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Simple and Practical Aerobic Oxidation of Alcohols Catalyzed by a (*μ*-Oxo)tetraruthenium Cluster[*]

Teruyuki Kondo[1#], Yu Kimura[1], Takashi Kanda[2], Daisuke Takagi[2], Kenji Wada[2], Akio Toshimitsu[3]

[1]*Advanced Biomedical Engineering Research Unit, Kyoto University, Kyoto, Japan*
[2]*Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, Japan*
[3]*Division of Multidisciplinary Chemistry, Institute for Chemical Research, Kyoto University, Kyoto, Japan*
E-mail: [#]*teruyuki@scl.kyoto-u.ac.jp*
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Abstract

A (*μ*-oxo)tetraruthenium cluster showed high catalytic activity for a simple and practical aerobic oxidation of alcohols to aldehydes and ketones under 1 atm of O_2 or *air*. After the reaction, this cluster catalyst was recovered from the reaction mixture, and we believe that this (*μ*-oxo)tetraruthenium cluster acts as an active catalytic species throughout the reaction.

Keywords: Ruthenium, Cluster, Catalyst, Aerobic Oxidation, Alcohol

1. Introduction

The selective oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones, respecttively, is a ubiquitous and pivotal reaction in organic synthesis and the chemical industry [1,2]. Such oxidation reactions have been performed traditionally with stoichiometric inorganic oxidants, represented by CrO_3, $KMnO_4$, MnO_2, and SeO_2 [3]. However, these oxidation methods have serious drawbacks, such as their cost and the production of environmentally hazardous/toxic byproducts. From both economic and environmental viewpoints [4], there is an urgent demand for greener, more atom-efficient methods that use O_2 and *air* as readily available terminal and ideal oxidants, and produce only H_2O as a byproduct. Among the various transition-metal catalysts, much attention has been focused on the ability of ruthenium catalysts, since they have often been used for hydrogenation and transfer hydrogenation reactions [5] as well as dehydrogenation and oxidation reactions [6,7]. In fact, some success has been realized using ruthenium catalysts in alcohol oxidation with $NaIO_4$ [8], *tert*-butyl hydroperoxide [9,10], chloramine-T [11], amine-*N*-oxide [11], iodosylbenzene [12], $NaBrO_3$ [13,14], benzoquinone/Co(salen) [15-17], H_2O_2 [18], and TEMPO [19] as oxidants. However, there are few examples of a ruthenium-catalyzed *real* aerobic oxidation of alcohols without hydrogen acceptors [20,21]. Most recently, Hill and

coworkers reported the ruthenium-catalyzed practical aerobic oxidation of alcohols in a continuous-flow reactor [22].

We have been interested in ruthenium chemistry, and have successfully synthesized many novel low-valent ruthenium complexes [23,24], which can be used as highly efficient catalysts for characteristic organic synthesis [25,26]. In addition, we have recently succeeded in the synthesis of a novel and isolable (*μ*-oxo)tetraruthenium cluster (**2**) [27] by an unusual reaction of a zero-valent ruthenium complex, Ru(η^6-cot)(η^2-dmfm)$_2$ (**1**) [cot = 1,3, 5-cyclooctatriene, dmfm = dimethyl fumarate] [28], with H_2O (**Scheme 1**).

Here, we report that this novel (*μ*-oxo)tetraruthenium cluster (**2**) efficiently catalyzes a simple, practical, and selective oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones, respectively, under 1 atm of O_2 or air.

2. Results and Discussion

Benzyl alcohol was smoothly oxidized in *N,N*-dimethylacetamide (DMA) at 80˚C for 20 h under 1 atm of O_2 (balloon) to give benzaldehyde in 95% yield (**Scheme 2**). Neither benzoic acid nor acetal of benzaldehyde was obtained at all.

