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A unique rate-accelerating effect of certain amino acids in the H_2O_2 oxidation of alkanes catalyzed by a dinuclear manganese complex containing 1,4,7-trimethyl-1,4,7-triazacyclononane☆

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Abstract—Certain amino acids used in small amounts (10 catalyst equiv) strongly accelerate the H_2O_2 oxidation of cyclohexane catalyzed by a dinuclear manganese(IV) complex with 1,4,7-trimethyl-1,4,7-triazacyclononane. The efficiency of the co-catalyst dramatically depends on the nature and structure of the acid. Pyrazine-2,3-dicarboxylic acid (2,3-PDCA) has been found to be the most efficient co-catalyst whereas picolinic acid is almost inactive in this oxidation. The highest rate has been attained when 2,3-PDCA was used in combination with trifluoroacetic acid.
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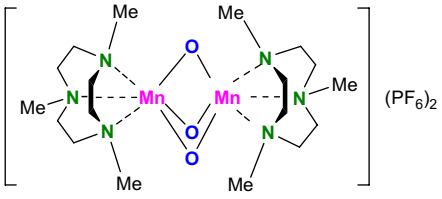
1. Introduction

Transition metal complexes are known to activate C–H bonds of various compounds including hydrocarbons (see reviews[1] and selected recent original papers[2]). Among these reactions, catalytic oxidations of alkanes under mild conditions are especially interesting both from practical and academic point of view. Some catalytic systems based on metal complexes in which a metal ion is surrounded by amino acid residues can be considered as models of reaction centers of oxidizing enzymes.[1d,3]

Manganese complexes (either isolated and fully characterized or prepared in situ from the ligand and a manganese ion) with 1,4,7-trimethyl-1,4,7-triazacyclononane (L) catalyze some oxidations of organic compounds (see very recent reviews[4] as well as brief surveys in our articles[5b,c,g,l]). The dinuclear manganese(IV) complex $[LMn(O)_3MnL](PF_6)_2$ was synthesized and characterized by Wieghardt and coworkers.[6] Earlier we discovered[5] that the system consisting of complex **1** and a carboxylic acid (co-catalyst) oxidizes various organic compounds with aqueous H_2O_2 in acetonitrile solution at room temperature. Thus, alkanes were transformed into the corresponding alkyl hydroperoxides, alcohols, and ketones,[5a–i,l] alcohols were oxidized to ketones or aldehydes,[5f,k] sulfides gave under the action of our system the corresponding sulfoxides.[5f] Olefins were transformed into the epoxides and diols.[5f,h–j] In some cases, water (for the oxidation of alkanes and olefins[5i]) in the absence of any organic liquid was used as a solvent. Carboxylic acids (usually acetic or oxalic) were used in a large excess with respect to the catalyst **1** (>1000 equiv of the acid for 1 equiv of the catalyst). No reactions occurred in the absence of acids. It is interesting that the analogues of complex **1** bearing only two methyl groups in each heterocyclic ring are much less efficient in the oxidations.[7]



Complex **1**

2. Results and discussion

In the present work, we compared the efficiency of alkane (cyclohexane) oxidation with the 'H_2O_2–**1**–carboxylic acid' system for various carboxylic acids added in small amounts (10 equiv for 1 equiv of **1**). All reactions were carried out in acetonitrile at 25 °C. The oxygenation of

☆ Part 9 from the series "Oxidations by the system 'hydrogen peroxide–$[Mn_2L_2O_3][PF_6]_2$ (L=1,4,7-trimethyl-1,4,7-triazacyclononane)–carboxylic acid'". For parts 1–8, see Refs. 5d–k, respectively.

Keywords: Homogeneous catalysis; Oxidation; Manganese complexes; Hydrogen peroxide; Alkanes.

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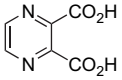
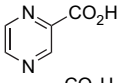
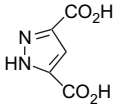
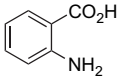
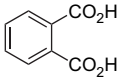
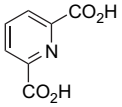
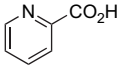
cyclohexane gives rise to the formation of the corresponding alkyl hydroperoxide as the main primary product, which further gradually decomposes to yield more stable products, cyclohexanone and cyclohexanol. The formation of alkyl hydroperoxides in addition to the corresponding alcohols and ketones was demonstrated by a method developed and used in our previous works.[1d,5a–h,8] More recently our method was used by other scientists in various oxidations.[9] Usually alkyl hydroperoxides are decomposed in the chromatograph to produce corresponding alcohol and ketone. If triphenylphosphine is added to the reaction solution ca. 10 min before the GC analysis, the alkyl hydroperoxide present is completely reduced to the corresponding alcohol. As a result, the chromatogram differs from that of a sample not subjected to the reduction (the alcohol peak rises, while the intensity of the ketone peak decreases). Comparing the intensities of peaks attributed to the alcohol and ketone before and after the reduction, it is possible to estimate the real concentrations of the three products (i.e., alcohol, ketone, and alkyl hydroperoxide) present in the reaction solution. As the main goal of this work was to study effects of various co-catalysts (carboxylic acids) on the alkane oxidation rates, in our kinetic studies presented below we usually measured the concentrations of cyclohexanone and cyclohexanol after the reduction with triphenylphosphine.

