur at the pK_a of the dihydrogen complex intermediate and has allowed a bracketing of the pK_a values of these important intermediates. Such a method may be useful for obtaining

pK_a values for dihydrogen complexes that catalyze D_2/H_2O exchange. In addition, the kinetic models presented herein may be usefully applied to the isotopic exchange reactions catalyzed by the hydrogenase enzymes.

Acknowledgements

P.S.W. acknowledges support from NIH MBRS (Grant 2 S06 GM08192-23) and from the Henry Dreyfus Teacher Scholar Awards Program.

Appendix A. Derivation of the integrated rate expressions (Eqs. (8)–(10))

Eqs. (5)–(7) suggest the following differential rate equation for $[D_2]$

$$\frac{-\mathrm{d}[D_2]}{\mathrm{d}t} = k_1[D_2] + k_2[D_2].$$

H_2O has been neglected in the differential rate equations because water is present in such large excess that it is assumed to have a constant concentration over the time of the reaction. Integration results in Eq. (8).

Eqs. (5)–(7) suggest the following differential rate equation for [HD].

$$\frac{\mathrm{d}[HD]}{\mathrm{d}t} = k_1[D_2] - \frac{1}{2}k_1[HD].$$

Substitution of Eq. (8) for $[D_2]$ results in

$$\frac{\mathrm{d}[HD]}{\mathrm{d}t} = k_1[D_2]_0 \mathrm{e}^{-(k_1+k_2)t} - \frac{1}{2}k_1[HD],$$

which is in the form

$$\frac{\mathrm{d}x}{\mathrm{d}t} = a\mathrm{e}^{-bt} - cx$$

where $a = k_1[D_2]_0$, $b = k_1 + k_2$, $c = 1/2k_1$, and $x = [HD]_t$.

The solution to the above differential equation is

$$x_t = \frac{a}{c-b}\mathrm{e}^{-bt} + K\mathrm{e}^{-ct}$$

where K is the constant of integration.

The constant of integration is determined by using the fact that at $t = 0$, $[HD] = 0$, thus:

$$K = -\frac{a}{c-b}, \quad \text{resulting in : } x_t = \frac{a}{c-b}\mathrm{e}^{-bt} - \frac{a}{c-b}\mathrm{e}^{-ct}.$$

Back substitution for a, b, c, and x results in Eq. (9). Finally, mass balance gives Eq. (10).

