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Aqueous organometallic reactions of rhodium porphyrins: equilibrium thermodynamics†

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The reactivity and equilibrium thermodynamic studies of tetra-*p*-sulfonatophenyl porphyrin rhodium hydride ([(TSPP)Rh–D]$^{-4}$) with CO, aldehydes and olefins that produce formyl, α-hydroxyalkyl and alkyl complexes have been explored in water and compared with the related reactions in non-aqueous media.

Current emphasis on developing organometallic processes in aqueous solution[1–4] stimulated this investigation of rhodium tetra-*p*-sulfonatophenyl porphyrin ((TSPP)Rh) reactivity in water. The (TSPP)Rh species have a remarkable range of organometallic reactions in water and this system provides an opportunity to obtain one of the most complete descriptions of equilibrium thermodynamics for organometallic transformations in water. Water soluble (TSPP)Rh(III) complexes react with hydrogen to form a rhodium hydride that is a weak acid in D_2O. Reactions of the rhodium hydride in D_2O with CO, aldehydes and olefins (Scheme 1) that produce formyl, α-hydroxyalkyl and alkyl complexes have comparable thermodynamics and larger reaction rates in water than analogous reactions in benzene.[5–7] These substrate reactions in water are thought to occur by ionic pathways that involve the rhodium(I) metal-centered nucleophile. An advantage of using aqueous solutions is the capability of tuning the equilibrium distribution of species by varying the hydrogen ion concentration. This approach is used to expand the range of rhodium hydride substrate equilibrium thermodynamic studies in water to olefins which have equilibrium constants too large for convenient direct measurement in both aqueous and hydrocarbon media.

Measurement of aqueous solution equilibria involving reactions of rhodium(III) porphyrins requires a knowledge of the equilibrium distributions of bis aquo $[(TSPP)Rh^{III}(D_2O)_2]^{-3}$ (**1**), mono hydroxo $[(TSPP)Rh^{III}(D_2O)(OD)]^{-4}$ (**2**) and bis hydroxo $[(TSPP)Rh^{III}(OD)_2]^{-5}$ (**3**) complexes (eqns. (1) and (2)).[8]

$$[(TSPP)Rh^{III}(D_2O)_2]^{-3} \rightleftharpoons [(TSPP)Rh^{III}(D_2O)(OD)]^{-4} + D^+ \quad (1)$$

$$[(TSPP)Rh^{III}(D_2O)(OD)]^{-4} \rightleftharpoons [(TSPP)Rh^{III}(OD)_2]^{-5} + D^+ \quad (2)$$

Equilibrium constants‡ for reactions (1) and (2) ((T = 298 K); K_1 = 1.4 ± 0.2 × 10^{-8}; K_2 = 2.8 ± 0.3 × 10^{-12}) were determined from the mole fraction averaged pyrrole chemical shifts for **1**, **2**, and **3** as a function of the concentration of D^+ in D_2O (Fig. 1A). At D^+ concentrations greater than 10^{-5} M the bis aquo complex **1** is effectively the only $(TSPP)Rh^{III}$ species present in D_2O while at D^+ less than 10^{-12} M the bis hydroxo complex **3** predominates (Fig. 1A).

Reaction of the bis aquo species $[(TSPP)Rh^{III}(D_2O)_2]^{-3}$ (**1**) with H_2/D_2 (0.5–0.8 atm) results in formation of a hydride complex $[(TSPP)Rh–D]^{-4}$ (**4**) in equilibrium with a rhodium(I) species $[(TSPP)Rh^I]^{-5}$ (**5**) (eqns. (3) and (4)). A rhodium(II) metal–metal bonded dimer $[(TSPP)Rh^{II}]_2^{-8}$ (**6**) also forms in the process from reaction of **1** with **5** (eqn. (5)), but at equilibrium the reaction of **6** with hydrogen effectively removes rhodium(II) species from the reaction system (eqn. (6)). Equilibrium constants‡ have been determined for reactions (3)–(6) which describe the distribution of the precursors for organometallic reactions (T = 298 K, K_3 = 0.3, K_4 = 8.0 ± 0.5 × 10^{-8}, K_5 = 4.2 ± 0.5 × 10^3, K_6 = 9.8 ± 0.8 × 10^2).

$$[(TSPP)Rh^{III}{}_{aq}]^{-3} + D_2 \rightleftharpoons [(TSPP)Rh–D]^{-4} + D^+ \quad (3)$$

$$[(TSPP)Rh–D]^{-4} \rightleftharpoons [(TSPP)Rh^I]^{-5} + D^+ \quad (4)$$

$$[(TSPP)Rh^I]^{-5} + [(TSPP)Rh^{III}{}_{aq}]^{-3} \rightleftharpoons [(TSPP)Rh^{II}]_2^{-8} \quad (5)$$

$$[(TSPP)Rh^{II}]_2^{-8} + D_2 \rightleftharpoons 2\ [(TSPP)Rh–D]^{-4} \quad (6)$$

