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## DIOXYGEN OXIDATION OF ALCOHOLS AND ALDEHYDES OVER A CERIUM DIOXIDE-RUTHENIUM SYSTEM

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**Abstract:** Treatment of cerium dioxide with small amounts of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  allows the mild preparation of an efficient heterogeneous system for the dioxygen oxidation of various alcohols and aldehydes.

Lanthanide compounds give useful transformations in organic chemistry<sup>1</sup>. After an extensive investigation of low valent lanthanides (e.g.  $\text{SmI}_2$ )<sup>2</sup>, we are now looking to the possibility of using  $\text{Ln(IV)}$  species for selective oxidations.

Oxidation of organic compounds with  $\text{Ce(IV)}$  species has been widely investigated<sup>3</sup>. The most useful reagent is ceric ammonium nitrate (CAN).

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The cheapest source of Ce(IV), which can be regenerated with molecular oxygen is undoubtedly  $\text{CeO}_2$ , but this compound is a poor oxidant of organic compounds. Although it has been found to be active in the oxidation of hydrocarbons<sup>4,5,6</sup>, the experimental conditions are rather drastic. It has been used in the oxidation of phenols to hydroperoxycyclohexadienones in the presence of hydrogen peroxide, but according to the author the results are hard to reproduce<sup>7</sup>. Onishi *et al.*<sup>8</sup> have studied the adsorption of  $\text{O}_2$  on the surface of  $\text{CeO}_2$ , which leads to superoxide species ( $\text{O}_2^-$  adds) or peroxide species ( $\text{O}_2^{2-}$  adds) according to the pre-treatment of  $\text{CeO}_2$ . This suggests the possibility of performing air oxidations with cerium oxide<sup>9</sup>. Imamura *et al.*<sup>10</sup>, for waste water treatment, have also performed the wet oxidation of alcohols, phenols, acetamide, polypropylene, glycol and acetic acid with molecular oxygen in the presence of some metal oxides impregnated with oxides of precious metals. It appears that the  $\text{CeO}_2$ - $\text{RuO}_2$  combination is the most efficient one, giving the complete oxidation of organic compounds to  $\text{CO}_2$  and water. Yamanaka *et al.*<sup>11,12</sup> have recently reported alkane dioxygen oxidations catalysed by Ln(III). The system needs Zn powder, acetic acid, water and methylene chloride. Unfortunately the yields are low.

The development of a new heterogeneous system for oxidations with the abundant and cheap oxidant molecular oxygen remains a stimulating challenge, although many approaches have already been described<sup>13</sup>. To this end, we have investigated the controlled dioxygen oxidation of organic compounds (Table), in the presence of a  $\text{CeO}_2$ -ruthenium system that we have prepared by a procedure inspired by that of Imamura<sup>10</sup>. This  $\text{CeO}_2$ -Ru (Ru 1.95 wt %) system is easily regenerated in the presence of water and formaldehyde and its effectiveness does not increase if the percentage of ruthenium is more than 2 wt %. In our experimental conditions, ruthenium is in a catalytic amount (3.3 mol eq.%) by respect to the organic substrates, while cerium dioxide is in a stoichiometric amount.

As indicated in the table, with our system, alkanes (entries 1 and 2) are not oxidised, contrary to the results of ref. 13, most probably because the catalyst preparation is different and the experimental conditions are milder.

Aliphatic primary and secondary alcohols (entries 3 and 5) are transformed into aldehydes, acids and ketones. Cyclic secondary alcohols (entries 7, 8 and 9) are easily oxidised into ketones, especially borneol and 2-adamantanol. Under the same conditions a tertiary alcohol such as 1-adamantanol remains unchanged. The rate of oxidation strongly depends on the structure of the alcohol : menthol or geraniol react much slower than isoborneol.

Benzylic secondary alcohols (entries 13 and 15) are easily oxidised into ketones at 110°C using toluene as solvent, probably because the aromatic structure stabilise the intermediate species (and also the ketones). Under the same conditions, 1-phenyl-1,2-ethanediol and phenol remain unchanged (entries 17 and 18). It was found that phenol (1 mol eq.) inhibits the oxidation of the alcohols.