References

[1] A.I. Krasna, D.J. Rittenberg, J. Am. Chem. Soc. 76 (1954) 3015–3020.
[2] M.W.W. Adams, L.E. Mortenson, J.-S. Chen, Biochim. Biophys. Acta 594 (1981) 105–176.
[3] P.A. Lespinat, Y. Berlier, G. Faque, M. Czechowski, B. Dimon, J. LeGall, Biochimie 68 (1986) 55–61.
[4] P.M. Vignais, Coord. Chem. Rev. 249 (2005) 1677–1690.
[5] D.J. Evans, C.J. Pickett, Chem. Soc. Rev. 32 (2003) 268–275.
[6] G. Henrici-Olivé, S. Olivé, J. Mol. Cat. 1 (1975/76) 121–135.
[7] (a) J.P. Collman, P.S. Wagenknecht, R.H. Hembre, N.S. Lewis, J. Am. Chem. Soc. 112 (1990) 1269–1271;
(b) J.P. Collman, P.S. Wagenknecht, J.E. Hutchison, N.S. Lewis, M.A. Lopez, R. Guilard, M. L'Her, J. Am. Chem. Soc. 114 (1992) 5654–5664.
[8] M. Zimmer, G. Schulte, X.-L. Luo, R.H. Crabtree, Angew. Chem. Int. Eng. 30 (1991) 193–194.
[9] A.C. Albeniz, M.D. Heinekey, R.H. Crabtree, Inorg. Chem. 30 (1991) 3632–3635.
[10] D. Sellmann, G.H. Rackelmann, F.W. Heinemann, Chem. Eur. J. 3 (1997) 2071–2080.
[11] (a) J.W. Tye, M.B. Hall, I.P. Georgakaki, M.Y. Darensbourg, Adv. Inorg. Chem. 56 (2004) 1–26;
(b) X. Zhao, I.P. Georgakaki, M.L. Miller, J.C. Yarbrough, M.Y. Darensbourg, J. Am. Chem. Soc. 123 (2001) 9710–9711;
(c) X. Zhao, I.P. Georgakaki, M.L. Miller, R. Mejia-Rodriguez, C. Chiang, M.Y. Darensbourg, Inorg. Chem. 41 (2002) 3917–3928.
[12] E.P. Cappellani, S.D. Drouin, G. Jia, P.A. Maltby, R.H. Morris, C.T. Schweitzer, J. Am. Chem. Soc. 116 (1994) 3375–3388.
[13] Y. Okhi, N. Matsuura, T. Marumoto, H. Kawaguchi, K. Tatsumi, J. Am. Chem. Soc. 125 (2003) 7978–7988.
[14] C. Larpent, H. Patin, J. Mol. Cat. 61 (1990) 65–73.
[15] G. Kovács, L. Nádasdi, F. Joo, G. Laurenczy, C. R. Acad. Sci. Paris, Ser. IIc: Chim. 3 (2000) 601–605.
[16] G. Kovács, L. Nádasdi, G. Laurenczy, F. Joó, Green Chem. 5 (2003) 213–217.
[17] G. Kovács, G. Schubert, F. Joó, I. Papai, Organometallics 24 (2005) 3059–3065.
[18] P. Egerer, H. Gunther, H. Simon, Biochim. Biophys. Acta 703 (1982) 149–157.
[19] N. Tamiya, S.L. Miller, J. Biol. Chem. 238 (1963) 2194–2198.
[20] D.J. Arp, R.H. Burris, Biochim. Biophys. Acta 700 (1982) 7–15.
[21] P.M. Vignais, M.-F. Henry, Y. Berlier, P.A. Lespinat, Biochim. Biophys. Acta 681 (1982) 519–529.
[22] N.A. Zorin, B. Dimon, J. Gagon, J. Gaillard, P. Carrier, P. Vignais, Eur. J. Biochem. 241 (1996) 675–681.
[23] H. McTavish, L.A. Sayavedra-Soto, D.J. Arp, Biochim. Biophys. Acta 1294 (1996) 183–190.
[24] M. Teixeira, G. Fauque, I. Moura, P.A. Lespinat, Y. Berlier, B. Prickril, H.D. Peck Jr., A.V. Xavier, J. Le Gall, J.J.G. Moura, Eur. J. Biochem. 67 (1987) 47–58.
[25] M. Bernhard, T. Buhrke, B. Bleijlevens, A.L. DeLacey, V.M. Fernandez, S.P.J. Albracht, B. Friedrich, J. Biol. Chem. 276 (2001) 15592–15597.
[26] P.M. Vagnais, B. Dimon, N.A. Zorin, M. Tomiyama, A. Colbeau, J. Bacteriol. 182 (2000) 5997–6004.
[27] (a) P.S. Wagenknecht, J.P. Penney, R.T. Hembre, Organometallics 22 (2003) 1180–1182;
(b) P.S. Wagenknecht, E.J. Sambriski, in: S.G. Pandalai (Ed.), Inorganic Chemistry, Transworld Research Network, Kerala, India, 2003, pp. 33–50.
[28] F. Joó, J. Kovács, Á. Kathó, A.C. Bényei, T. Decuir, D.J. Darensbourg, Inorg. Synth. 32 (1998) 1–8.
[29] R. Cramer, Inorg. Synth. 28 (1990) 86–87.
[30] W.A. Herrmann, C.W. Kohlpaintner, Inorg. Synth. 32 (1998) 8–25.
[31] Though $Rh(TPPMS)_3Cl$ catalyzes the hydrogenation of bicarbonate [32], we observe no evidence of that under the conditions employed in this article.
[32] F. Joó, G. Laurenczy, L. Nádasdi, J. Elek, Chem. Comm. (1999) 971–972.
[33] J.P. Collman, P.S. Wagenknecht, N.S. Lewis, J. Am. Chem. Soc. 114 (1992) 5665–5673.