A Novel Ru(VII)/Ru(IV) Mediatory System for Electrooxidation of Primary and Secondary Alcohols, Leading to Aldehydes and Ketones

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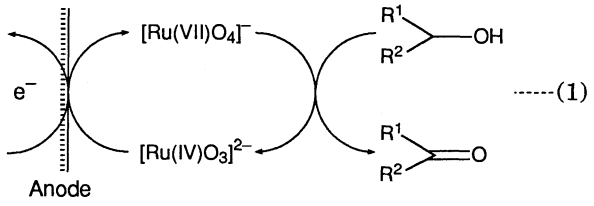
A soluble Ru(VII)/Ru(IV) redox system in MeCN/H_2O(9/1 v/v)-Bu_4NOH-(Pt/Pt) was found to be a mild oxidizing method for the electrochemical conversion of primary and secondary alcohols into their corresponding aldehydes and ketones under basic conditions.

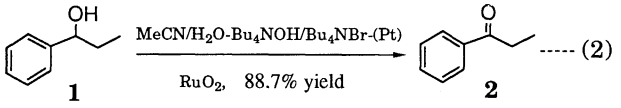
It has been demonstrated that a double mediatory Ru(VIII)/Ru(IV)–$[Cl]^+$/$[Cl]^-$ system is a versatile electrooxidation of alcohols.[1,2] The procedures are able to be used for the oxidation of a wide range of alcohols. A characteristic feature of the Ru(VIII)/Ru(IV)–$[Cl]^+$/$[Cl]^-$ mediatory system has to be generation of octa-valent ruthenium (RuO_4) as an active oxidant derived from ruthenium dioxide (RuO_2) as a black solid. The presence of halide ion is essential for the generation of RuO_4 in the double mediatory system which, occasionally, causes to produce halogenated materials as by-products.[2b] In order to avoid the unexpected halogenation, we have looked for the other system which works without aid of halogen species as a co-oxidant. Ruthenium based oxidation catalyst, $[RuO_4]^{2-}$/$[S_2O_4]^{2-}$, has been used for alcohol oxidation in strongly basic aqueous media.[3] Tetraalkylammonium perruthenates $[R_4N]^+[RuO_4]^-$ with *N*-methylmorpholine *N*-oxide as a co-oxidant are also developed for the same purpose.[4]

Described herein is a novel Ru(VII)/Ru(IV) redox mediator system for the electrooxidation of alcohols under minimum use of halogen species as shown in Scheme 1.



------(1)

Recently, we examined the possibility in the electrooxidation of alcohols using hepta-valent perruthenate$[Ru(VII)O_4]^-$ species [4] as a redox catalyst. Characteristic features of the system are as follows: 1) capability of the Ru(VII) species under basic conditions as a recyclable mediator and 2) creation of a soluble Ru(VII)/Ru(IV) redox systems in either Bu_4NOH/Bu_4NBr or Bu_4NOH medium. First, we studied electro- generation of the ruthenate $[Ru(VII)O_4]^-$ in a Bu_4NOH/Bu_4NBr system as a recyclable mediator: [Method A] A mixture of 1-phenylpropan-1-ol **1** (1.00 mmol), RuO_2 (0.1 mmol), Bu_4NOH (0.5 mmol), and Bu_4NBr (0.5 mmol) in MeCN/water (9/1, 10 mL) was placed in a glass tube cell fitted with platinum foils (1.5 X 2.0 cm^2) as electrodes. The mixture was electrolyzed under a constant current density of 50 mA/cm^2 (applied voltage 10 V) by passage of 5.0 F/mol of electricities. The routine workup of the crude product afforded the corresponding carbonyl compound **2**. The results obtained by change of additives under similar electrolysis conditions are indicated in Table 1.



1 2 ----- (2)

Table 1. Effect of additives in electrolysis system

Entry	RuO_2	Bu_4NOH	Bu_4NBr	**2** Yield/%
1	0.1 eq.	0.5 eq.	0.5 eq.	88.7
2	0.1 eq.	0.5 eq.	-	83.3
3	0.1 eq.	-	0.5 eq.	69.6
4	-	0.5 eq.	0.5 eq.	17.9
5	0.01 eq.	0.25 eq.	0.25 eq.	85.2

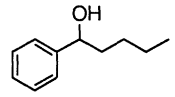
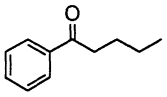
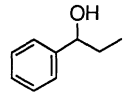
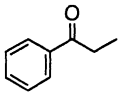
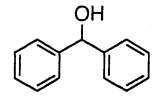
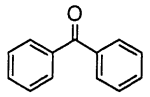
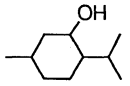
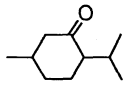
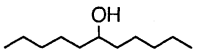
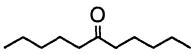
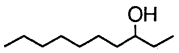
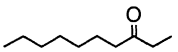
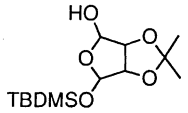
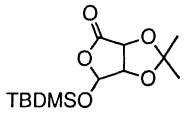
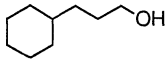
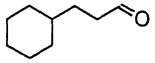
The figures (Table 1., Entries 1 and 2) demonstrate that bromide ion is not always essential for the oxidation of the alcohol **1**. For example, the presence of Bu_4NOH and Bu_4NBr in the system gave the desired ketone in 88.7 % yield (Entry 1). Happily enough, the similar conversion of **1** to **2** smoothly proceeded in 83.3 % yield in the absence of bromide ion (Entry 2). These results reveal that Ru(VII) species can play a role for the oxidation of alcohols under the both conditions, suggesting that soluble lower-valent ruthenium species are generated in the course of the reaction even if recyclable bromide ions are absent. Lack of Bu_4NOH in the above conditions seems to be less favor on oxidizing the alcohol (Entry 3). The absence of RuO_2 in the electrolysis media resulted in an unsatisfactory conversion yield (Entry 4).

