Monatshefte für Chemie 131, 1321–1326 (2000)

Monatshefte für Chemie
Chemical Monthly

Oxidation of Alcohols by $[Cp^*Rh(ppy)(OH)]^+$

Ulrich Kölle* and **Holger Fränzl**

Institute of Inorganic Chemistry, Technical University of Aachen, D-52074 Aachen, Germany

Summary. Rh(III) polypyridine complexes ($[Cp^*Rh(ppy)(H_2O)]^{2+}$; ppy = 2,2′-bipyridine, 2,2′-bipyridine-4,4′-dicarboxylate, *o*-phenanthroline, tetrahydro-4,4′-dialkyl-*bis*-oxazole) oxidize in organic or aqueous alkaline solution primary and secondary alcohols to aldehydes or ketones and are thereby reduced to the Rh(I) complexes $Cp^*Rh(ppy)$. The Rh(III) form can be regenerated by oxidants like pyruvate or oxygen, making the reaction *quasi*-catalytic. The reaction follows an autocatalytic pathway; hydrogen transfer from the α-CH_2 group of an alcoholate complex $[Cp^*Rh(ppy)(OR)]^+$ to $Cp^*Rh(I)(ppy)$ is suggested to yield the Rh(II) intermediate $Cp^*Rh(ppy)H$ as the key and rate determining step. The knowledge of Rh(III)/Rh(I) redox potentials allows to estimate the thermodynamic driving force of the reaction which is not more than about 300 mV.

Keywords. Alcohol oxidation; $Cp^*Rh(ppy)$ complex; Kinetics.

Introduction

Cleavage of $[Cp^*RhCl_2]_2$ with various polypyridines easily leads to mononuclear polypyridine derivatives $Cp^*Rh(ppy)Cl_2$ (**1** [1, 2]). Polypyridines different from *bipy* (2,2′-bipyridine) and *o*-phenanthroline derivatives have been applied in the same reaction by *Kaim* an coworkers [3]. Complexes **1** hydrolyze in water to aquaions $[Cp^*Rh(ppy)H_2O]^{2+}$ (**2**). The water soluble complexes **2** are stable towards hydrolytic loss of Cp^* and *ppy* ligands over a wide *pH* range. The pK_s value of the water molecule in **2a** ($ppy = 2,2'$-bipyridine) has been determined as 8.2 ± 0.15 [4] which means that the species present in water at $pH > 10$ are hydroxo complexes $[Cp^*Rh(bipy)(OH)]^+$ (**3**). Compounds **1–3** are reduced in cyclic voltammetry and by suitable reducing agents (cobaltocene) to intense blue or violet Rh(I) complexes $Cp^*Rh(bipy)$ (**4**, $\lambda_{max} = 512$ nm), where reduction potentials for Rh(III)/Rh(I) have been found to be around $-0.6 - -0.95$ V *vs.* SCE depending on *ppy* and *pH* [2].

The system **2/3** has previously been utilized as a catalyst for the reduction of protons to hydrogen, a reaction that could be effected with visible light using illuminated TiO_2 colloid as the electron donor [1]. Other groups have immobilized the system for the same purpose on an electrode surface [5] or applied it for *e.g.* the regeneration of *NAD*H from NAD^+ [6]. Analogous Ir complexes have been prepared and are effective photocatalysts for the water gas shift reaction [7]. In the present communication we report on the oxidation of alcohols by the system **2/3**.

