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## OXIDATION OF ALCOHOLS WITH HYDROGEN PEROXIDE CATALYZED BY SOLUBLE IRON AND OSMIUM DERIVATIVES

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### Abstract

Osmium chloride  $\text{OsCl}_3$  efficiently catalyzes (yields of products up to 90%, turnover numbers (TON) up to 1500) the oxidation of 2-cyanoethanol with hydrogen peroxide to produce the corresponding aldehyde and acid. Oxidation of isopropanol over  $\text{OsCl}_3$  gave acetone in 58% yield. The reactions were carried out either in acetonitrile or without any solvent. The analogous iron compound  $\text{FeCl}_3$  was found to be less efficient in the oxidation of 2-cyanoethanol (yields of products up to 67%, TON up to 135). Oxidation of isopropanol in this case gave acetone (yield 53%) and acetic acid (yield 11%). Some other soluble derivatives of iron or osmium exhibited noticeably lower catalytic activity in the alcohol oxidation with  $\text{H}_2\text{O}_2$ .

*Keywords:* Alcohols, homogeneous catalysis, hydrogen peroxide, iron complexes, osmium complexes, oxidation

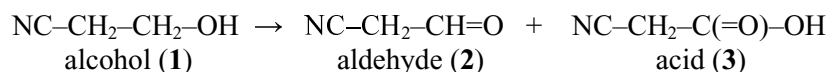
### INTRODUCTION

Hydrogen peroxide oxidation of alcohols to produce the corresponding ketones, aldehydes and carboxylic acids (see recent reviews [1–7]) can be catalyzed by both

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soluble (homogeneously) [8–29] and insoluble (heterogeneously) [30–38] metal-containing compounds. In the present work, we investigated in detail the oxidation of 2-cyanoethanol (**1**) with hydrogen peroxide catalyzed by certain soluble iron and osmium compounds. Alcohol **1** is a relatively inert compound, because generally primary alcohols are less reactive than secondary alcohols, and, in addition, the electron-withdrawing CN-group leads to lower reactivity of this compound in comparison with other primary alcohols. The selective and efficient formation of cyanoacetic acid (**3**) as well as cyanoacetic aldehyde (**2**) by the oxidation of inexpensive 2-cyanoethanol (**1**) is a reaction of certain industrial interest.



Some other alcohols, including secondary ones (*e.g.* isopropanol), were also studied as substrates in less detail in order to compare the behavior of alcohols of different structures. The reactions were carried out both in acetonitrile and without any solvent. In addition, the effects of added diamines (2,2'-bipyridine and phenanthroline) on the reaction rates and product yields were examined, because it is known [41] that such additives can dramatically enhance the efficiency of metal-catalyzed hydrocarbon oxygenations.

## EXPERIMENTAL

Hydrogen peroxide solution (aqueous 35%, Fluka) was used as received. The experiments on alcohol oxidations were carried out in air in thermostated Pyrex cylindrical vessels (total volume 5 mL) with vigorous stirring. In a typical experiment, initially, a portion of the aqueous solution of H<sub>2</sub>O<sub>2</sub> was added to the solution of the catalyst (and co-catalyst) in the alcohol. Since we have found that cyanoacetic acid is extensively decarboxylated in the GC injector, concentrations of 2-cyanoethanol, cyanoacetaldehyde and cyanoacetic acid were determined by <sup>1</sup>H NMR (Bruker 400 MHz) after addition of D<sub>2</sub>O and nitromethane as an internal standard.

## RESULTS AND DISCUSSION

We have found that simple salt, aqueous iron trichloride (see catalytic oxidations of alkanes with this compound [39–41]), in the oxidation of **1** with H<sub>2</sub>O<sub>2</sub> is the most efficient catalyst among all checked iron-containing compounds. The results of the oxidations under different conditions are summarized

**Table 1**  
Oxidation of 2-cyanoethanol (**1**) with H<sub>2</sub>O<sub>2</sub> catalyzed by FeCl<sub>3</sub><sup>a</sup>

Run	Solvent (mL)	Co-catalyst (M)	H <sub>2</sub> O <sub>2</sub> (mL)	Time (h)	T (°C)	Conv. of <b>1</b> (%)	Yields of products <sup>b</sup> (%)		TON
							-al ( <b>2</b> )	acid ( <b>3</b> )	
1	none	none	1.5	24	20	31	20	13	60
2	none	bipy (0.05)	1.5	24	20	65	34	28	115
3	none <sup>c</sup>	none	0.8	3	50	70	23	38	100
4	none <sup>c</sup>	bipy (0.05)	0.8	3	50	65	25	32	95
5	none	phen (0.05)	1.5	24	20	67	31	36	125
6	MeCN (0.6)	none	0.8	3	70	72	0.2	67	135
7	MeCN (0.6)	bipy (0.05)	0.8	3	70	66	2	55	115
8	MeCN (0.6) <sup>d</sup>	bipy (0.05)	0.8	3	60	55	8	40	100
9	MeCN (0.6) <sup>d</sup>	phen (0.05)	0.8	3	60	35	12	24	70

<sup>a</sup> Conditions. All reactants were mixed in the beginning of the reaction at room temperature. Volume of alcohol **1** used in all reactions was 0.1 mL. Concentration of FeCl<sub>3</sub> was 5 × 10<sup>-3</sup> M.