Instead of the Bu_4NOH/Bu_4NBr system, an alternative tactics for the oxidation which would provide a solution for the suppression of the undesired halogenation is thought to be a recyclable RuO_2/Bu_4NOH system. In this connection, the things which should be clarified are the following items: 1) without aid of halide ion, whether RuO_2 can be oxidized under basic conditions or not, and 2) whether the intermediary Ru(IV) complex is recycled well under the employed conditions.

Our successful electrolysis condition for the novel recyclable RuO_2/Bu_4NOH system was as follows: [Method B] A mixture of the alcohol **1** (3.00 mmol), RuO_2 (0.02 mmol), and Bu_4NOH (0.50 mmol) in Acetone/Water (9/1, 10 mL) was placed in a glass cell fitted with platinum foils (1.5 X 2.0 cm^2) as electrodes. The mixture was electrolyzed under a constant current density of 10 mA/cm^2 (applied voltage 5 V) by passage of 5.0 F/mol of electricities. The routine workup of the crude product afforded the corresponding carbonyl compound **2**. The results are indicated in Table 2.

The direct evidences on working the Ru(VII)/Ru(IV) redox as a mediator system have been obtained by measurement of UV spectra. It is known that ruthenium complex solutions show

Table 2. Oxidation of alcohols by a Ru(VII)/Ru(IV) redox system

Entry	Substrate	Product	Yield/%
1			94.2 [a]
2			83.3 [a] 82.8 [b]
3			91.7 [a] 99.8 [b]
4			94.4 [b]
5			87.6 [b]
6			92.6 [b]
7			85.2 [b]
8			69.4 [b]
9	$CH_3(CH_2)_9-CH_2OH$	$CH_3(CH_2)_9-CHO$	73.7 [b]
10	$Ph(CH_2)_2-CH_2OH$	$Ph(CH_2)_2-CHO$	63.3 [b]

[a]Alcohol **1** (3.0 mmol), RuO_2 (0.02 mmol), *n*-Bu_4NOH (0.50 mmol), Acetone (9 mL), Water (1mL), (Pt) - (Pt), 5 F/mol. 10.0 mA/cm^2; Using a commutator (every 10 min).

[b]Alcohol **1** (1.0 mmol), RuO_2 (0.05 mmol), *n*-Bu_4NBr (0.25 mmol), *n*-Bu_4NOH (0.25 mmol), MeCN (9 mL), Water (1 mL), (Pt)-(Pt), 16.6 mA/cm^2, 5.0 F/mol; Using a commutator (every 10 min).

their typical colors depending on their valents.[5] The UV spectra of a deep green (dark-green) solution of the electrogenerated Ru species were superimposable with that of the authentic Ru(VII), demonstrating the formation of Ru(VII) species under the employed conditions.[6] The diagram of the correlation of oxidation potentials and pH equilibrium suggests the formation of Ru(VII) species under the employed electrolysis condition at pH 10-11 ranges. Actually, the reaction proceeded at nearly pH 10. Under these conditions, tetra-, hexa-, and hepta-valent ruthenium species tend to generate *in situ* . When the electrolysis was terminated before the end, the electrolysis solution showed a red-brown color which was well in accordance with that of reported one.[6]

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Reference and Notes

1 a) S. Torii, T. Inokuchi, and T. Yukawa, *Chem. Lett.*, **1984**, 1063; b) S. Torii, T. Inokuchi, S. Matsumoto, T. Saeki, and T. Oki, *Bull. Chem. Soc. JPN.*, **62**, 2108 (1989); c) T. Inokuchi, S. Tanigawa, M. Kanazaki, and S. Torii, *Synlett*, **1991**, 707; d) S. Torii, T. Inokuchi, and Y. Hirata, *Synthesis*, **1987**, 377.

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5 The actual valency of the generated low-valent ruthenium species is still vague. Under the passage of electricity, the electrolysis solution shows a dark green color, indicating that the rate of the electrooxidation of Ru(IV) to Ru(VII) is faster than that of consumption of Ru(VII) for the alcohol oxidation. The soluble Ru(IV) complexes would be existing as a soluble complex, i.e., $RuO_2{\cdot}H_2O{\cdot}$ ROH, $RuO_2{\cdot}2ROH$, before discharge of electrons. Decreasing of the concentration of the substrate alcohol in the final stage of the reaction tends to deposit ruthenium dioxide as a black powder precipitates. The plausible equilibrium be tween $RuO_2{\cdot}2H_2O$ and substrate alcohol is shown in equations (3) and (4).

$$Bu_4NOH + ROH \rightleftharpoons Bu_4NOR + H_2O \quad \text{-------- (3)}$$

$$RuO_2{\cdot}2H_2O \underset{+H_2O}{\overset{Bu_4NOR}{\rightleftharpoons}} RuO_2{\cdot}H_2O{\cdot}ROH \underset{+H_2O}{\overset{Bu_4NOR}{\rightleftharpoons}} RuO_2{\cdot}2ROH \quad \text{---- (4)}$$

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