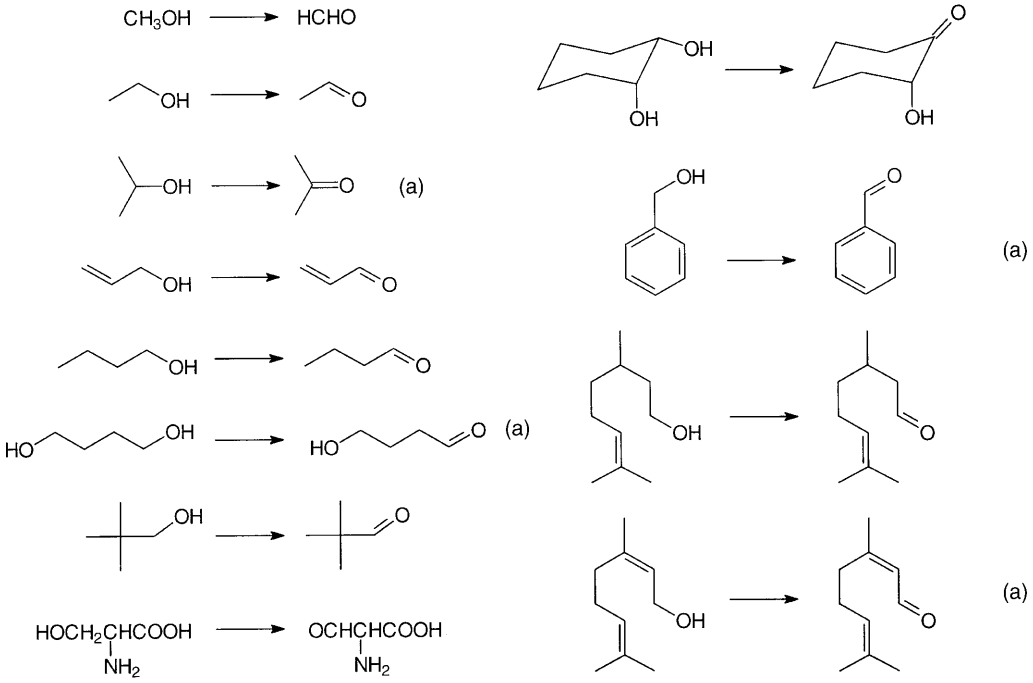
* Corresponding author

1: $Cp^*Rh(ppy)Cl_2$
2: $[Cp^*Rh(ppy)H_2O]^{2+}$
3: $[Cp^*Rh(ppy)(OH)]^+$
4: $Cp^*Rh(ppy)$

ppy = 2,2′-bipyridine (**a**), 2,2′-bipyridine-4,4′-dicarboxylate (**b**), *o*-phenanthroline (**c**), tetrahydro-4,4′-dialkyl-*bis*-oxazole (**d**)

Results and Discussion

When a deaerated aqueous solution of **3b** at $pH > 10$ is treated with a primary or secondary alcohol at ambient or slightly elevated temperature, the development of an intense characteristic blue color within some minutes indicates the formation of the Rh(I) complex **4b**. The formation of an aldehyde or ketone can be shown by precipitation of the corresponding 2,4-dinitrophenylhydrazone. For other polypyridines such as 2,2′-bipyridine or *o*-phenanthroline, the Rh(I) complex is insoluble in water and will precipitate from an aqueous solution. A homogeneous reaction is achieved in tetrahydrofurane, dimethylformamide, acetonitrile, or the alcohol as the solvent. Since the Rh(I) complexes are air sensitive, their formation can only be observed under anaerbic conditions. It was verified that the same mixture does not give any oxidation products in the presence of oxygen. The reaction has been applied to a variety of different alcohols with and without additional functional groups (Scheme 1).



Scheme 1. Alcohols that effect the reduction of $[Cp^*Rh(III)(ppy)(OH)]^+$ to $Cp^*Rh(I)(ppy)$; carbonyl compounds marked with (a) were identified as 2,4-dinitrophenylhydrazones

In some cases, the oxidation product of the alcohol was identified as the aldehyde or ketone by conversion to the respective 2,4-dinitrophenylhydrazone. GC analysis of the reaction mixture did not show any carboxylic acid or other oxidation products after several cycles. The overall reaction is thus as formulated in Eq. (1). In the presence of an excess of alcohol, the conversion of Rh(III) to Rh(I) was quantitative.

