Water-soluble diruthenium complexes bearing acetate and carbonate bridges: highly efficient catalysts for aerobic oxidation of alcohols in water

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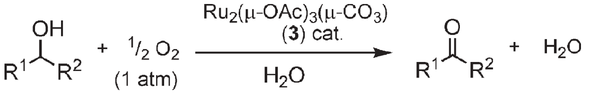
The aerobic oxidation of alcohols in water can be performed efficiently in the presence of a catalytic amount of the water-soluble diruthenium complex $Ru_2(\mu\text{-}OAc)_3(\mu\text{-}CO_3)$ under an atmospheric pressure (1 atm) of O_2.

The aerobic oxidation of alcohols that proceeds in water is important from environmental and economical viewpoints, not only as a practical process for the production of carbonyl compounds, but also as a model system for a variety of oxidative transformations.[1] Although a number of homogeneous catalysts have been used for the oxidation of alcohols with molecular oxygen, most of the reported reactions are carried out in organic solvents.[2] This is probably due to difficulties in the preparation of homogeneous catalysts that exhibit a balance between reactivity and stability in the presence of water and O_2. Most of the reported reactions in water employed heterogeneous catalysts,[3,4] the low catalytic activities of which generally have been compensated by the supplementary use of less green additives such as phase transfer catalysts and strong bases.

The homogeneous water-soluble-catalyst based methods are promising strategies for aerobic oxidations in water because of the good controllability of the catalysts. However, the reported methods are limited to reactions that use water-soluble palladium phenanthroline[5] and biquinoline[6] catalysts under a pressure of air. We have found that a series of water-soluble acetate-bridged diruthenium complexes exhibit extremely high catalytic activity in the aerobic oxidation of alcohols in water. The reaction can be performed both in water and water–organic solvent biphasic systems under an atmospheric pressure (1 atm) of molecular oxygen (eqn (1)).



(1)

The catalytic activities of various water-soluble ruthenium complexes were examined for the aerobic oxidation of 1-phenylethanol (**1**) to acetophenone (**2**) in a toluene–water biphasic system under an O_2 atmosphere (1 atm) at 80 °C. The initial rates of formation of **2** (k_{obs} = d[**2**]/dt) were evaluated by GLC analysis of the reaction mixture until 10% conversion of **1** (Table 1). The acetate-bridged diruthenium complexes $Ru_2(OAc)_3(CO_3)$ (**3**) and $[Ru_2(OAc)_4](OAc)$ (**4**)[7] were found to be effective catalysts (entries 1 and 2). $[Ru_2(OAc)_4]_2(SO_4)$ (**5**)[8] exhibited moderate activity (entry 3), while the other water-soluble mono- and multinuclear catalysts, including $RuCl_3$, $K_2[RuCl_5(H_2O)]$ and $[Ru_3O(OAc)_6(H_2O)_3](OAc)$, exhibited lower catalytic activities (entries 4–6). Conventional ruthenium catalysts for the aerobic oxidation of alcohols, such as RuO_2, $RuCl_2(PPh_3)_3$ and Ru/C, are water-insoluble and inactive.

The effect of μ-bridged ligands was examined using a series of diruthenium complexes. Tetrakis-carbonate, -sulfate and -phosphate complexes—$K_3[Ru_2(CO_3)_4]$,[9] $K_3[Ru_2(SO_4)_4]$[10] and $K_4[Ru_2(HPO_4)_3(PO_4)]$,[10] respectively—exhibited almost no catalytic activity under the reaction conditions (entries 7–9). The acetate complex with one μ-carbonate bridge, **3**, exhibited the highest catalytic activity among all the examined catalysts (entry 1). The di- and tri-carbonate complexes formulated as $[Ru_2(OAc)_{4-n}(CO_3)_n]$ (n = 2, 3), which can be prepared *in situ* using 1 : 2 and 1 : 3 mixtures of $Ru_2(OAc)_4Cl$ and K_2CO_3, exhibited moderate catalytic activity. Complex **3** was the sole catalyst that achieved almost >99% conversion of the alcohol. In the case of the other active catalysts such as **4** and **5**, the catalysis degraded significantly during the reaction in water and the catalysts deactivated completely at *ca.* 90% conversion.

