Aerobic oxidation of alcohols catalyzed by rhodium(III) porphyrin complexes in water: reactivity and mechanistic studies[†]

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Selective oxidation of alcohol in water using molecular oxygen as the terminal oxidant is mediated by rhodium porphyrin complexes. Addition of methanol to an aqueous solution of (TSPP)Rh(III) resulted in observation of the key intermediate porphyrin rhodium(III) methoxide species. The activation parameters for β C–H elimination of Rh–alkoxide were evaluated.

Oxidation of olefins by dioxygen in water has recently been accomplished using rhodium(III) tetra(*p*-sulfonatophenyl) porphyrin (TSPP)Rh(III).^{1,2} Rapid quantitative aerobic oxidation of (TSPP)Rh(I) to (TSPP)Rh(III) gives this system the capability of undergoing oxidation processes where dioxygen functions as the terminal oxidant. Rhodium porphyrins have a wide range of substrate reactions in water³⁻⁶ and a focus of interest is in exploring the scope of useful oxidation processes for rhodium(III) and related group nine Co(III) and Ir(III) porphyrins. Oxidation of primary and secondary alcohols to aldehydes and ketones ranks among the most important functional group transformations and catalytic aerobic alcohol oxidation is a major topic in transition metal catalysis research.⁷⁻¹³ Complexes of palladium,⁷ copper,⁸ gold,⁹ ruthenium¹⁰ and platinum¹¹ have been applied as homogeneous water soluble catalysts and there have also been several reports of heterogeneous catalysts used for the oxidation of alcohols in water using molecular oxygen.¹² However, reports on oxidation of alcohols catalyzed by rhodium complexes are rare.¹³ This article reports on aerobic oxidation of aliphatic, allylic, and benzylic alcohols in water catalyzed by water soluble rhodium porphyrin complexes. Kinetic-mechanistic studies for the oxidation processes in water are reported, including the product forming step where β -H elimination from a metal alkoxide produces a ketone and metal hydride.

Aqueous solutions of (TSPP)Rh^{III} are observed to catalyze selective oxidation of benzyl alcohol to benzaldehyde using dioxygen as the terminal oxidant (eqn (1)).

$$C_6H_5CH_2OH + \frac{1}{2}O_2 \rightleftharpoons C_6H_5CHO + 2H_2O \qquad (1)$$

In a typical oxidation experiment, benzyl alcohol (0.68 g) and (TSPP)Rh^{III} (3.6 mg) and 1.5 ml of a buffer solution are added to a 40 ml vacuum adapted flask, which is subsequently

evacuated, pressurized with oxygen to one atmosphere, and heated at 80 °C for 7 h. Dependence of the turnover numbers and selectivity on pH to form benzaldehyde in the (TSPP)Rh^{III} catalyzed benzyl alcohol oxidation was measured and are reported in Table 1. (TSPP)Rh^{III} is a robust catalyst and does not degrade to an observable extent under these conditions. The reported turnover numbers thus reflect the relative reaction rates, which can be increased by increasing the oxygen pressure and alcohol substrate concentration. Turnover numbers for benzyl alcohol increase substantially (60-560) and high selectivity is retained as the pH increases (pH = 9.2-13.2) (Table 1). High selectivity for the formation of aldehydes and ketones is partly ascribed to the extraction of product to the excess alcohol, which protects against over oxidation to carboxylic acids.14

A broad range of alcohol substrates can be oxidized by (TSPP)Rh^{III} in water including benzylic, aliphatic, and heteroatom bearing alcohols (Table 2). Benzylic alcohols have relatively weak benzylic C-H bonds and react substantially faster than primary or secondary aliphatic alcohols (Table 2). Reactions of benzyl alcohols containing electron donating groups on the phenyl ring react faster than those with electron withdrawing groups (Table 2, entry 1, 2, 3 and 6). The low solubility of methyl substituted benzyl alcohols in aqueous solution resulted in a slower oxidation reaction rate (Table 2, entry 4, 5). The oxidation process tolerates a variety of functional groups, such as methoxy, C=C double bonds, and thiofuran groups (entry 2, 3, 7 and 8). Alcohols with higher water solubility give higher TON or reaction rates relative to the less soluble alcohols (Table 2, entry 8, 10-12).

