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HIGHLY EFFICIENT OXIDATION OF ALCOHOLS BY THE SYSTEM "HYDROGEN PEROXIDE–[LMn(O)$_3$MnL](PF$_6$)$_2$ (L = 1,4,7-TRIMETHYL-1,4,7-TRIAZACYCLONONANE)–OXALIC ACID"[≠]

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Abstract

The dinuclear manganese(IV) complex [LMn(O)$_3$MnL](PF$_6$)$_2$ (1, L = 1,4,7-trimethyl-1,4,7-triazacyclononane) catalyzes the extremely efficient oxidation of alcohols with hydrogen peroxide at room temperature. Oxalic acid is an obligatory co-catalyst. The oxidation of isopropanol, for example, yields acetone with turnover numbers up to 40000 after 5–10 h in the absence of a solvent. 2-Cyanoethanol was oxidized by this system with somewhat lower efficiency (conversion 70%). The catalytically active cation from salt 1 was obtained in an insoluble form containing a heteropoly anion [Mn$_2$O$_3$(TMTACN)$_2$]$_2$[SiW$_{12}$O$_{40}$]. Oxidation of 2-cyanoethanol using this heterogenized catalyst and oxalic acid gave the oxo-products with the 54% total yield.

Keywords: Alcohols, oxidation, hydrogen peroxide, homogeneous catalysis, manganese complexes

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[≠] Part 8 of the series "oxidations by the system hydrogen peroxide–[Mn$_2$L$_2$o$_3$][PF$_6$]$_2$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane)–carboxylic acid". For parts 1–7, see [8–14], respectively. Parts of the present work were reported at the *13th International Congress on Catalysis*, Paris, 2004 and published in a preliminary form in *Chemistry Preprint Archive*, **5**, 19 (2004) (go for free to http://www.sciencedirect.com/preprintarchive)

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INTRODUCTION

Oxidation of alcohols and phenols constitutes an important field of contemporary metal-complex catalysis (see, for example, [1–7]). Hydrogen peroxide is widely used as an oxidant in these transformations. In our previous publications, we have described a system consisting of dinuclear manganese(IV) complex salt $[LMn(O)_3MnL](PF_6)_2$ (catalyst **1**; L = 1,4,7-trimethyl-1,4,7-triazacyclononane, TMTACN), carboxylic acid (co-catalyst, usually acetic acid), and aqueous H_2O_2, which efficiently oxidizes alkanes and certain other organic compounds in acetonitrile at room temperature [8–14]. In the present work, we found that the “catalyst **1**–oxalic acid–H_2O_2” system highly efficiently oxidizes isopropanol (**2**) to the corresponding ketones, as well as transforms the relatively inert primary alcohol 2-cyanoethanol into the corresponding aldehyde and acid with a moderate yield. The reactions were carried out both in acetonitrile and without any solvent.

EXPERIMENTAL

Hydrogen peroxide solutions (aqueous 70% “Peróxidos do Brasil” and 35% “Fluka”) were used as received. The experiments on alcohol oxidations were carried out typically without solvent at 25ºC in thermostated Pyrex cylindrical vessels (total volume 12 mL) with vigorous stirring. The total volume of the reaction solution was 5 or 2 mL. In a typical experiment, initially, a portion of the aqueous solution of H_2O_2 was added to the solution of the catalyst and oxalic acid in the alcohol. Acetonitrile in a low concentration was used as an internal standard for a quantitative analysis of unreacted isopropanol, produced acetone, and in some cases of acetic acid by gas chromatography (GC, HP Series 6890 instrument). After given time intervals, samples (about 0.2 mL) were taken. The reaction was typically quenched by addition of solid MnO_2 to decompose an excess of hydrogen peroxide and filtered. As we found that cyanoacetic acid is extensively decarboxylated in the GC injector, concentrations of 2-cyanoethanol, cyanoacetaldehyde and cyanoacetic acid were determined by ^{1}H NMR (Brucker 400 MHz).