Complex **3** was prepared by the reaction of fully acetate-bridged diruthenium complexes, such as **4** and $Ru_2(OAc)_4Cl$, with one equivalent of K_2CO_3 in water. It was characterized using ^1H NMR and IR spectra and elemental analysis.[11,12] The paramagnetic ^1H NMR spectra of **3** in D_2O showed characteristic 2 : 1 signals of *cis-* and *trans-*acetate bridges at −43.5 and −41.7 ppm, while those

Table 1 The catalytic activity of water-soluble ruthenium complexes in the oxidation of 1-phenylethanol (**1**) to acetophenone (**2**) with molecular oxygen in water[a]

Entry	Catalyst	Rate × 10^5/M s^{-1}
1	$Ru_2(OAc)_3(CO_3)$ (**3**)	1.36
2	$[Ru_2(OAc)_4](OAc)$ (**4**)	0.97
3	$[Ru_2(OAc)_4]_2(SO_4)$ (**5**)	0.35
4	$RuCl_3$	0.08
5	$K_2[RuCl_5(H_2O)]$	0.08
6	$[Ru_3O(OAc)_6(H_2O)_3](OAc)$	0.46
7	$K_3[Ru_2(CO_3)_4]$	<0.01
8	$K_3[Ru_2(SO_4)_4]$	No reaction
9	$K_4[Ru_2(HPO_4)_3(PO_4)]$	No reaction

[a] Reaction conditions: 1-phenylethanol (**1**) (2.0 mmol), Ru catalyst (10 mol% per Ru atom), H_2O (3.0 mL), toluene (2.0 mL), 353 K, O_2 (1 atm). The initial rate (k_{obs} = d[**2**]/dt) was determined by GLC analysis during the period of 0–2 h (conversion <10%).

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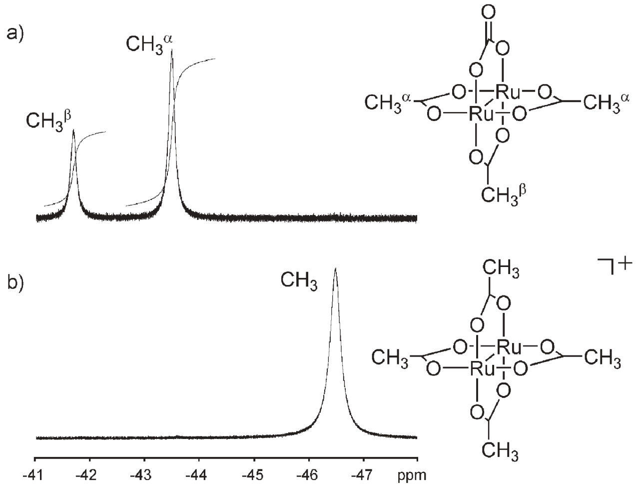
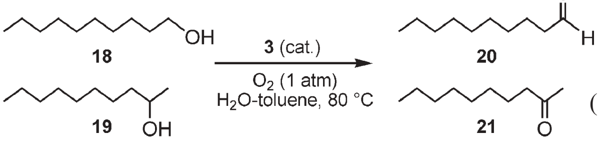


Fig. 1 500 MHz ^{1}H NMR spectra (D_2O, 298 K) of (a) $Ru_2(\mu\text{-}OAc)_3(\mu\text{-}CO_3)$ (**3**) and (b) $[Ru_2(\mu\text{-}OAc)_4]PF_6$.

of $[Ru_2(OAc)_4]PF_6$[13] showed one broad signal at −46.5 ppm (Fig. 1).

A variety of alcohols can be conveniently oxidized with an aqueous solution of a catalytic amount of **3** under an atmospheric pressure of O_2. The representative results are listed in Table 2. By this reaction, activated alcohols such as aromatic, allylic and α-keto alcohols can be converted into the corresponding carbonyl compounds (entries 1–10).[14] Primary aliphatic diols such as 1,2-cyclohexanedimethanol can be converted into the corresponding lactones (entry 11). It is noteworthy that the oxidation of **1** proceeds twice as fast in water (entry 2) than in the toluene–water biphasic system. In all the cases, the product carbonyl compounds can be readily isolated by removing the catalyst in the aqueous phase.

One important feature of the present aerobic oxidation is the high reusability of the catalyst. The aqueous catalyst phase can be stored after the reaction and reused for the next run without a loss of efficiency or selectivity (Table 3). Furthermore, the present reaction exhibits a high chemoselectivity toward primary hydroxy groups in the presence of secondary ones. For example, the treatment of a 1 : 1 mixture of 1-decanol (**18**) and 2-decanol (**19**) yielded 1-decanal (**20**) and 2-decanone (**21**) in a ratio of 14 : 1 (eqn (2)).