Among the solvents examined, toluene also gave the good results, and benzaldehyde was obtained in 94% yield, while in dioxane, propionitrile, and pyridine the conversion of benzyl alcohol decreased drastically to
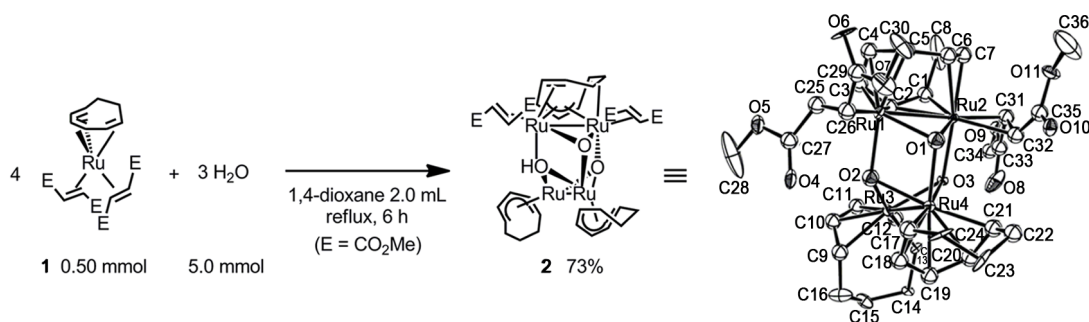
Scheme 1. Synthesis of 2 by the reaction of 1 with H₂O.
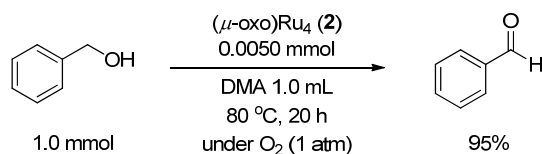
Scheme 2. Aerobic oxidation of benzyl alcohol to benzaldehyde catalyzed by 2.

give benzaldehyde in only 33%, 7%, and 2% yield, respectively.

Thus, the oxidation of primary alcohols bearing heteroaromatic rings, such as 2-thiophenemethanol and 2-pyridinemethanol, proceeded at an elevated temperature of 110°C (**Table 1**, Entries 3 and 4) to give the corresponding aldehydes in good to high yields, while with aliphatic alcohols, such as 1-octanol and cyclohexanemethanol, the yield of the desired aldehydes decreased somewhat due to the formation of carboxylic acids (overoxidation) and esters (Tischenko-type-reaction) (Entries 5 and 6).

Secondary alcohols were also converted into the corresponding ketones when the reaction was carried out at 130°C (**Table 2**). For example, benzophenone was obtained quantitatively by the aerobic oxidation of diphenylmethanol (Entry 1). Methyl 2-hydroxy-2-phenylacetate was also converted into methyl 2-oxo-2-phenylacetate in 81% yield (Entry 3). In all reactions, no ketals were formed at all.

The present catalyst system is highly active, and the oxidation of benzyl alcohol proceeded smoothly at 110 °C for 48 h under 1 atm of *air* (balloon) to give benzaldehyde in 87% yield with 95% selectivity (**Scheme 3**), while benzaldehyde was obtained in only 26% yield under an argon atmosphere[a]. Diphenylmethanol also gave benzophenone in 93% yield under 1 atm of *air*.

After the reactions, (*μ*-oxo)tetraruthenium cluster (**2**) was recovered in 20% yield by simple column chromatography, which was confirmed by ^{1}H NMR [27]. In

[a]Under an argon atmosphere, catalytic dehydrogenation of benzyl alcohol occurred to give benzaldehyde in 26% yield together with the formation of H₂ (0.20 mmol), which was confirmed by a careful GC analysis of the gas phase.

**Table 1. Aerobic oxidation of primary alcohols to aldehydes catalyzed by 2[a].**

Entry	Alcohol	Temp.(°C)	Product	Yield (%)[b]
1	(benzyl alcohol)	80	(benzaldehyde)	95 (92)
2	(2-thiophenemethanol)	80	(2-thiophenecarboxaldehyde)	45
3	(2-thiophenemethanol)	110	(2-thiophenecarboxaldehyde)	94 (88)
4	(2-pyridinemethanol)	110	(2-pyridinecarboxaldehyde)	53 (50)
5[c]	(1-octanol)	80	(octanal)	43
6[d]	(cyclohexanemethanol)	80	(cyclohexanecarboxaldehyde)	28

[a](**2**) (0.0050 mmol), alcohol (1.0 mmol), DMA (1.0 mL) for 20 h under an O₂ (1 atm, balloon). [b]GLC yield (isolated yield). [c]Octyl octanoate (12%) was generated together with a small amount of octanoic acid (below 10%). [d]Cyclohexanecarboxylic acid (21%), and cyclohexylmethyl cyclohexanecarboxylate (15%) were generated.

Table 2. Aerobic oxidation of secondary alcohols to ketones catalyzed by 2[a].

