

## Hydrogen Peroxide Oxidation of 2-Cyanoethanol Catalyzed by Metal Complexes

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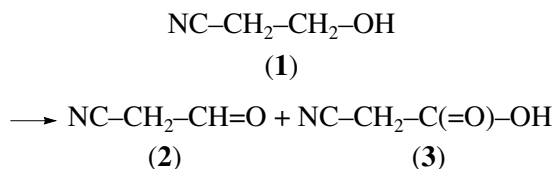
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**Abstract**—Oxidation of 2-cyanoethanol, a relatively inert primary alcohol, with several systems (both homogeneous and heterogenized) based on transition metal complexes was studied. The oxidation was performed under homogeneous conditions with 35% hydrogen peroxide upon catalysis by the chlorides FeCl<sub>3</sub> or OsCl<sub>3</sub>. The best result was obtained upon the oxidation catalyzed by OsCl<sub>3</sub> at 70°C for 3 h in the absence of solvent: the total yield of the corresponding aldehyde and cyanoacetic acid reached 90%, and the turnover number was 1500. The systems [LMn<sup>IV</sup>(O)<sub>3</sub>Mn<sup>IV</sup>L]<sub>n</sub>(X)<sub>m</sub>–oxalic acid (where L = 1,4,7-trimethyl-1,4,7-triazacyclononane) also catalyze oxidation of 2-cyanoethanol with yields of 50–70% either under homogeneous conditions (X = PF<sub>6</sub><sup>-</sup>, n = 1, and m = 2) or with the use of the catalyst in the heterogenized form (as insoluble heteropoly acid salt), where X = W<sub>12</sub>SiO<sub>40</sub><sup>4-</sup>, n = 2, and m = 1.

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### INTRODUCTION

Oxidation of alcohols into the corresponding aldehydes, ketones, and carboxylic acids is an important process in petrochemical synthesis. Transition metal complexes are known to catalyze the conversion of primary alcohols into the corresponding aldehydes and carboxylic acids by the action of hydrogen peroxide [1–9]. Preparation of cyanoacetic acid (compound **3**) and the corresponding aldehyde (compound **2**) from 2-cyanoethanol (compound **1**) is of practical importance:



Note, however, that primary alcohols usually exhibit a much lower reactivity in oxidation reactions; moreover, compound **1** is even less amenable to oxidation because of the presence of the electron-withdrawing cyano group in the molecule. Therefore, it was of interest to study transformations of this compound under the action of various oxidizing systems based on metal complex catalysts in order to find the most effective and selective oxidants. We decided to study first the applicability of the systems that had been developed earlier and appeared to be efficient in the oxidation of some

organic substrates, in particular, alkanes, olefins, and alcohols. Iron(III) chloride [10], as well as its compound with bipyridyl or other nitrogen ligands [10–13], was supposed to be the simplest and least expensive catalyst. We also used osmium(III) chloride (this metal is an iron analogue in the periodic table) for the oxidation of alkanes [14, 15]. The attempt to use, for the first time, organometal iron and osmium derivatives (metallocenes, carbonyls) as catalysts in these reactions was also of interest. We found earlier that alkanes, olefins, and alcohols were efficiently oxidized with hydrogen peroxide in acetonitrile in the presence of the binuclear manganese(IV) complex [LMn<sup>IV</sup>(O)<sub>3</sub>Mn<sup>IV</sup>L](PF<sub>6</sub>)<sub>2</sub> (**4**), where L = 1,4,7-trimethyl-1,4,7-triazacyclononane, as a catalyst and a carboxylic acid (in particular, oxalic acid (**5**)) as a cocatalyst [1, 5, 7, 8, 16–23]. In the present work, we attempted to oxidize cyanoethanol in the presence of this homogeneous catalyst, as well as of its heterogenized form (**6**) [24].