(2)

$k_{obs(prim)} = 2.84(11) \times 10^{-6}$ Ms^{-1} k_{prim}/k_{sec} = 14:1
$k_{obs(sec)} = 2.10(11) \times 10^{-7}$ Ms^{-1}

The chemoselectivity of the present oxidation strongly suggests that the reaction proceeds *via* the formation of an alkoxy–ruthenium complex and subsequent β-hydrido elimination.[15] Work is in progress to provide definitive mechanistic information and to apply the present method to other systems.

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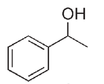
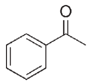
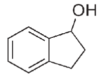
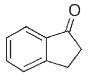
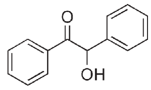
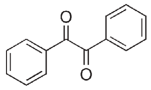
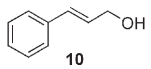
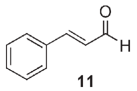
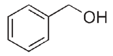
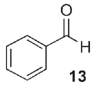
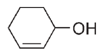
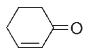
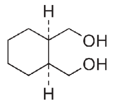
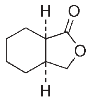
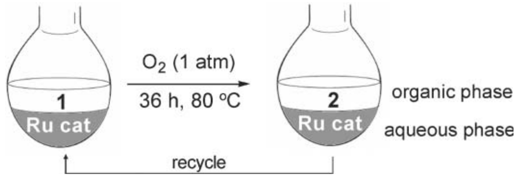
Table 2 Ruthenium-catalyzed oxidation of alcohols with molecular oxygen in water[a]

Entry	Substrate	Time/h	Conversion (%)[b]	Product	Yield (%)[b]
1	 **1**	36	99	 **2**	99
2[c]		15	99		99 (95)[d]
3	 **6**	36	99	 **7**	99
4[e]		36	99		99
5[f]	 **8**	8	99	 **9**	93
6[e,f]		8	99		91
7	 **10**	5	98	 **11**	95
8	 **12**	5	99	 **13**	21[g]
9[h]		5	99		99
10[e]	 **14**	30	99	 **15**	73
11[e]	 **16**	72	99	 **17**	86[i]

[a] The reactions were carried out as follows: a mixture of $Ru_2(OAc)_3(CO_3)$ (**3**) (0.05 mmol), alcohol (1.0 mmol), H_2O (1.5 mL), and toluene (0.5 mL) was stirred under an oxygen atmosphere (1 atm) at 80 °C. [b] Determined by GLC analysis. [c] Without toluene. [d] Isolated yield. [e] A mixture of $Ru_2(OAc)_4Cl$ (0.05 mmol) and K_2CO_3 (0.05 mmol) in H_2O was used as the catalyst. [f] Toluene (1 mL) was used for the complete dissolution of the substrate. [g] The major product was benzoic acid (76%). [h] The reaction was carried out in the presence of 2,6-di-*tert*-butyl-4-methylphenol (0.10 mmol). [i] Determined by ^{1}H NMR analysis. The corresponding cyclic hemiacetal was also formed in a 7% yield.

Table 3 Aerobic oxidations of **1** with recycled catalyst



Run	Conversion of **1** (%)[a]	Yield of **2** (%)[a]
1[b]	99	99
2[c]	99	99
3[c]	99	99

[a] Determined by GLC analysis. [b] The reaction was carried out as described in the text. [c] The aqueous phase from the previous run was reused instead of a recharge of catalyst and water.

Notes and references

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11 Characterization data of **3**: IR (KBr) 1635 (C=O), 1578 (O–C–O, sym.), 1444 (O–C–O, asym.) cm^{-1}. UV-vis (H_2O) λ_{max} (log ε): 424 (2.78) nm. ^{1}H NMR (D_2O) δ −43.5 (br, *cis*-O_2CCH_3, 6H), −41.7 (br, *trans*-O_2CCH_3, 3H). ^{13}C NMR (D_2O) δ −143.6 (*trans*-$O_2C\mathit{C}H_3$), −138.6 (*cis*-$O_2C\mathit{C}H_3$). Anal. Calcd for $C_7H_9O_9Ru_2{\cdot}H_2O$: C, 18.39; H, 2.42%. Found: C, 18.64; H, 2.54%.

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14 A typical procedure for the aerobic oxidation of **1**: a mixture of **1** (122 mg, 1.0 mmol) and **3** (22.9 mg, 0.05 mmol) in water (1.5 mL) and toluene (0.5 mL) was stirred at 80 °C for 36 h under an O_2 atmosphere (1 atm, O_2 balloon). After extraction with toluene and filtration through a pad of silica gel, ketone **2** (114 mg, 95%) was obtained in a pure form (GLC yield, 99%).

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