RESULTS AND DISCUSSION

The experimental results on the oxidation of isopropanol by the system under consideration are presented in Fig. 1, and conditions are given in the caption to this Figure. It can be seen (curve A) that in the absence of oxalic acid, the yield of acetone (**3**) is very low. This yield is much higher in the presence of

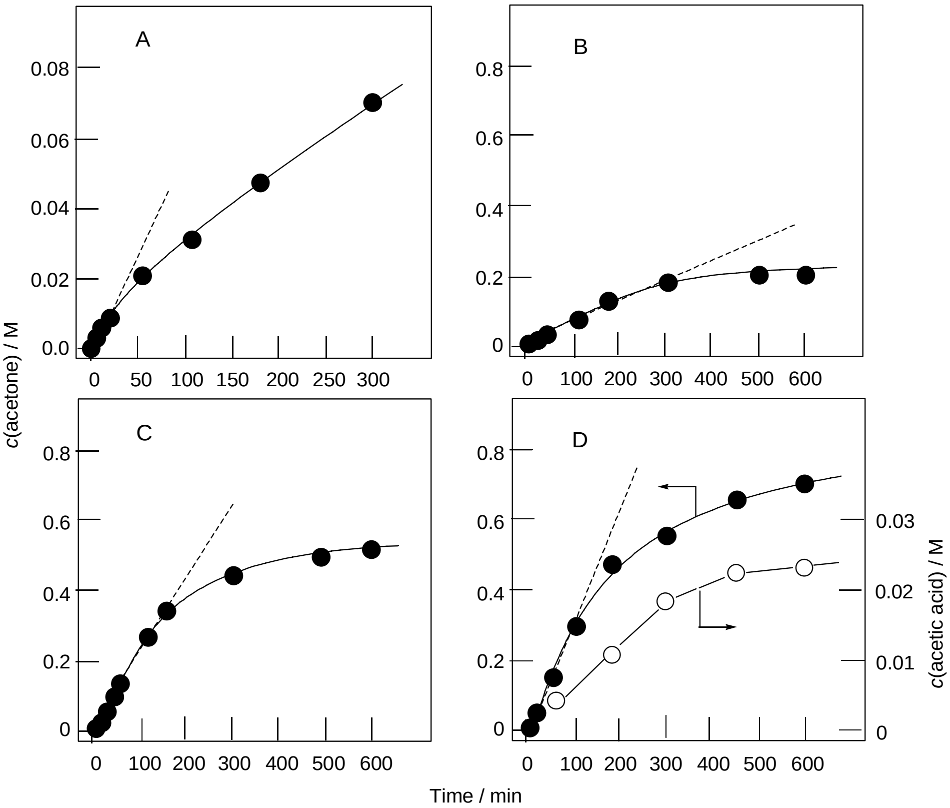

Fig 1. Oxidation of isopropanol to acetone (and acetic acid, which is shown only in graph D) by H_2O_2 (70% aqueous) without any solvent catalyzed by **1** and oxalic acid under different conditions. Graph A: complex **1**, 1.84×10^{-5} M; no oxalic acid. Graph B: complex **1**, 0.6×10^{-5} M; oxalic acid, 0.05 M. Graph C: complex **1**, 1.84×10^{-5} M; oxalic acid, 0.05 M. Graph D: complex **1**, 2.2×10^{-5} M; oxalic acid, 0.05 M. In all cases: H_2O_2, 0.81 M; MeCN, 1.4 M; water was added and total concentration of H_2O was 6.2 M. Total volume of the reaction solution was 5 mL; 25°C. Initial rates W_0 of oxidation presented in the subsequent Figures were calculated from the slopes of straight dotted lines