<sup>b</sup> Yields are based on initial alcohol and were determined by <sup>1</sup>H NMR.

<sup>c</sup> Concentration of FeCl<sub>3</sub> was 1 × 10<sup>-2</sup> M.

<sup>d</sup> Temperature was gradually (during 3 h) increased from 0 to 60°C

in Table 1. The reaction proceeds with 30–70% conversion and gives both acid **3** and aldehyde **2**. The maximum yield of **3** was 67% (run 6). The maximum turnover number (total moles of products produced per one mole of a catalyst; TON = 135) was also attained under conditions of run 6. In contrast to alkane oxidation by H<sub>2</sub>O<sub>2</sub> catalyzed by FeCl<sub>3</sub>, where addition of 2,2'-bipyridine (bipy) enhances dramatically (up to 40 times) the initial oxidation rate [41], in the oxidation of alcohol **1**, the effect of added bipy is weaker. Nevertheless, at room temperature (the reaction time is 24 h), the addition of bipy significantly improves the yields of products and TON (compare runs 1 and 2). In the presence of phenanthroline (phen) under the same conditions, the oxidation is also more efficient (compare runs 1 and 5). At high temperature (70°C, 3 h), the addition of bipy results in a slight decrease in the product yields (compare runs 6 and 7).

Iron chloride also catalyzes the hydrogen peroxide oxidation of secondary alcohols (Table 2). It is interesting that the addition of bipy decreases the yield of acetone in the solvent-free oxidation of isopropanol (compare runs 1 and 2) and increases the yield of acetophenone in the biphasic oxidation of 1-phenylethanol (compare runs 3 and 4).

**Table 2**  
Oxidation of secondary alcohols with H<sub>2</sub>O<sub>2</sub> catalyzed by FeCl<sub>3</sub>

Run	Co-catalyst (amount)	H <sub>2</sub> O <sub>2</sub> (mL)	Time (h)	T (°C)	Ketone <sup>a</sup> (%)	Acetic acid <sup>a</sup> (%)
Oxidation of isopropanol to acetone <sup>b</sup>						
1	none	0.4	3	55	53	11
2	bipy (0.05 M)	0.4	3	55	33	5
Oxidation of 2-phenylethanol to acetophenone <sup>c</sup>						
3	none	0.4	3	60	17	
4	bipy (0.027 mmol)	0.4	3	60	36	

<sup>a</sup> Yields are based on initial alcohol.

<sup>b</sup> Conditions: isopropanol, 0.2 mL; FeCl<sub>3</sub>, 2×10<sup>-2</sup> M.

<sup>c</sup> Conditions: 2-phenylethanol, 0.2 mL (1.4 mmol); FeCl<sub>3</sub>, 0.012 mmol; the reaction proceeded in two phases

We also checked some other iron derivatives, which turned out to be much less efficient catalysts in the oxidation of alcohol **1**. For example, ferrocene (5×10<sup>-3</sup> M) and bipy (2×10<sup>-2</sup> M) catalyzed the oxidation of **1** (0.1 mL) with H<sub>2</sub>O<sub>2</sub> (0.5 mL) (other conditions: MeCN, 0.4 mL; 60°C; 2 h) yielding aldehyde **2** (8%) and acid **3** (25%). A carbonyl derivative Fe<sub>3</sub>(CO)<sub>12</sub> (3×10<sup>-3</sup> M) gave under the same conditions only low yields of products **2** (9%) and **3** (14%).

It was interesting to compare the catalytic activity of iron chloride with that of osmium chloride, taking into account that osmium is an analogue of iron in the Periodic System. Earlier, we have demonstrated that osmium chlorides are efficient in catalytic H<sub>2</sub>O<sub>2</sub> oxidation of alkanes [42–45] (see also recent publications on oxidation catalysis by osmium complexes [46–49]). In this work, it turned out that OsCl<sub>3</sub> is noticeably more efficient than FeCl<sub>3</sub> in the oxidation of **1** (Table 3). Indeed, in run 7, the total maximum yield of **2** and **3** was 90%, and the TON attained 1500. As it follows from comparison of runs 7 and 8, the addition of bipy under these conditions slightly decreases the catalyst efficiency. In contrast, the efficiency of the oxidation in the presence of a small amount of acetonitrile can be improved by adding bipy (compare runs 1 and 2). It can be seen that in all cases, substantial amounts of aldehyde **2** were formed and only in run 6 did the use of phenanthroline as a co-catalyst result in the predominant formation of acid **3**.