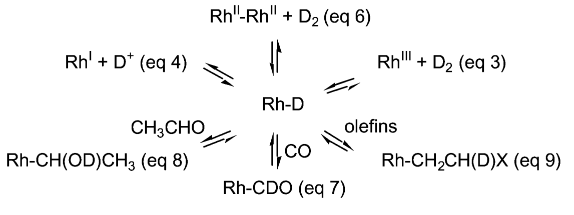
Aqueous solutions of the rhodium hydride complex **4** react with CO (P_{CO} ~ 0.2–0.9 atm; $[D^+] < 10^{-5}$) within the time needed to record the ^1H NMR to produce an equilibrium distribution with a formyl complex (eqn. (7)).

$$[(TSPP)Rh–D]^{-4} + CO \rightleftharpoons [(TSPP)Rh–CDO]^{-4} \quad (7)$$

The formyl complex is most convincingly identified by ^{13}C NMR of **7** prepared by using ^{13}CO in reaction (7). The ^{13}C NMR for the formyl group of $[(TSPP)Rh–^{13}CDO]^{-4}$ in D_2O ($\delta_{13_{CHO}}$ = 218.7 ppm) appears as an approximate 1:2:2:1 quartet that results from the near equal coupling of D and ^{103}Rh with ^{13}C ($2J_{^{13}C–D} + J_{^{103}Rh–^{13}C}$ = 78 Hz) (Fig. 2A).

When the ^1H derivative of **7** ($[(TSPP)Rh–^{13}CHO]^{-4}$) is formed in H_2O, the ^{13}C NMR of the $Rh–^{13}CHO$ unit manifests a $^{13}C–H$ coupling constant of 166 Hz which gives a calculated value for $J_{^{13}C–D}$ of 25.5 Hz (($J_{^{13}C–H}/J_{^{13}C–D}$) = 6.51) and a value of 27 Hz is derived for $J_{^{103}Rh–^{13}C}$.

The equilibrium constant‡ for reaction (7) (K_7(298 K) = 3.0 ± 0.3 × 10^3) was determined in D_2O by integration of the porphyrin pyrrole ^1H NMR for **4** and **7** and the solubility of CO in water.[9]



Scheme 1 Formation and representative small molecule reactions of (TSPP)Rh–D in D_2O.

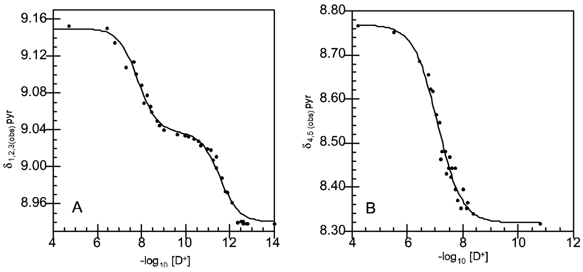


Fig. 1 Determination of acid dissociation constants at 298 K. (A) $[(TSPP)Rh^{III}(D_2O)_2]^{-3}$, K_1 = 1.4 ± 0.2 × 10^{-8} $[(TSPP)Rh^{III}(D_2O)(OD)]^{-4}$, K_2 = 2.8 ± 0.3 × 10^{-12}. (B) $[(TSPP)Rh-D]^{-4}$, K_4 = 8.0 ± 0.5 × 10^{-8}.

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b2/b212027e/

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Solutions of $[(TSPP)Rh–D]^{-4}$ (**4**) in D_2O react with acetaldehyde to form an α-hydroxy ethyl complex $[(TSPP)Rh–CH(OD)CH_3]^{-4}$ (**8**) (eqn. (8)) during the time required to record the ^1H NMR. The equilibrium constant for reaction (8) was obtained by integration of the ^1H NMR for each of the constituents in the equilibrium distribution of **4**, **8** and CH_3CHO ($K_8(298\ K) = 1.4 \pm 0.1 \times 10^3$). Equilibrium constants for reactions of **4** with olefins (eqn. (9)) are too large for accurate direct measurement.

$$[(TSPP)Rh–D]^{-4} + CH_3CHO \rightleftharpoons [(TSPP)Rh–CH(OD)CH_3)]^{-4} \quad (8)$$

$$[(TSPP)Rh–D]^{-4} + CH_2{=}CH(X) \rightleftharpoons [(TSPP)Rh–CH_2CH(D)X]^{-4} \quad (9)$$

The equilibrium constant for reaction (9) was derived indirectly from a thermodynamic cycle by measuring the equilibrium constant for reaction of the rhodium(I) complex (**5**) with olefins and D_2O in basic solution (eqns. (10) and (11)) in combination with the equilibrium constants (298 K) for reactions (4) ($K_4 = 8.0 \times 10^{-8}$) and (11) ($K_{11} = [D_2O]/K_w(D_2O) = 4.1\times 10^{16}$) ($K_9 = K_{10}K_4K_{11} = 3.3 \times 10^9 K_{10}$).

$$[(TSPP)Rh^I]^{-5} + CH_2{=}CH(X) + D_2O \rightleftharpoons [(TSPP)Rh–CH_2CH(D)X]^{-4} + OD^- \quad (10)$$

$$OD^- + D^+ \rightleftharpoons D_2O \quad (11)$$

The equilibrium constant‡ for reaction (10) using methyl acrylate ($CH_2{=}CHCO_2CH_3$) is 0.086 ($K_{10}(298\ K) = 0.086$) which permits evaluation of the equilibrium constant for addition of the Rh–H (**4**) to methyl acrylate (K_9(methyl acrylate) $= 2.8 \times 10^8$).