$$[Cp^*Rh(ppy)(OH)]^+ + RCH_2OH + OH^- \longrightarrow Cp^*Rh(ppy) + RCHO + 2H_2O \quad (1)$$

Though the reduction of Rh(III) to Rh(I) with concomitant aldehyde/ketone formation due to the involvement of Rh(I) in the reaction cycle (see below) only proceeds under anaerobic conditions, the whole reaction can still be made *quasi*-catalytic if oxygen is admitted after one cycle to reoxidize Rh(I) to Rh(III). In this way, many cycles (more than 10, depending on *ppy* and *pH*) have been effected.

Reaction scheme and kinetics

As mentioned above, the reaction only proceeds in deaerated solutions, and there is always an induction period before the development of the blue color commences. The length of this induction period varies between seconds and several minutes depending on the reaction medium and the deaeration procedure; it can be shortened by adding a small amount of Rh(I) complex to the deaerated solution. These observations strongly suggest an autocatalytic pathway with the participation of the Rh(I) complex. Since the product-forming step of an alcohol to aldehyde conversion is the abstraction of the α-hydrogen we suggest that Rh(I) is effective in this step. A Rh(II) hydride formed this way would be rapidly converted to Rh(I) and a proton as outlined below ($RH = Cp^*Rh(ppy)$).

$$RH(III)(OH)^+ + RCH_2OH \rightleftharpoons RH(III)OCH_2R^+ + H_2O \quad (2)$$

$$RH(III)OCH_2R^+ + RH(I) \longrightarrow RH(II)^+ + RH(II)H + RCHO \quad (3)$$

$$RH(II)^+ + RH(II)H \longrightarrow RH(I) + RH(I)H^+ \quad (4)$$

$$RH(I)H^+ + OH^- \longrightarrow RH(I) + H_2O \quad (5)$$

The 1st step in the sequence, *i.e.* complexation of the alcohol to Rh(III) either as an alcoholate as given in Eq (2) or as an alcohol complex, is inferred from the observation that the reaction is strongly inhibited by stronger, σ-donors such as amines which obviously block the residual coordination site at Rh(III) for alcohol complexation. It further accounts for the fact that the reaction requires alkaline conditions, since formation of a Rh(III) alcoholate is feasible only at high *pH*. Formation of an alcoholate by the hydrogen donating alcohol is invoked in transfer hydrogenations, particularly those catalyzed by Rh(*ppy*) complexes [8]. Deprotonation of protonated Rh(I) (Eq. (5)) would proceed completely at $pH \geq 9$ where the alcohol oxidation is still very slow. A pK_a around 8 was evaluated from spectroelectrochemistry for $Cp^*Rh(I)(bipy)H^+$ (*bipy* = 4,4′-dicarboxylato-2,2′-bipyridine). In these experiments, the reduction of $Cp^*Rh(bipy)(H_2O)^{2+}$ gives the colored Rh(I)

complex *Cp**Rh(I)(*bipy*) only at $pH \geq 8$. Below this *pH*, the reduction product is the much less colored protonated complex *Cp**Rh(I)(*bipy*)H^+. In the 2nd step (Eq. (3)), a hydrogen atom is abstracted from the α-CH_2 group of the alcohol by Rh(I) generating formally two Rh(II) complexes. Though transfer of hydrogen, *e.g.* in alcohol dehydrogenase to NAD^+ to give *NAD*H, may be viewed as hydride transfer as well as the corresponding step in transfer hydrogenations (1st half of Eq. (6)), in a recent system detected by *Wieghardt* and coworkers [9], where alcohols have been oxidized aerobically by a Cu bisphenolamine complex, α-hydrogen transfer is considered a radical transfer step.

