

Catalytic Oxidation of Tetrahydrofuran in the Presence of Transition Metal Complexes under Aerobic Conditions†

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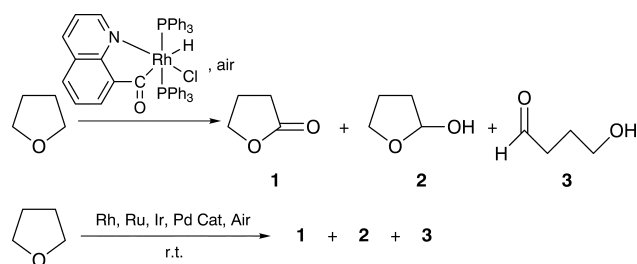
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Upon stirring a THF solution of a transition metal under an aerobic atmosphere, γ -butyrolactone and a small amount of lactol and 4-hydroxybutyraldehyde are formed; the turnover number of this catalytic oxidation process can reach 150 when $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ is used.

Oxygenation of the α -carbon of diethyl ether using metals or metal oxides has been widely studied.¹ For example, RuO_4 ,² CrO_3 ,³ and KMnO_4 ⁴ are among the stoichiometric oxidants. It has also been reported that $[\text{Rh}(\text{NBD})(\text{PMe}_2\text{Ph})][\text{BF}_4]$ (NBD = 2,5-norbornadiene) can catalyse the aerobic oxidation of ethers to esters with coproduction of formic acid in the presence of carbon dioxide and oxygen as in the corresponding catalytic oxygenation of the α -carbon of ethers using transition metals.⁵ Furthermore, Komatsu and co-workers⁶ elucidated that treatment of benzyl ethyl ether with a catalytic amount of a binuclear copper(II) complex of 7-azaindole under an oxygen atmosphere at 80 °C produced ethyl benzoate and that this oxidation reaction involves an outer-sphere electron transfer between metal and ether and the reactivity depends on the ionization of ethers.

Recently, I found that air-stable rhodium complexes such as acylrhodium(II) hydrides⁷ can easily catalyse the oxidation of tetrahydrofuran (THF) under aerobic conditions to give γ -butyrolactone **1**, a small amount of the corresponding lactol (**2**), and 4-hydroxybutyraldehyde **3** (Scheme 1). Further investigations showed that many simple transition metals also can catalyse this oxidation when a THF solution of a complex of Rh, Ru, Ir, or Pd is stirred in an open flask and a high yield of the corresponding lactone was formed. Herein I report the details of this interesting oxidation reaction.

A THF (30 ml) solution of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ (35 mg, 0.05 mmol) was stirred under aerobic conditions at room temperature for 48 h. The reaction mixture was analysed by GC and GC-MS. the product yields were determined by GC analysis using naphthalene as internal standard. The solvent was removed under reduced pressure and the residue purified by chromatography to give compound **1** which was further confirmed by ¹H NMR analysis. Some other catalysts were also examined under the same reaction conditions and their turnover numbers are summarized in Table 1. It is clear that the turnover numbers highly depend on the solubility of the catalyst used in THF, that is the homogeneous



Scheme 1

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1 Yields of lactone from THF (30 ml) in the presence of catalysts (0.05 mmol) under an aerobic atmosphere

Catalyst	Turnover number ^a		
	1	2	3
Rh/C	20	—	—
$\text{RhCl}(\text{CO})(\text{PPh}_3)_2$	94	4	5
$[\text{Rh}(\text{COD})\text{Cl}]_2$	90	4	5
	19	—	—
$\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$	64	2	4
$\text{RuH}_2(\text{PPh}_3)_4$	50	2	3
$\text{IrCl}(\text{CO})(\text{PPh}_3)_2$	150	4	3
Pd/C	10	—	—
$\text{Pd}(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$	6	—	—
$\text{Pd}(\text{PPh}_3)_4$	22	10	50

^aThe turnover number is based on the amount of the catalyst.

reaction phase gave a higher turnover. Soluble Vaska-type complexes of Rh or Ir in THF usually give a high turnover number, but sterically hindered catalysts only give a low turnover. Apparently some transition metals are much more effective than the binuclear copper(II) complex reported by Komatsu and co-workers⁶ even under mild conditions.

A control experiment was carried out under a nitrogen atmosphere using $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ as catalyst. it was confirmed by GC that, in the absence of oxygen, no reaction product is formed. The oxidation mechanism of this reaction is still obscure at present. Further study on the oxidation of other ethers or heteroatomic compounds is in progress.

Experimental

Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. Gas chromatographic analyses of compounds **1**, **2** and **3** were performed on a 50 m capillary column (Shimadzu CBP20) at 90–180 °C on a Shimadzu 14A instrument. ¹H NMR spectra were determined for solutions in CDCl_3 with tetramethylsilane as internal standard on a JNM-GX270 spectrometer, mass spectra on a JMS D-300 instrument. All the solid compounds reported in this paper gave satisfactory C, H, N microanalyses with a Perkin-Elmer Model 240 analyzer. The acylrhodium(III) complex,⁷ rhodium and iridium Vaska-type catalysts,^{8,9} were prepared according to the literature. The other transition metals were commercially available.

γ -Butyrolactone **1**: δ_{H} (CDCl_3) 2.26 (2 H, q, *J* 6.6, CH_2), 2.46 (2 H, t, *J* 7.0, CH_2) and 4.32 (2 H, t, *J* 6.9 Hz, CH_2); HRMS (EI) *m/z* 86.0362 (M^+); calc. for $\text{C}_4\text{H}_6\text{O}_2$ 86.0368.

Quinolinecarbaldehyde: δ_{H} (CDCl_3) 7.45–7.60 (1 H, m, Ar), 7.68 (1 H, t, *J* 7.7, Ar), 8.08 (1 H, d, *J* 8.1, Ar), 8.23 (1 H, d, *J* 8.2, Ar), 8.32 (1 H, d, *J* 7.4, Ar), 9.05 (1 H, d, *J* 0.2 Hz, Ar) and 11.45 (1 H, s, $\text{CH}=\text{O}$); MS (EI) *m/z* 157 (M^+) (Found: C, 76.49; H, 4.51; N, 8.9. $\text{C}_{10}\text{H}_7\text{NO}$ requires C, 76.42; H, 4.49; N, 8.91%).

Acylrhodium(III) hydride: δ_{H} (CDCl_3) -11.93 (1 H, dt, J_{PH} 6.0, J_{RH} 15.0), 6.80–8.10 (35 H, m, Ar) and 8.85 (1 H, d, J 5.0 Hz, Ar) (Found: C, 67.49; H, 4.57; N, 1.70. $\text{C}_{46}\text{H}_{37}\text{ClINOP}_2\text{Rh}$ requires C, 67.37; H, 4.55; N, 1.71%).

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