oxalic acid (compare with curves B, C and D). The reaction proceeds with an induction period. We measured for various conditions (different concentrations of the components) both initial rate W_0 of the reaction and concentration of acetone after 5 h. Initial rates were calculated from slopes of straight dotted lines as shown in Fig. 1. These lines correspond to the maximum rates of acetone accumulation in the beginning of the reaction. Usually we used isopropanol in excess in comparison with hydrogen peroxide, and it is possible to say that isopropanol was not only a substrate but also the solvent. Moreover, acetonitrile was added to the reaction mixture as an internal standard and a solvent for stock solutions of catalyst **1** and oxalic acid. Water was also added to dilute 70% hydrogen peroxide. As a result, the reaction solution used, for example, in the experiment shown in Fig. 1, line D, contained the following concentrations of the components (M): catalyst **1**, 2.2×10^{-5}; oxalic acid, 0.05; hydrogen peroxide, 0.81; isopropanol, 5.74; water, 6.2; MeCN, 1.14. These concentrations correspond to the following ratio of the reactants: [**1**] : [oxalic acid] : $[H_2O_2]_0$: $[\text{isopropanol}]_0$ = 1 : 2270 : 36820 : 260900. As follows from Fig. 1, graph D, the reaction after 10 h gave acetone (0.7 M) and acetic acid (0.023 M). That means that the turnover number (TON, *i.e.*, total moles of products produced per one mole of a catalyst) of the reaction attained 32860. The yield of both products based on hydrogen peroxide was 89%. Using lower concentrations of **1** we were able to obtain very high TONs. For example, at [**1**] = 1×10^{-5} M, TON = 39000 (in previous studies, alcohol oxidation with H_2O_2 usually attained TONs of 2–250). Acetone was not produced at all in the absence of catalyst **1**.

Table 1

Oxidation of isopropanol (**2**) to acetone (**3**) and acetic acid (**4**) with H_2O_2 at various concentrations (M) of catalyst **1** [a]

Time(min)	[**1**] = 0.6×10^{-5}		[**1**] = 1.0×10^{-5}		[**1**] = 1.4×10^{-5}		[**1**] = 1.84×10^{-5}		[**1**] = 2.2×10^{-5}	
	[**3**]	[**4**]	[**3**]	[**4**]	[**3**]	[**4**]	[**3**]	[**4**]	[**3**]	[**4**]
3	0.005		0.005		0.003				0.006	
5	0.006		0.005		0.002				0.006	
10	0.012		0.004		0.006				0.009	
15			0.005		0.009				0.012	
30	0.012		0.015		0.022		0.041		0.036	
60	0.039		0.049		0.075		0.126		0.125	
120	0.105		0.121		0.183		0.294		0.285	
180	0.142	0.009	0.221		0.277				0.471	0.011
300	0.185	0.014	0.325	0.006	0.383	0.018	0.584	0.011	0.555	0.019
430	0.213		0.389	0.007	0.539	0.023			0.661	0.023
600	0.215								0.696	0.023

[a] Conditions: H_2O_2 (70% aqueous), 0.81 M; oxalic acid, 0.05 M (added as a stock solution in 0.2 mL of MeCN); H_2O, 0.5 mL; total volume of the reaction solution in isopropanol was 5 mL; 25°C

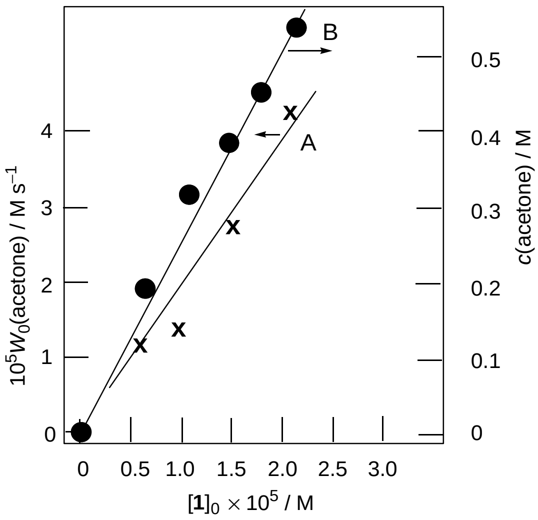

Fig. 2. Initial rate of the isopropanol oxidation (line A) and concentration of acetone after 300 min (line B) *vs* concentration of catalyst **1**. Conditions: H_2O_2, 0.81 M; oxalic acid, 0.05 M; water was added and total [H_2O] was 6.2 M. Total volume of the reaction solution in isopropanol was 5 mL; 25°C