Entry	Alcohol	Product	Yield (%)[b]
1	(diphenylmethanol)	(benzophenone)	(97)
2	(1-phenylethanol)	(acetophenone)	74 (62)
3	(methyl 2-hydroxy-2-phenylacetate)	(methyl 2-oxo-2-phenylacetate)	(81)
5	(2-octanol)	(2-octanone)	67
6[c]	(cyclooctanol)	(cyclooctanone)	87 (78)

[a](**2**) (0.0050 mmol), alcohol (1.0 mmol), DMA (1.0 mL) at 130 °C for 20 h under an O₂ (1 atm, balloon). [b]GLC yield (isolated yield). [c]At 160 °C.
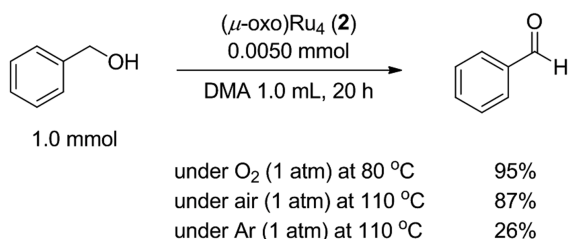
Scheme 3. Oxidation of benzyl alcohol to benzaldehyde under O₂, *air* and Ar atmosphere.

addition, mononuclear $Ru(\eta^6\text{-cot})(\eta^2\text{-dmfm})_2$ (**1**), which is the starting material for the synthesis of (μ-oxo) tetra-ruthenium cluster (**2**), showed no catalytic activity in either the absence or presence of a small amount of H_2O. No induction period was observed, and benzaldehyde was generated from the initial stage of the reaction (**Figure 1**).

Based on the results described above, we believe that a (μ-oxo)tetraruthenium cluster (**2**) acts as an active catalytic species throughout the reaction [29,30]. There are two possible catalytic cycles to be considered (A and B), which are illustrated in **Scheme 4**. In catalytic cycle A, the reaction starts with the alcoholysis of a hydroxo-Ru(II) bond in **2** with an alcohol to give an (alkoxo)Ru-(II) cluster together with H_2O. Oxidation of the alkoxo-attached ruthenium atom with O_2 then occurs to give a cluster containing an (alkoxo)(peroxo)Ru(III) part, followed by β-hydrogen elimination from an alkoxo functionality and hydrogen transfer to a peroxyo group to give a (hydroperoxo)Ru(II) cluster and the corresponding aldehyde. Final alcoholysis of a (hydroperoxo)Ru(II) cluster would give H_2O_2 with the regeneration of an (alkoxo)Ru(II) cluster. In the other possible catalytic cycle B, a (μ-oxo)-tetraruthenium cluster (**2**) is first converted into an (alkoxo)(hydroxo)Ru(II) cluster by addition of an alcohol to

a bridging oxo-Ru bond. Subsequent β-hydrogen elimination releases an aldehyde, and a (hydrido)(hydroxo)Ru(II) cluster is formed. Insertion of O_2 into a hydrido-Ru bond gives a (hydroperoxo)(hydroxo)Ru(II) cluster, and subsequent hydrogen abstraction from a hydroxo functionality gives H_2O_2 with the regeneration of **2**. After the reaction, no peroxide was detected in the reaction mixture by a peroxide test (see Experimental), and we consider that H_2O_2 is decomposed immediately to H_2O and O_2 under the present reaction conditions.

Although there is not yet much evidence for full consideration and discussion of the mechanism, the recent study on the mechanism of ruthenium-catalyzed alcohol oxidation, in which the active [Ru]-OH species could be generated, supports the mechanism according to the catalytic cycle B [19,31,32], and the real oxidant in the present reaction is O_2, not H_2O_2. A further mechanistic study including observation of KIE (Kinetic Isotope Effect) for alcohols is now in progress.
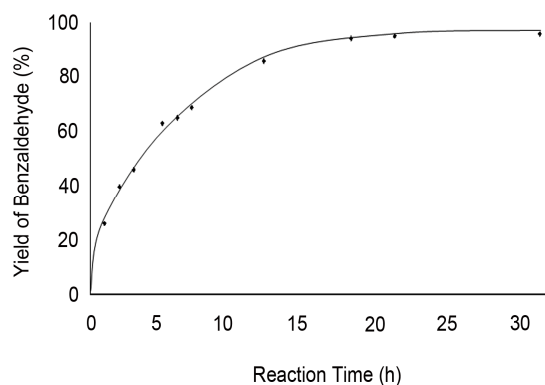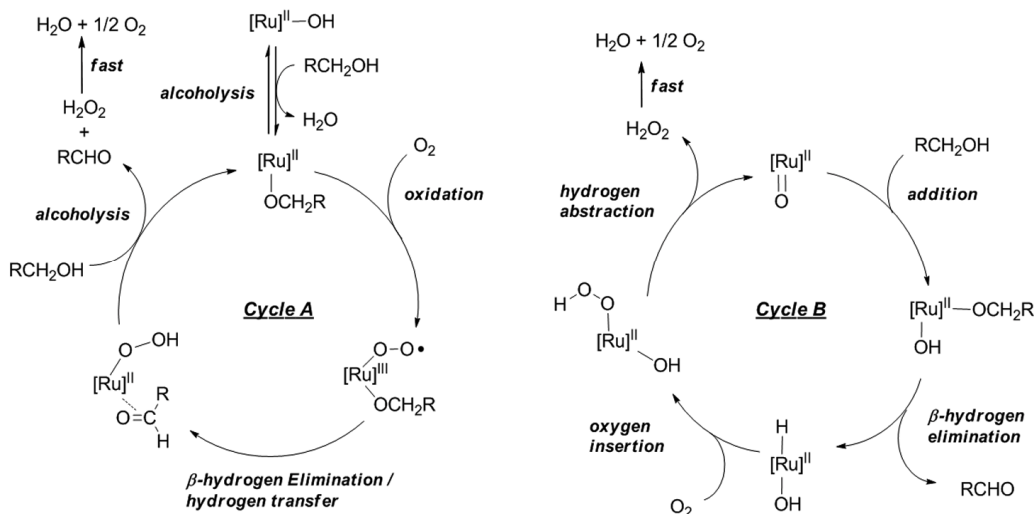