Table 1 Catalytic aerobic oxidation of benzyl alcohol mediated by (TSPP)Rh^{III} in water at different pH values

^{.CH₂OH}(TSPP)Rh^{III} O₂, 80 °C, 7h

Entry	pН	Buffer	TON ^a	Selectivity ^b		
1	9.2	0.050 M Na ₂ B ₄ O ₇	60	>99%		
2	10.2	0.19 M NaHCO ₃ /0.17 M Na ₂ CO ₃	100	>99%		
3	11.2	0.025 M NaHCO ₃ /0.22 M Na ₂ CO ₃	220	>99%		
4	12.2	1.1 M Na ₂ CO ₃	150	>99%		
5	13.2	0.16 M NaOH	560	>99%		

TON = $n(\text{benzaldehyde})/n((\text{TSPP})\text{Rh}^{\text{III}})$, GC yield. ^b Selectivity = $n(\text{benzaldehyde})/(n(\text{benzyl alcohol})_{\text{initial}} - n(\text{benzyl alcohol})_{\text{recycle}}),$ GC results.

Stoichiometric oxidation of isopropanol. Reaction of (TSPP)Rh^{III} with aqueous isopropanol in the absence of dioxygen gives stoichiometric formation of acetone and

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Entry	1	2	3	4	5	6	7	8	9^d	10	11	12
Substrate	Стон	Н3СО ОН	H ₃ CO H ₃ CO OCH ₃	н _з с Он	СССН3	_F СССОН	Сусон	Отон	∕∕∕он	~~~́	€рон	⊖-он
Solubility ^{b} TON ^{c} Selectivity ^{c}	0.36 560 >99%	0.18 690 94%	0.25 590 95%	0.058 290 >99%	0.056 320 91%	0.23 350 90%	0.44 640 94%	0.032 70 >99%	0.27 23 77%	0.49 90 >99%	1.1 210 >99%	0.41 80 >99%
^a [NaOH] =	= 0.16 M.	b mol l ⁻¹ in p	ure D ₂ O at 29	9.5 K, see ES	SI for deta	uiled measur	rement pr	ocedure. ^{<i>c</i>} G	C results. ^d	14.4 mg	catalyst w	vas used.

Table 2 Catalytic aerobic oxidation of various alcohols mediated by (TSPP)Rh^{III}_{aq} in water^a

(TSPP)Rh–H (eqn (2)) which at high pH gives (TSPP)Rh^I (eqn (3)).

$$CH_{3}CH(OH)CH_{3} + [(TSPP)Rh^{III}]^{-3} \rightleftharpoons$$
$$[(TSPP)Rh-H]^{-4} + H^{+} + CH_{3}C(O)CH_{3} \qquad (2)$$

$$[(TSPP)Rh-H]^{-4} + OH^{-} \rightleftharpoons [(TSPP)Rh^{1}]^{-5} + H_{2}O \quad (3)$$

Progress of reaction eqn (2) is conveniently followed by the appearance of acetone and the disappearance of (TSPP)Rh^{III} in the ¹H NMR spectra. Degassed samples of (TSPP)Rh^{III} and isopropanol containing a buffer solution at pH = 11.2 were heated directly in the NMR apparatus and the time dependence of the reaction eqn (2) was evaluated. The rates for oxidation reactions were observed to increase as (TSPP)Rh^I was produced (Fig. 1A), which complicates analysis of the kinetic data. The kinetic observations for the reaction (2) were simplified by addition of methyl iodide, which serves as a trap for (TSPP)Rh^I by rapidly reacting to form an unreactive methyl complex (TSPP)Rh–CH₃ (eqn (4)).

$$[(TSPP)Rh^{I}]^{-5} + CH_{3}I \rightleftharpoons [(TSPP)Rh-CH_{3}]^{-4} + I^{-} (4)$$

Under the conditions of rapid trapping of (TSPP)Rh(1), reaction eqn (2) shows first order dependencies on both (TSPP)Rh¹¹¹ and isopropanol (Fig. 1B–C). Evaluating the rate constants for the reaction eqn (2) using $CH_3CH(OH)CH_3$ and $CD_3CD(OD)CD_3$ at 308 K and pH of 11.2 in D_2O



Fig. 1 A: concentration changes of (TSPP)Rh^{III} upon reaction with alcohol, [isopropanol] = 0.16 M at 313.2 K; B: saturated with CH₃I, [isopropanol] = 0.32 M at 313.2 K; C: dependence of the observed rate constant, k_{obs} , on the concentration of ((CH₃)₂CHOH) at 308 K; D: comparison of k_{obs} of reactions of (TSPP)Rh^{III} with regular and deuterated isopropanol ((CD₃)₂CDOD) 0.32M at 308 K, respectively. [(TSPP)Rh^{III}] = 2.0×10^{-3} M, pH = 11.2.