Electron transfer between protonated and unprotonated Rh(II) species (Eq. (4)) forms protonated and unprotonated Rh(I) complexes, where the former will be deprotonated at the *pH* given. Note that the seeming contradiction in oxidation states in Eq. (4) is due to the fact that the Rh bound hydrogen is counted (by convention) as a hydride at the left hand side but as a proton at the right hand side.

Equations (2)–(5) not only take care of the fact that the reaction requires alkaline conditions and accounts for the overall autocatalytic pathway, but also explains why it does not proceed under aerobic conditions: rapid reoxidation of any Rh(I) formed quenches step two and thus the whole cycle. It also rules out the 2nd mechanistic alternative, *i.e.* deprotonation of the Rh(III)alcoholate complex at the α-CH_2 group, or the hydride derived thereof by β-insertion (Eq. (6)). It has, however, been observed that under strong alkaline conditions, *i.e.* at $pH \geq 13$, the reaction mechanism changes. The induction period is shortened or even absent, and the time profile of Rh(I) after about one half life resembles more that of an ordinary 1st order reaction. Operation of Eq. (6) would readily account for this behavior.

$$RH(\mathrm{III})\mathrm{OCH_2}R \longrightarrow RH(\mathrm{I})\mathrm{H}^+ + R\mathrm{CHO} \xrightarrow{\mathrm{OH}^-} RH(\mathrm{I}) + \mathrm{H_2O} \qquad (6)$$

A kinetic run at 23°C of a solution containing $1.12 \cdot 10^{-3}\,M$ **1c** (*ppy* = *o*-phenanthroline) and $0.01\,M$ KOH in $2\,\mathrm{cm}^3$ *i*-propanol was simulated according to the reaction scheme with the CKS kinetic simulator [8]. A starting concentration of $5 \cdot 10^{-5}\,M$ Rh(I) was given to initiate the reaction, and the initial concentrations of alcohol and water were set to $0.1\,M$ for practical reasons (to keep the required number of particles and thus the time for simulation within a reasonable limit). The equilibrium of Eq. (2) was fixed arbitrarily to $K_2 = 10$ with rate constants $k_2 = 5 \cdot 10^5$, $k_{-2} = 5 \cdot 10^4$, and $k_4 = k_5 = 5 \cdot 10^4\,M^{-1} \cdot \mathrm{min}^{-1}$ to ensure the pre-equilibrium and the consecutive ractions to be fast in comparison to the rate determining step (Eq. (3)). The simulated curve (Fig. 1) was obtained with $k_3 = 700\,M^{-1} \cdot \mathrm{min}^{-1}$. Though the simulated curve is somewhat more curved than the experimental one, where also the beginning of the reaction is lacking, the order of the slow reaction, *i.e.* Eq. (3), is well reproduced. Note that the rate constant k_3 has no real significance; only the product $K_2 \cdot k_3 = 7 \cdot 10^4\,M^{-1} \cdot \mathrm{min}^{-1}$ can be deduced from the observed kinetics.

A 1st order dependence of the rate on $[OH^-]$ and thus a strong support for the participation of Eq. (2) in the reaction scheme was revealed when a kinetic run at 1/10 of the base concentration was simulated with the same rate constant and gave very good agreement between experimental and simulated slopes in the nearly linear part of the *c vs. t* curve.