Addition reactions of $[(TSPP)Rh–D]^{-4}$(**4**) with CO, aldehydes and olefins to produce formyl (**7**), α-hydroxyalkyl (**8**), and alkyl (**9**) derivatives are analogous to previously observed substrate reactions of (TPP)Rh–H in benzene.[5–7] Measurement of the equilibrium constant (298 K) to produce the formyl complex (Rh–CDO) by reaction (7) in water gives a $\Delta G°_7$(298 K) of -4.7 kcal mol^{-1} which compares with a $\Delta G°$(298 K) of -3.7 kcal mol^{-1} to produce (TPP)Rh–CHO from reaction of (TPP)Rh–H with CO in benzene.[10] Solvation of the formyl complex in water is undoubtedly very different from that in benzene, yet there is only a small net change in $\Delta G°$(298 K) for the process in water compared to benzene.

Reaction of the hydride **4** with acetaldehyde in D_2O occurs with regioselectivity to form an α-hydroxyalkyl $[(TSPP)Rh–CH(OD)CH_3]^{-4}$, in preference to an alkoxide. The hydride **4** reacts with olefins that have either electron withdrawing or releasing substituents to give anti-Markovnikov regioselectivity which suggests that the steric demands of the porphyrin may have a dominant influence. Anti-Markovnikov regioselectivity is also observed for (por)Rh–H addition reactions in benzene and appears to be a characteristic feature of rhodium porphyrin hydride reactions with olefins.

Substrate reactions of $[(TSPP)Rh–D]^{-4}$ in D_2O are observed to occur substantially faster than the analogous reactions in benzene. The ability of water to support ionic processes is a probable origin for the enhanced kinetics in water. Concerted reactions of (por)Rh–H with substrates are extremely slow because the coordination positions adjacent to the Rh–H unit are occupied by the porphyrin pyrrole nitrogen donors. Relatively rapid substrate reactions of (por)Rh–H require facile access of the substrate to the rhodium center and sequential addition of the (por)Rh and H fragments. Reactions of (por)Rh–H complexes with CO and olefins in benzene are catalyzed by $(por)Rh^{II\cdot}$ metalloradicals and provide a radical chain pathway for stepwise addition.[11] The rhodium hydride is observed to be a weak acid in water and thus a facile source of $[(TSPP)Rh^I]^{-5}$ (**5**) which functions as a metal-centered nucleophile in water. Substrate reactions of **4** in water thus have a potential alternate pathway for reaction involving the stepwise addition of the rhodium(I) nucleophile and proton fragments of **4** (eqns. (12) and (13)).

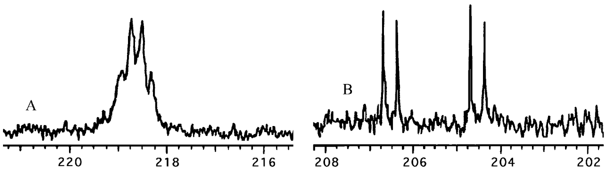

Fig. 2 (A) ^{13}C NMR of $[(TSPP)Rh–^{13}CDO]^{-4}$ in D_2O. $2J_{^{13}C–D} + J_{^{103}Rh–^{13}C} = 78$ Hz. (B) ^{13}C NMR of $[(TSPP)Rh–^{13}CHO]^{-4}$ in DMF. $J_{^{13}C–H} = 166$ Hz.

$$(por)Rh^{I}{:}^- + H_2CO \rightleftharpoons (por)Rh–CH_2O^- \quad (12)$$

$$(por)Rh–CH_2O^- + H^+ \rightleftharpoons (por)Rh–CH_2OH \quad (13)$$

Relatively fast reactions of **4** with aldehydes and olefins activated by electron withdrawing groups are consistent with the rhodium(I) species having a prominent role in the reaction of **4** in water. Reaction of **4** with CO in water by this unusual pathway is plausible, but is speculative at this time.

The equilibrium thermodynamic studies reported in this article provide a foundation for obtaining thermodynamic measurements on a much wider scope of substrate reactions available to (TSPP)Rh species in the +1 to +3 oxidation state in water. Our continuing studies in this area include a focused effort to elucidate the mechanism for CO activation in water and the development of strategies to exploit the rapid reactions of **4** in aqueous substrate transformations.

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‡ The dimensionless equilibrium constants (K_1–K_{11}) (298 K) are associated with a standard state of unit molar concentration for each constituent.

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