yields a deuterium kinetic isotope effect (KIE) of 1.46 $(k_{\rm H}/k_{\rm D}(308 \text{ K}) = 1.46)$ (Fig. 1D). Activation parameters for the stoichiometric oxidation of isopropanol (eqn (2)) were evaluated from the temperature dependence of the rate constants for reaction eqn (2) $(\Delta H^{\neq} = 21.8 \text{ kcal mol}^{-1}, \Delta S^{\neq} = -2.9 \text{ eu}, \Delta G^{\neq}$ (298 K) = 22.7 kcal mol⁻¹ (Fig. 2). The activation parameters and deuterium isotope effect measured for the reaction eqn (2) are close to the values reported for β C–H elimination processes for Pd–alkoxide ($\Delta H^{\neq} = 20.25 \pm 0.89 \text{ kcal mol}^{-1}, \Delta S^{\neq} = -5.4 \pm 2.7 \text{ eu}$)¹⁵ and Ir–methoxide ($\Delta H^{\neq} = 24.1 \pm 1.8 \text{ kcal mol}^{-1}, \Delta S^{\neq} = 0.6 \pm 5.9 \text{ eu}, \Delta G^{\neq}$ (298 K) = 23.9 ± 3.6 kcal mol}^{-1}

Direct observation of rhodium porphyrin alkoxide complexes in water. Metal alkoxide complexes are generally invoked as key intermediates in the oxidation of alcohols catalyzed by transition metal complexes.^{7d–f,15,17–20} Adding methanol to an aqueous solution of (TSPP)Rh^{III} resulted in observation of a complex equilibrium distribution of nine rhodium(III) porphyrin, water, methanol, hydroxide and methoxide species (see ESI † for details). An equilibrium distribution of a rhodium(III) bis hydroxo complex ([(TSPP)Rh^{III}(OD)₂]⁻⁵) (1), mono alkoxide ([(TSPP)Rh^{III}OD(OCH₃)]⁻⁵) (2), and bis alkoxide ([(TSPP)Rh^{III}(OCH₃)₂]⁻⁵) (3), are the predominant species that occur throughout the basic range ([OD⁻] > 0.025 M) as shown in Fig. 3.

Equilibrium constants at 298 K for the formation of complexes 2 and 3 were determined from the intensity integrations of the ¹H NMR spectra of pyrrole hydrogens of complexes 1–3 in combination with the concentration of methanol ($K_5 = 25 \pm 5$, $K_6 = 5.5 \pm 1$) (eqn (5, 6)).



Fig. 2 Determination of activation parameters for oxidation of isopropanol by (TSPP)Rh^{III} in water using (Na₂CO₃/NaHCO₃) buffer at pH = 11.2 (CH₃CH(OH)CH₃ + [(TSPP)Rh^{III}]⁻³ + OH⁻ \rightleftharpoons [(TSPP)Rh-H]⁻⁴ + CH₃C(O)CH₃ + H₂O).

1500 2000

Time/s

-2.0



Fig. 3 The ¹H NMR (400 MHz, D_2O) spectrum of the equilibrium distribution of complexes **1–3** in water ([CH₃OH] = 2.8 M, [NaOH] = 0.030 M), where a and b designate the pyrrole and alkoxide hydrogens, respectively, in species **1–3**.

Mechanistic features for aerobic oxidation of alcohols in water catalyzed by (TSPP)Rh^{III}. The proposed mechanism for the aerobic oxidation of alcohols catalyzed by (TSPP)Rh^{III} in basic aqueous solution is given in Scheme 1. Displacement of hydroxide ion by alcohols and subsequent deprotonation to alkoxide complexes are directly observed in the (TSPP)Rh^{III} catalyst system. The rate determining step is Rh–alkoxide β -C–H elimination which produces the carbonyl product and (TSPP)Rh–H. Rapid quantitative reaction of oxygen with (TSPP)Rh–H/(TSPP)Rh(1) to regenerate (TSPP)Rh^{III} completes the catalytic cycle.



Scheme 1 Proposed mechanism for catalytic oxidation of alcohols in water, mediated by (TSPP)Rh^{III}.

In summary, a broad range of alcohol substrates are catalytically oxidized by (TSPP)Rh^{III} in water using oxygen as the terminal oxidant. The (TSPP)Rh^{III} catalyst system in water permits direct observation of alkoxide intermediates and evaluation of the activation parameters for the rate determining Rh–alkoxide β C–H elimination. Development of this new aqueous catalyst system that uses dioxygen without the need for co-catalysts, suggests that this prototype catalyst system may find applications in a wide range of "green" oxidation chemistry.

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