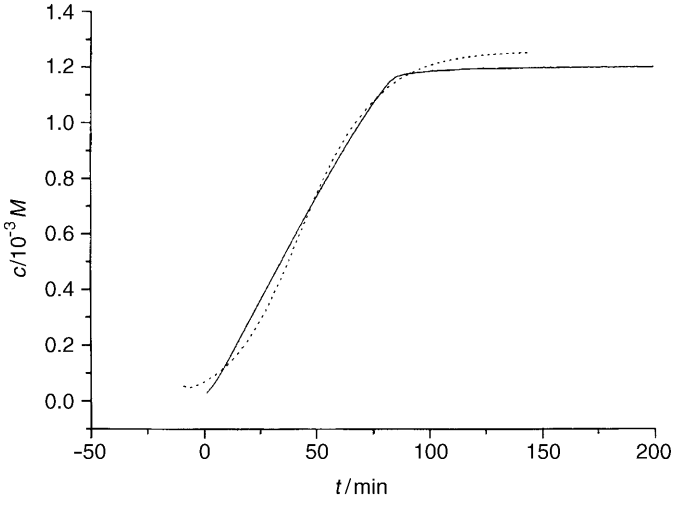


Fig. 1. Experimental (———) and simulated (· · · · · ·) concentration time profile for the reaction a 1.2 m*M* solution of **2c** ($L = o$-phenanthroline) with *i*-propanol in 0.01 *M* KOH according to Eqs. (2)–(5)

Thermodynamics

Alcohol oxidation catalyzed by metal complexes has utilized strongly oxidizing metals in high oxidation states such as Mn(III), Co(III), and Ni(III) in most cases. The formation of oxidation products beyond the aldehyde/ketone stage is a frequently encountered problem, in particular with oxidation of primary alcohols. In contrast, the redox couple **2b/4b** for example is characterized by potentials of −0.56 (E_p^c) and −0.50 (E_p^a) V vs. SCE. The corresponding values for **2a/4a** are −0.66 and −0.54 V [2]. On the other hand, the driving force for Eq. (7) can be estimated as −0.8 V *vs.* SCE at *pH* 13.

$$C_2H_5OH + 2OH^- \longrightarrow CH_3CHO + 2H_2O + 2e^- \quad (7)$$

This leaves an overall driving force for Eq. (1) of only −150 to −250 mV ($\Delta G^\circ = -0.3 - -0.5$ kJ/mol), much less than is typical for alcohol oxidation by high oxidation state transition metal complexes. The low driving force may be responsible for the clean oxidation in particular of primary alcohols to aldehydes. It may find application in cases where substrates feature oxidation sensitive functionalities such as conjugated multiple bonds. The small driving force, on the other hand, can lead to a reversal of the reaction for activated, *i.e.* stronger oxidizing carbonyl compounds. It was found that *e.g.* pyruvate readily oxidizes Rh(I) back to Rh(III), presumably with formation of lactate, under the same conditions where ordinary alcohols are reduced.

$$CH_3C(O)COO^- + Rh(I) + 2H_2O \longrightarrow CH_3CH(OH)COO^- + Rh(III)OH^+ + OH^- \quad (8)$$

Experimental

Rh(III)*ppy* complexes **2/3** were prepared as previously described [1, 2]. For alcohol oxidation experiments they may be generated *in situ* by adding an equivalent of the respective polypyridine to a slurry of $[Cp^*RhCl_2]_2$ in methanol.

Pentamethylcyclopentadienyl-(4S,4′S)-4,4′,5,5′-tetrahydro-4,4′-methyl-bisoxazole-chlororhodium tetrafluoroborate (**2d**)

2d was prepared analogously to the polypyridine complexes [2] after dehalogenation of $[Cp^*RhCl_2]_2$ with one equivalent of $AgBF_4$ in methanol or acetone. ^{1}H NMR (300 MHz, δ, acetone-d_6): 1.63, 1.91 (d, $J = 6.3$ Hz, Me), 1.95 (s, 15H, Cp^*), 3.58 (m, 2H, H4), 4.8 (m, 2H, H4′), 5.11 (m, 2H, H5) ppm; cyclic voltammogram (CH_2Cl_2:acetonitrile = 1:1, Bu_4NPF_6, $v = 200$ mV/s): $E_p^c = -0.94$ (irrev), $E_p^a = -0.43$ (irrev).