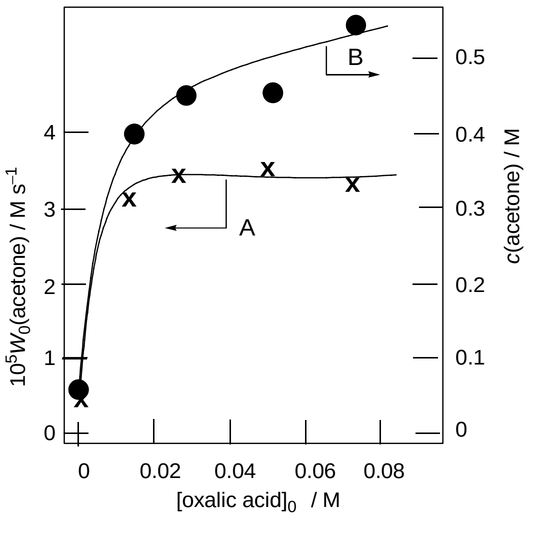

Fig. 3. Initial rate of the isopropanol oxidation (curve A) and concentration of acetone after 300 min (curve B) *vs* concentration of oxalic acid. Conditions: complex **1**, 1.84×10^{-5} M; H_2O_2, 0.81 M; water was added and total H_2O, 6.2 M. Total volume of isopropanol solution was 5 mL; 25°C

The analysis of oxidation reactions carried out at different concentrations of complex **1** (Table 1) indicates that the reaction is of the first order with respect to the catalyst (see also Fig. 2). It is interesting that the yield of the products after 5 h also linearly depends on [**1**] (Fig. 2, line B). Figure 3 demonstrates that the initial rate of the acetone formation does not depend on the concentration of oxalic acid, when [oxalic acid] > 0.01 M, whereas at relatively high concentrations of oxalic acid, the yield of acetone grows insignificantly with increase in the concentration of the acid (Fig. 3, curve B). The initial reaction rate as well as the acetone yield after 300 min also do not depend on initial concentration of hydrogen peroxide at $[H_2O_2]_0 > 0.5$ M (Fig. 4). The oxidation of isopropanol with acetonitrile as a solvent was also carried out, and the result is presented in Fig. 5. In this case, TONs are also high and attain 20600 after 5 h.

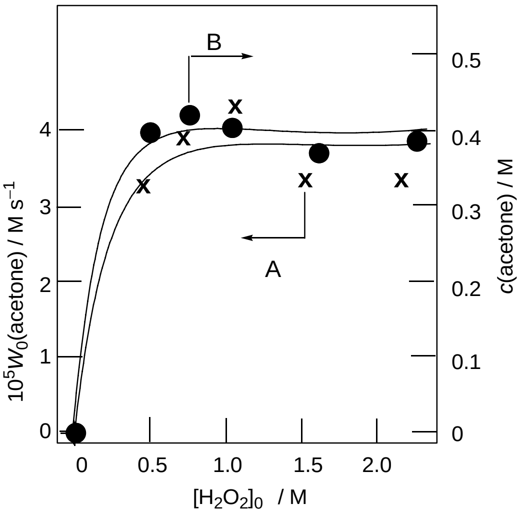

Fig. 4. Initial rate of the isopropanol oxidation (curve A) and concentration of acetone after 300 min (curve B) *vs* concentration of H_2O_2. Conditions: complex **1**, 1.84×10^{-5} M; oxalic acid, 0.05 M; water was added and total H_2O concentration was 6.2 M. Total volume of isopropanol solution was 5 mL; 25°C

We have found that some amount of acetic acid (**4**) is produced during isopropanol oxidation. This prompted us to study in more detail the oxidation of acetone to acetic acid under similar conditions. It turned out that acetic acid is produced from acetone even in the absence of catalyst **1** and oxalic acid (Table 2). As expected (see Table 1), our catalytic system oxidizes acetone to acetic acid much more efficiently in comparison with pure hydrogen peroxide.