### EXPERIMENTAL

The synthesis and the structure of complex **4** were described earlier [25, 26]. Catalyst **6** was prepared using the procedure described elsewhere [24] as insoluble orange powder by mixing a solution of complex **4** in acetonitrile with a solution of H<sub>4</sub>W<sub>12</sub>SiO<sub>40</sub> in aque-

Hydrogen peroxide oxidation of 2-cyanoethanol (**1**) catalyzed by different metal complexes

Run no.	Catalyst	Co-catalyst	Solvent	<i>T</i> , °C	Time, h	Conversion of <b>1</b> , %	Yield of <b>2</b> , %	Yield of <b>3</b> , %	Notes
1	FeCl <sub>3</sub>	None	MeCN	70	3	72	0.2	67	<i>a</i>
2	FeCl <sub>3</sub>	2,2'-Bipyridyl	MeCN	70	3	66	2	55	<i>a, b</i>
3	FeCl <sub>3</sub>	<i>o</i> -Phenanthroline	MeCN	60	3	35	12	24	<i>a, c</i>
4	FeCl <sub>3</sub>	None	None	20	24	31	20	13	<i>d</i>
5	FeCl <sub>3</sub>	2,2'-Bipyridyl	None	20	24	65	34	28	<i>b, d</i>
6	FeCl <sub>3</sub>	None	None	50	3	70	23	38	<i>e</i>
7	FeCl <sub>3</sub>	2,2'-Bipyridyl	None	50	3	65	25	32	<i>b, e</i>
8	FeCl <sub>3</sub>	<i>o</i> -Phenanthroline	None	20	24	67	31	36	<i>c, d</i>
9	OsCl <sub>3</sub>	None	MeCN	50	2	18	15	0	<i>f</i>
10	OsCl <sub>3</sub>	2,2'-Bipyridyl	MeCN	50	2	35	30	0	<i>f, g</i>
11	OsCl <sub>3</sub>	2,2'-Bipyridyl	MeCN	70	4	85	50	30	<i>h</i>
12	OsCl <sub>3</sub>	2,2'-Bipyridyl	MeCN	70	4	88	39	44	<i>i</i>
13	OsCl <sub>3</sub>	<i>o</i> -Phenanthroline	MeCN	70	4	99	1	57	<i>j</i>
14	OsCl <sub>3</sub>	None	None	70	3	97	20	70	<i>k</i>
15	OsCl <sub>3</sub>	2,2'-Bipyridyl	None	70	3	97	24	63	<i>b, k</i>
16	<b>4</b>	<b>5</b>	MeCN	22	24	43	10	33	<i>l</i>
17	<b>4</b>	<b>5</b>	MeCN	22	48	60	22	48	<i>m</i>
18	<b>4</b>	<b>5</b>	MeCN	22	29	70	48	22	<i>n</i>
19	<b>4</b>	<b>5</b>	None	22	28	53	40	13	<i>o</i>
20	<b>4</b>	<b>5</b>	None	50	4	60	22	38	<i>p</i>

Notes: In all reactions performed at temperatures higher than room temperature, the reactants were mixed at room temperature, after which the temperature increased to the required level for some minutes.

*a* Substrate **1** (0.1 ml), FeCl<sub>3</sub> ( $5 \times 10^{-3}$  mol l<sup>-1</sup>), MeCN (0.6 ml), and H<sub>2</sub>O<sub>2</sub> (0.8 ml) were used.

*b* The concentration of 2,2'-bipyridyl was 0.05 mol l<sup>-1</sup>.

*c* The concentration of *o*-phenanthroline was 0.05 mol l<sup>-1</sup>.

*d* Substrate **1** (0.1 ml), FeCl<sub>3</sub> ( $5 \times 10^{-3}$  mol l<sup>-1</sup>), and H<sub>2</sub>O<sub>2</sub> (1.5 ml) were used.

*e* Substrate **1** (0.1 ml), FeCl<sub>3</sub> ( $1 \times 10^{-2}$  mol l<sup>-1</sup>), and H<sub>2</sub>O<sub>2</sub> (0.8 ml) were used.

*f* Substrate **1** (0.1 ml), OsCl<sub>3</sub> ( $1 \times 10^{-3}$  mol l<sup>-1</sup>), MeCN (0.1 ml), and H<sub>2</sub>O<sub>2</sub> (0.8 ml) were used.

*g* The concentration of 2,2'-bipyridyl was  $4 \times 10^{-3}$  mol l<sup>-1</sup>.