This cheap CeO<sub>2</sub>-Ru system is easy to prepare and store and allows the clean and selective dioxygen oxidation of various alcohols and aldehydes. The products are isolated by a simple filtration and the system is easily regenerated. We are currently investigating the scope of this oxidation procedure by dioxygen.

## EXPERIMENTAL

**Preparation of the oxidation system:** In a typical preparation, 5.16 g of CeO<sub>2</sub> (30 mmol), 10 mL of H<sub>2</sub>O, 260 mg of RuCl<sub>3</sub>·3H<sub>2</sub>O (1 mmol) and 0.6 mL of 37% aqueous formaldehyde, are placed in a flask fitted with a refrigerant. The mixture is heated with vigorous stirring for two hours at 90°C. The initially brown aqueous phase becomes colourless, and the cerium dioxide turns grey. 3 mL of aqueous NaOH (3N) are then added, and the mixture is heated at 100°C for an

**Table**

Entry <sup>a</sup>	Reaction time (h) temperature (°C)	Substrate	Products and isolated yield (%)
1	6 ; 140	octane	no reaction
2	6 ; 110 <sup>b</sup>	adamantane	no reaction
3	8 ; 140	1-octanol	octanoic acid ; >95
4	6 ; 140	octanal	octanoic acid ; >95
5	6 ; 140	2-octanol	2-octanone ; 96
6	6 ; 110 <sup>b</sup>	1-adamantanol	no reaction
7	1 ; 80 <sup>b</sup>	2-adamantanol	2-adamantanone ; >95
8	1 ; 110 <sup>b</sup>	borneol	camphor ; >95
9	6 ; 110 <sup>b</sup>	isoborneol	camphor ; >95
10	6 ; 110 <sup>b</sup>	nopol	no reaction
11	6 ; 110 <sup>b</sup>	menthol	menthone ; 15
12	6 ; 110 <sup>b</sup>	geraniol	geranial ; 5
13	9 ; 140	benzylic alcohol	benzaldehyde ; 80 <sup>c</sup>
14	6 ; 140	benzaldehyde	benzoic acid ; 83
15	6 ; 140	benzhydrol <sup>d</sup>	benzophenone ; >95
16	4.5 ; 110 <sup>b</sup>	1-phenyl-1-ethanol <sup>d</sup>	acetophenone ; >95
17	6 ; 110 <sup>b</sup>	1-phenyl-1,2-ethanediol	no reaction
18	6 ; 110 <sup>b</sup>	phenol	no reaction

a) Molar ratio CeO<sub>2</sub>/Substrate = 1. b) Toluene as solvent. c) Benzoic acid is obtained in 20 % yield. d) Molar ratio CeO<sub>2</sub>/Substrate = 0.5.

additional hour. The grey solid is filtered on filter-paper and washed with water. After drying in air for 8 h at 100°C, 5.44 g of a grey powder are obtained (98% yield based on Ce-RuO<sub>2</sub>). The same procedure is used to regenerate the system, except that there is no need to add further amounts of ruthenium chloride.

**Oxidation of organic compounds. General Procedure:** In a typical experiment, to a 100 mL Schlenk tube fitted with a refrigerant and corked with a rubber septum, are added 12.5 mmol of organic compound and 2.15 g of the CeO<sub>2</sub>-Ru system (12.5 mmol CeO<sub>2</sub> ; 0.41 mmol Ru). This mixture is magnetically stirred and 5 mL of toluene are also added if necessary. Oxygen gas is bubbled at the surface of the mixture by means of a metal cannula. Reactions are monitored by gas chromatography on a 8000 GC Fisons series with a flame ionisation detector (DB1 - 30 m column). Finally, the reaction mixture is mixed with diethyl ether, the crude organic material is separated from CeO<sub>2</sub>-Ru by filtration, the solvent is removed and the crude material is purified by distillation.

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