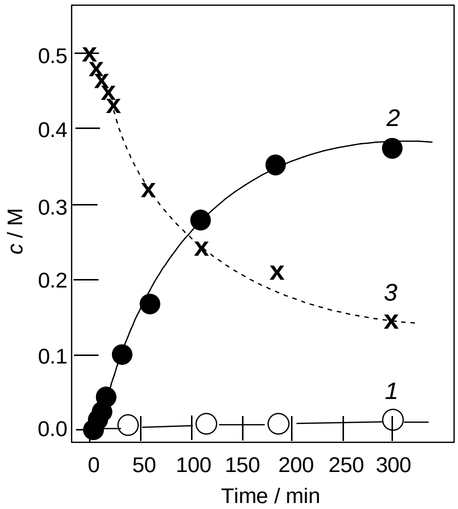

Fig 5. Oxidation of isopropanol by H_2O_2 (70% aqueous) to acetone in acetonitrile as a solvent. Accumulation of acetone is depicted with curves 1 (in the absence of oxalic acid as a co-catalyst) and 2 (at [oxalic acid] = 0.05 M). Consumption of isopropanol (at [oxalic acid] = 0.05 M) is depicted with curve 3. Conditions: isopropanol, 0.5 M; H_2O_2, 0.81 M; complex **1**, 1.84×10^{-5} M. Total volume of the reaction solution was 5 mL; 25°C

Table 2

Oxidation of acetone to acetic acid with H_2O_2 catalyzed by complex **1** and oxalic acid (concentration of acetic acid, M, and turnover number, TON, are given) [a]

Time (min)	In the presence of complex **1**		In the absence of complex **1** [b]
	Acetic acid [**4**] (M)	TON	Acetic acid [**4**] (M)
5	0.011	210	0.008
15	0.031	610	0.013
30	0.035	708	0.013
60	0.042	848	0.011
120	0.070	1400	0.014

[a] Conditions: H_2O_2 (70% aqueous), 0.4 M; oxalic acid, 0.05 M; complex **1**, 5×10^{-5} M; total volume of acetone solution was 5 mL; 25°C.

[b] Experiments were carried out in the presence of oxalic acid but without complex **1**

The selective and efficient formation of cyanoacetic acid (**7**) as well as of aldehyde (**6**) by oxidation of the inexpensive 2-cyanoethanol (**5**) is a reaction of certain industrial interest. To test the catalytic system "**1**–H_2O_2–oxalic acid" in this transformation, we carried out experiments under various reaction conditions summarized in Table 3. The highest conversion (run 3) was attained when H_2O_2 was added to the reaction mixture drop by drop during the reaction. In this case, yields of corresponding aldehyde **6** and acid **7** were 48 and 22%, respectively. At a higher temperature (60°C, run 7), rapid catalyst deactivation

Table 3

Oxidation of 2-cyanoethanol (**5**) with H_2O_2 (35% aqueous) catalyzed by complex **1** in the presence of oxalic acid

$NC–CH_2–CH_2–OH$ → $NC–CH_2–CH=O$ + $NC–CH_2–C(=O)–OH$
alcohol (**5**) aldehyde (**6**) acid (**7**)

Run	Solvent	T (°C)	Time (h)	Method	Conversion of **5** (%)	Composition of the reaction mixture (%)		
						-ol (**5**)	-al (**6**)	acid (**7**)
1[a]	MeCN	22	24	*A*	43.5	56.5	10	33.5
2[b]	MeCN	22	48	*A*	60	40	22	38
3[c]	MeCN	22	5+24	*B*	70	30	48	22
4[d]	none	22	4+24	*C*	53	47	40	13
5[e]	none	40	3	*A*	65	35	50	15
6[f]	none	50	4	*A*	60	40	44	16
7[g]	none	60	4+24	*C*	18	82	17	1

Methods. *A*: all reactants are mixed at the beginning of the reaction; *B*: H_2O_2 is added to the reaction mixture drop by drop; *C*: a solution of **1** in **5** is added to the mixture of all other reactants drop by drop.