Figure 1. Time-course of aerobic oxidation of benzyl alcohol to benzaldehyde catalyzed by 2.

Scheme 4. Possible catalytic cycles for (μ-oxo)Ru₄ (2)-catalyzed aerobic oxidation of primary alcohols to aldehydes.

3. Experimental

3.1. Materials

Alcohols were obtained commercially and purified before use by standard procedures. Anhydrous DMA and dioxane were obtained commercially and used as received. Anhydrous toluene, THF, and CH_2Cl_2 were obtained by filtration through a drying column on a Glass Contour system [33], and used after bubbling with argon. $Ru(\eta^6\text{-cot})$-$(\eta^2\text{-dmfm})_2$ (**1**) and (μ-oxo)tetraruthenium cluster (**2**) were prepared as described in the literature [27,28]. Quantofix® peroxide test paper was used to detect H_2O_2.

3.2. General

GLC analyses were carried out on a Shimadzu GC14BPF (FID) gas chromatograph equipped with a glass column (2.8 mm i.d. × 3 m) packed with Silicone OV-17 (2% on Chromosorb W(AW-DMCS), 60 mesh - 80 mesh). The formation of hydrogen was analyzed carefully by a Shimadzu 8AIT (TCD) gas chromatograph equipped with a stainless column (3.0 mm i.d. × 2 m) packed with MS-5A. GC/MS analyses were performed using a Shimadzu Parvum2 mass spectrometer connected to a Shimadzu GC-2010 gas chromatograph [column: J & W Scientific capillary column DB-1, 0.25 mm i.d. × 25 m (film thickness 0.25 μm)]. ^{1}H-NMR spectra were recorded at 400 MHz, and ^{13}C-NMR spectra were recorded at 100 MHz. Samples were analyzed in $CDCl_3$, and the chemical shift values are expressed relative to Me_4Si as an internal standard. IR spectra were obtained on a JASCO FT/IR-4200 spectrometer.

3.3. General Procedure for the (μ-Oxo)Tetraruthenium Cluster-Catalyzed Oxidation of Alcohols to Aldehydes and Ketones

A mixture of alcohol (1.0 mmol), (μ-oxo)tetraruthenium cluster (**2**) (0.0050 mmol), and *N,N*-dimethylacetamide (1.0 mL) was placed in a 20 mL Pyrex flask equipped with a magnetic stirring bar and a reflux condenser under a flow of argon. The reaction vessel was then connected to a balloon containing O_2 or *air* (1 atm). The reaction was carried out at 80˚C - 110 ˚C (for primary alcohols) or 130 ˚C (for secondary alcohols) for 20 h with stirring. After being allowed to cool, the reaction mixture was analyzed by GLC. The products were isolated by Kugelrohr distillation, if necessary, followed by silica gel column chromatography (KANTO CHEMICAL, Silica Gel 60N (spherical, neutral), 40 μm - 50 μm, eluent: hexane/EtOAc = 8/1), and identified by comparing the spectral (^{1}H and ^{13}C NMR spectra [34]) and analytical data with those of authentic samples.

4. Conclusions

One of the major goals of catalysis today is the design of environmentally benign and highly atom-efficient processes to replace traditional waste-forming reactions, including some of the most fundamental synthetic methods. Our method for the catalytic oxidation of alcohols to aldehydes and ketones can be used with a wide range of alcohols, is highly atom-efficient, and is particularly convenient with respect to a simple operation under 1 atm of O_2 or *air* as the *real* oxidants.

5. Acknowledgements

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