**Table 3**Oxidation of 2-cyanoethanol (**1**) with H<sub>2</sub>O<sub>2</sub> (35% aqueous) catalyzed by OsCl<sub>3</sub><sup>a</sup>

Run	OsCl <sub>3</sub> (M)	MeCN (mL)	Co-catalyst (M)	Time (h)	T (°C)	Conv. of <b>1</b> (%)	Yields of products <sup>b</sup> (%)		TON
							-al ( <b>2</b> )	acid ( <b>3</b> )	
1	1×10 <sup>-3</sup>	0.1	none	2	50	18	15	0	225
2	1×10 <sup>-3</sup>	0.1	bipy (4×10 <sup>-3</sup> )	2	50	35	30	0	450
3	5×10 <sup>-3</sup>	0.6	bipy (5×10 <sup>-2</sup> )	4	70	85	50	30	160
4	5×10 <sup>-3</sup>	0.6	bipy (1×10 <sup>-1</sup> )	4	70	75	45	21	130
5	1×10 <sup>-2</sup>	0.6	bipy (5×10 <sup>-2</sup> )	4	70	88	39	44	80
6	5×10 <sup>-3</sup>	0.6	phen (5×10 <sup>-2</sup> )	4	70	99	1	57	120
7	1×10 <sup>-3</sup>	none	none	3	70	97	20	70	1500
8	1×10 <sup>-3</sup>	none	bipy (5 × 10 <sup>-2</sup> )	3	70	97	24	63	1490

<sup>a</sup> Conditions. All reactants were mixed in the beginning of the reaction at room temperature. Volume of alcohol **1** used in all reactions was 0.1 mL; H<sub>2</sub>O<sub>2</sub>, 0.8 mL.

<sup>b</sup> Yields are based on the initial alcohol and were determined by <sup>1</sup>H NMR.

The oxidation of heptanol-1 (0.1 mL, 0.53 M) gave under similar conditions (OsCl<sub>3</sub>, 5×10<sup>-3</sup> M; H<sub>2</sub>O<sub>2</sub>, 1 mL, 6.7 M; bipy, 5×10<sup>-2</sup> M; MeCN, 0.4 mL; 60°C; 2 h) predominantly the corresponding aldehyde. In this case, a mixture of the aldehyde (0.34 M; 64%), heptanoic acid (0.016 M; 3%) and initial heptanol-1 (0.17 M; 33%) (the total yield of products 67%, 0.36 M, TON = 72) was formed. We have also found that a trinuclear hydrido carbonyl complex H<sub>2</sub>Os<sub>3</sub>(CO)<sub>10</sub> (for the chemistry of this compound, see, *e.g.*, [50]) catalyzes the oxidation of alcohols in the absence of a diamine. For example, the oxidation of 0.1 mL of alcohol **1** (conditions: catalyst, 2×10<sup>-4</sup> M; H<sub>2</sub>O<sub>2</sub>, 0.5 mL; MeCN, 0.3 mL; 50°C; 3 h) yielded **2** (28%) and **3** (8%) and the reaction of isopropanol (0.1 mL) under the same conditions gave acetone with 58% yield based on initial alcohol. Another complex containing the triosmium carbonyl fragment, namely (2,3-η-1,4-diphenylbut-2-en-1,4-dione)undecacarbonyl triangulotri-osmium (for synthesis, see [51]), which has been shown to be very active in alkane oxidations with peroxides [52], exhibited a relatively low activity in the oxidation of **1** (at [catalyst] = 1×10<sup>-4</sup> M, conversion was only 17% and aldehyde **2** was the sole product). However, the efficiency was improved when the catalyst is used in a higher concentration (1×10<sup>-3</sup> M) and bipy (5×10<sup>-2</sup> M) is added. In this case, the oxidation of 0.1 mL of alcohol **1** (H<sub>2</sub>O<sub>2</sub>, 0.2 mL; MeCN, 0.15 mL; 60°C; 6 h) yielded **2** (28%). Finally, we have found that decamethylsmocene (Me<sub>5</sub>C<sub>5</sub>)<sub>2</sub>Os is absolutely inactive in the oxidation of **1**.

In conclusion, in the present work, we have demonstrated that OsCl<sub>3</sub> efficiently catalyzes the oxidation of various alcohols with hydrogen peroxide, whereas an analogous compound FeCl<sub>3</sub> is a less efficient catalyst. By varying the conditions (temperature, solvent, additives), it is possible to change the selectivity of the reaction, *e.g.*, to control the aldehyde/acid ratio in the oxidation of the primary alcohol. The other osmium derivatives checked turned out to be less active (for example, a trinuclear hydrido carbonyl complex) or absolutely inactive (decamethylsmocene).

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