Details:

[a] Amounts: **5**, 0.1 mL; H_2O_2, 0.5 mL; **1**, $1×10^{-4}$ M; oxalic acid, 0.006 g (0.025 M), CH_3CN, 1 mL.

[b] Amounts: **5**, 0.1 mL; H_2O_2, 1.5 mL; **1**, $0.7×10^{-4}$ M; oxalic acid, 0.006 g (0.017 M), CH_3CN, 1 mL.

[c] Amounts (after addition of H_2O_2 during 5 h): **5**, 0.1 mL; H_2O_2, 1.5 mL; **1**, $0.7×10^{-4}$ M; oxalic acid, 0.006 g (0.017 M), CH_3CN, 1 mL.

[d] Amounts (and concentrations after addition of a solution of **1** – 0.0002 g – in **5** – 0.1 mL – during 4 h): **5**, 0.1 mL; H_2O_2, 0.5 mL; oxalic acid, 0.006 g. After addition of a solution of **1** in **5** during 4 h the resulting solution was kept at room temp. 24 h.

[e] Amounts: **5**, 0.1 mL; H_2O_2, 0.5 mL; **1**, 0.0002 g; oxalic acid, 0.006 g (0.017 M).

[f] Amounts: **5**, 0.1 mL; H_2O_2, 0.5 mL; **1**, 0.0002 g; oxalic acid, 0.006 g (0.017 M).

[g] Amounts (and concentrations after addition of a solution of **1** – 0.0002 g – in **5** – 0.1 mL – during 4 h): **5**, 0.1 mL; H_2O_2, 0.5 mL; oxalic acid, 0.006 g. After addition of a solution of **1** in **5** during 4 h the resulting solution was kept at room temp. 24 h.

resulted in a conversion of only 18%. At room temperature, similar results were obtained using a heteropolyacid-immobilized derivative **8** of complex **1**. This species was obtained by mixing complex **1** and $H_4SiW_{12}O_{40}$ in an appropriate solvent. The resulting material was characterized [15] as $[Mn_2O_3(TMTACN)_2]_2[SiW_{12}O_{40}]\cdot xH_2O$ (x = 2–4) (**8**). As previously reported [15], complex **8** is virtually insoluble in most solvents, so that it can undergo at least three recycling cycles with a moderate activity loss (the yield was reduced by *ca.* 40% for the third cycle). Cyanoethanol (0.2 mL) was oxidized by hydrogen peroxide (0.8 mL, 35% aqueous) in the presence of about 6 mol % of **8** (5 mg) and oxalic acid (6 mg). The oxidation at 22°C after 24 h gave aldehyde **6** (yield 33%) and acid **7** (21%).

We have also found that combination of catalyst **1** with either acetic acid or sodium carbonate gives rise to the very low (5%) yield of oxygenates in the cyanoethanol (**5**) oxidation. Sodium oxalate as a co-catalyst or a mixture of sodium oxalate with oxalic acid did not give higher yields. Experiments on **1**-catalyzed oxidation of **5** with *meta*-chloroperbenzoic acid in the presence of oxalic acid or with peroxyacetic acid were unsuccessful. Analogously, oxidations of **5** with combinations of $MnSO_4$ or $Mn(ClO_4)_2$ with sodium ascorbate in the presence also of 1,4,7-trimethyl-1,4,7-triazacyclononane (see [16]) did not give noticeable amounts of oxygenates.

In conclusion, the unique system described in this work, consisting of hydrogen peroxide as an oxidant, complex **1** as a catalyst, and oxalic acid as a co-catalyst, very efficiently oxidizes secondary alcohols to the corresponding ketones under mild conditions (room temperature, a few hours). Under similar conditions, the system less efficiently converts relatively inert 2-cyanoethanol into a mixture of 2-cyanoacetaldehyde and cyanoacetic acid.

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