*h* Substrate **1** (0.1 ml), OsCl<sub>3</sub> ( $5 \times 10^{-3}$  mol l<sup>-1</sup>), 2,2'-dipyridyl ( $5 \times 10^{-2}$  mol l<sup>-1</sup>), MeCN (0.6 ml), and H<sub>2</sub>O<sub>2</sub> (0.8 ml) were used.

*i* Substrate **1** (0.1 ml), OsCl<sub>3</sub> ( $1 \times 10^{-2}$  mol l<sup>-1</sup>), 2,2'-dipyridyl ( $5 \times 10^{-2}$  mol l<sup>-1</sup>), MeCN (0.6 ml), and H<sub>2</sub>O<sub>2</sub> (0.8 ml) were used.

*j* Substrate **1** (0.1 ml), OsCl<sub>3</sub> ( $5 \times 10^{-3}$  mol l<sup>-1</sup>), *o*-phenanthroline ( $5 \times 10^{-2}$  mol l<sup>-1</sup>), MeCN (0.6 ml), and H<sub>2</sub>O<sub>2</sub> (0.8 ml) were used.

*k* Substrate **1** (0.1 ml), OsCl<sub>3</sub> ( $1 \times 10^{-3}$  mol l<sup>-1</sup>), and H<sub>2</sub>O<sub>2</sub> (0.8 ml) were used.

*l* Substrate **1** (0.1 ml), catalyst **4** ( $1 \times 10^{-4}$  mol l<sup>-1</sup>), **5** (0.006 g, 0.025 mol l<sup>-1</sup>), CH<sub>3</sub>CN (1 ml), and H<sub>2</sub>O<sub>2</sub> (0.5 ml) were used.

*m* Substrate **1** (0.1 ml), catalyst **4** ( $0.7 \times 10^{-4}$  mol l<sup>-1</sup>), **5** (0.006 g, 0.017 mol l<sup>-1</sup>), CH<sub>3</sub>CN (1 ml), and H<sub>2</sub>O<sub>2</sub> (1.5 ml) were used.

*n* The oxidant H<sub>2</sub>O<sub>2</sub> (1.5 ml) was added dropwise to the reaction mixture containing other components for 5 h, after which the solution obtained was stirred for 24 h. The amounts and concentrations of other components after the addition of H<sub>2</sub>O<sub>2</sub> were the same as in run 17 (see note *m*).

*o* The solution of catalyst **4** (2 mg) in substrate **1** (0.1 ml) was added dropwise to the mixture of **4** (6 mg) with H<sub>2</sub>O<sub>2</sub> (0.5 ml) for 4 h, after which the solution obtained was stirred for 24 h.

*p* Substrate **1** (0.1 ml), catalyst **4** (2 mg), co-catalyst **5** (0.006 g), and H<sub>2</sub>O<sub>2</sub> (0.5 ml) were used.

ous ethanol (in the ratio [4] : [H<sub>4</sub>W<sub>12</sub>SiO<sub>40</sub>] = 2 : 1) with the yield >85%. Other reagents used were commercially available. Oxidation reactions of alcohol **1** were performed in a glass cylindrical vessel surrounded by a jacket with water circulating through a thermostat. The volume of the solution was 1–2 ml. Since cyanoacetic acid produced from 2-cyanoethanol was completely decarboxylated in the chromatograph evaporator, the oxidation products of this alcohol were determined by the <sup>1</sup>H NMR technique (using a Bruker 400 MHz spec-

trometer) using D<sub>2</sub>O and nitromethane as internal standards.

## RESULTS AND DISCUSSION

In this work, we thoroughly studied the oxidation of 2-cyanoethanol with three systems containing 35% hydrogen peroxide that were used earlier for the oxidation of alkanes and some other organic compounds. The table presents the results of the experiments.

First, we found that the simplest system consisting of hydrogen peroxide and iron(III) chloride [10, 13] is useful for fairly effective conversion of alcohol **1** into oxo derivatives **2** and **3** (table, runs 1–8). The conversion of **1** reached 30–70%, and the maximum yield of acid **3** was 67% (run 1). The maximum turnover number (TON) (i.e., the number of moles of all products formed per mole of catalyst) reached 135 (run 1). We showed earlier that the rate of the cyclohexane oxidation reaction was substantially higher in the presence of 2,2'-bipyridyl in the reaction solution [13]. A comparison of runs 5 and 4 shows that the addition of 2,2'-bipyridyl leads to a double increase in the product yield in the case of oxidation of alcohol **1** at room temperature. However, the addition of the diamine does not lead to a noticeable improvement of the oxidation characteristics at elevated temperatures.