Pentamethylcyclopentadienyl-(4S,4′S)-4,4′,5,5′-tetrahydro-4,4′-i-propyl-bisoxazole-chlororhodium tetrafluoroborate (**2e**)

^{1}H NMR (300 MHz, δ, CD_2Cl_2): 1.00, 1.07 (d, $J = 6.5$ Hz, 2H each, Me), 1.5 (m, 3H, $CH(Me)_2$ and CH_2), 1.87 (s, 15 H, Cp^*), 4.3 (dd, $J = 7.3$, 8.6 Hz, 2H, H4), 4.51 (d, $J = 8.6$ Hz, 2H, H4′), 4.77 (m, 2H, H5) ppm.

Oxidation of alcohols was conducted in 5 cm^3 septum sealed vessels charged with a 10^{-3} –10^{-4} *M* solution of the Rh(III) complex in H_2O (*ppy* = 2,2′-bipyridine-4,4′-dicarboxylate), *THF*, *DMF*, or the alcohol as solvent, to which 0.1 *M* aqueous KOH and the alcohol were added. Experiments with alcohols collected in Scheme 1 were performed with $\sim 10^{-3}$ *M* **3a**, 10^{-2} *M* KOH, and 10^{-2} *M* alcohol in *THF*:H_2O = 1:1 to ensure the solubility of **4a**. After deaerating the vessels with Ar by means of a syringe needle, the reaction starts by developing a blue to violet color. Repeated reduction and reoxidation of the blue solution was effected by injecting air slightly less than required for stoichiometric reoxidation of Rh(I). In one experiment, a 20 cm^3 septum sealed vessel was charged in the same way, and after the reduction had come to completion once, oxygen was continuously injected by means of an automatic pipette (Metrohm 702 Titrino) at a rate ensuring the presence of residual Rh(I) throughout. Polypyridine complexes generally allowed many reduction-reoxidation cycles. Bisoxazole complexes which in cyclic voltammetry showed similar reduction-oxidation behavior and developed dark red solutions in the presence of alcohol and base gave only one cycle.

Kinetic measurements were performed in a 5 mm optical glass cell fitted with a rubber seal. The absorption of the Rh(I) phenanthroline complex at 700 nm was followed with a J&M Tidas diode array spectrophotometer at 1 min intervals. The reaction scheme was simulated with the CKS, Vers. 1, kinetic simulator program [10] and compared with the experimental curves using Origin 6.0®.

References

[1] Kölle U, Grätzel M (1987) Angew Chem **99**: 572; (1987) Angew Int Ed Engl **26**: 567
[2] Kölle U, Kang B-S, Infelta P, Comte P, Grätzel M (1989) Chem Ber **122**: 1869
[3] Ladwig M, Kaim W (1991) J Organomet Chem **419**: 233; Kaim W, Reinhardt R, Sieger M (1994) Inorg Chem **33**: 4453
[4] Dadci L, Elias H, Frey U, Hörnig A, Kölle U, Merbach AE, Paulus H, Schneider JS (1995) Inorg Chem **34**: 306
[5] a) Cosnier S, Deronzier A, Vlachopoulos N (1989) J Chem Soc Chem Commun 1259; b) Caix C, Chardon-Noblat S, Deronzier A, Moutet J-C, Tingry S (1997) J Organomet Chem **540**: 105
[6] Ruppert R, Herrmann S, Steckhan E (1987) Tetrahedron Lett **28**: 6538; (1988) J Chem Soc Chem Commun 1150
[7] a) Ziessel R (1988) J Chem Soc Chem Commun 16; b) Ziessel R (1991) Angew Chem **103**: 863
[8] a) Zassinovich G, Mestroni G, Gladiali S (1992) Chem Rev **92**: 1051; b) Gladiali S, Mestroni G (1998) In: Beller M, Bolm C (eds) Transition Metals for Organic Synthesis, vol 2, Wiley-VCH, p 97 ff
[9] Chaudhuri P, Hess M, Weyhermüller T, Wieghardt K (1999) Angew Chem **111**: 1165
[10] Chemical Kinetics Simulator (1995) IBM Almaden Research Center

Received July 27, 2000. Accepted September 18, 2000