The use of some other iron derivatives instead of iron(III) chloride did not give good results: the oxidation catalyzed by ferrocene ( $5 \times 10^{-3}$  mol l<sup>-1</sup>) and 2,2'-bipyridyl ( $2 \times 10^{-2}$  mol l<sup>-1</sup>) (conditions: 0.1 ml **1**, 0.5 ml H<sub>2</sub>O<sub>2</sub>, 0.4 ml MeCN, 2 h at 60°C) gave aldehyde **2** (8%) and acid **3** (25%). Using iron carbonyl Fe<sub>3</sub>(CO)<sub>12</sub> ( $3 \times 10^{-3}$  mol l<sup>-1</sup>) as the catalyst led to even lower yields of **2** (9%) and **3** (14%).

It is interesting that osmium(III) chloride, which was earlier found to exhibit a markedly higher activity than FeCl<sub>3</sub> in the oxidation of alkanes [14, 15], also turned out to be a much more effective catalyst in the oxidation of alcohol **1** (see runs 9–15 in table). The maximum TON was found to be 1500 (run 14), with the yield of the products reaching 90%. A comparison of runs 14 and 15 shows that the addition of 2,2'-bipyridyl practically does not improve the method. However, the product yield is increased by the addition of 2,2'-bipyridyl upon the reaction in the presence of a small amount of acetonitrile (cf. runs 10 and 9). The osmium chloride-catalyzed oxidation of **1** leads to the formation of significant amounts of aldehyde **2**, and we failed to obtain acid **3** as a single product unless *o*-phenanthroline was used as a cocatalyst (run 13). The use of another osmium derivative, carbonylhydride H<sub>2</sub>Os<sub>3</sub>(CO)<sub>10</sub>, gave **2** (28%) and **3** (8%) with moderate yields (under the following conditions: catalyst ( $2 \times 10^{-4}$  mol l<sup>-1</sup>), H<sub>2</sub>O<sub>2</sub> (0.5 ml), and MeCN (0.3 ml), for 3 h at 50°C).

Decamethylsoscene (Me<sub>5</sub>C<sub>5</sub>)<sub>2</sub>Os turned out to be a completely inactive catalyst in oxidation of **1**.

We also studied a third system consisting of the binuclear manganese(IV) complex LMn<sup>IV</sup>(O)<sub>3</sub>Mn<sup>IV</sup>L](PF<sub>6</sub>)<sub>2</sub> (compound **4**), where L = 1,4,7-trimethyl-1,4,7-triazacyclononane [1, 5, 7, 8, 16–23], and oxalic acid (compound **5**). The results are presented in the table (runs 16–20). The highest conversion was reached when hydrogen peroxide was added dropwise to the reaction solution (run 18). In this case, the

yields of aldehyde **2** and acid **3** were 48 and 22%, respectively.

Apart from catalyst **4**, which is completely soluble in acetonitrile and alcohol **1**, we used heterogenized catalyst **6** prepared by mixing a solution of complex **4** with the heteropoly acid H<sub>4</sub>W<sub>12</sub>SiO<sub>40</sub> [24]. As shown earlier [24], catalyst **6** has the formula [Mn<sub>2</sub>O<sub>3</sub>(TMTACN)<sub>2</sub>]<sub>2</sub>[W<sub>12</sub>SiO<sub>40</sub>] · xH<sub>2</sub>O (where x = 2–4) and is practically insoluble in most solvents. Catalyst **6** can be filtered off after the oxidation process and can be used in a few new runs with some loss of the initial activity. The oxidation of alcohol **1** (0.2 ml) with hydrogen peroxide (0.8 ml) in the presence of catalyst **6** (6 mol %, 5 mg) and oxalic acid (6 mg), after stirring for 24 h at 22°C, led to the formation of **2** and **3** with yields of 33 and 21%, respectively.

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