It can be seen from the data of Figure 1 (curve 1) that accumulation of the oxygenates proceeds relatively slowly if acetic acid (**2**) is used as a co-catalyst. As there is no autoacceleration in this case, the initial rate of the reaction equals the maximum rate $W_0=W_{max}=0.7\times10^{-6}$ M s^{-1} (see also Table 1). Oxalic acid, **3** (as well as other dicarboxylic acids, malonic, **4**, and glutaric, **5**) is a more efficient co-catalyst (curves 2–4 in Fig. 1). The behavior of the system containing a carboxylic acid with strong electron-withdrawing susbstituents (namely trifluoroacetic, **6**, and trichloroacetic, **7**) is absolutely different (Fig. 2, curves 1 and 2) from those found for acids **2**–**5**. The kinetic curves of oxygenate accumulation have in these cases a sigmoid shape, which is much more pronounced when **7** is used as a co-catalyst. In the latter case the W_{max}/W_0 ratio attains 8.3 (see Table 1).

Table 1. Initial (W_0) and maximum (W_{max}) rates of the cyclohexane oxidation co-catalyzed by various carboxylic acids

Co-catalyst	Reaction rate$\times10^6$, M s^{-1}	
	W_0	W_{max}
CH_3CO_2H (**2**)	0.7	0.7
$(CO_2H)_2$ (**3**)	1.4	1.4
$CH_2(CO_2H)_2$ (**4**)	1.5	1.5
$(CH_2)_3(CO_2H)_2$ (**5**)	1.4	1.4
CF_3CO_2H (**6**)	2.0	16.0
CCl_3CO_2H (**7**)	1.0	8.3
 (**8**)	8.3	8.3
 (**9**)	2.6	2.6
 (**10**)	1.0	2.1
 (**11**)	0.5	1.2
 (**12**)	0.5	0.5
 (**13**)	0.6	0.6
 (**14**)	0.3	0.3

The most striking feature of the reaction under discussion was found by us when we used pyrazine-2,3-dicarboxylic

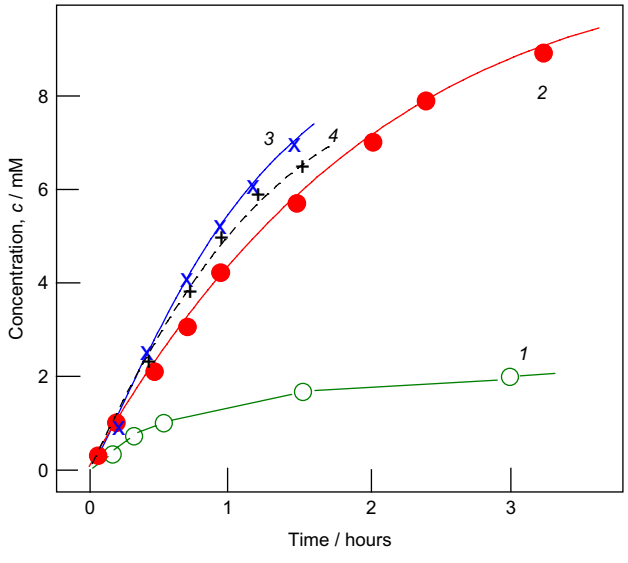


Figure 1. Accumulation of sum of oxygenates (after reduction of the samples with PPh_3) in the cyclohexane oxidation co-catalyzed by acetic acid **2** (curve 1), oxalic acid **3** (curve 2), malonic acid **4** (curve 3), and glutaric acid **5** (curve 4).

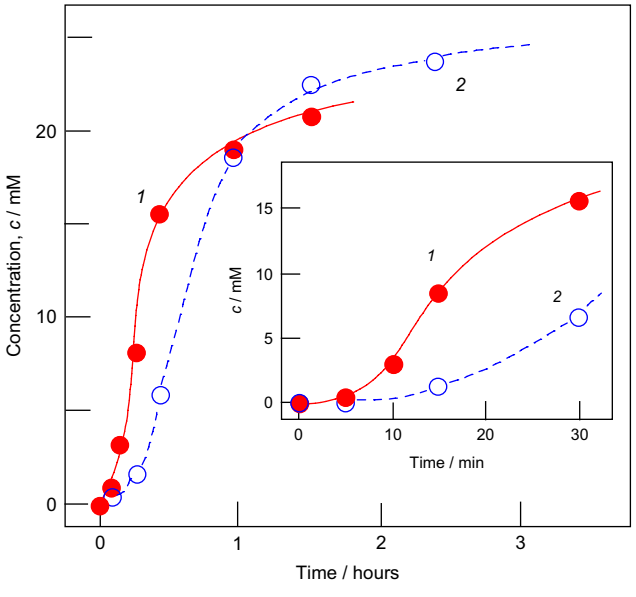


Figure 2. Accumulation of sum of oxygenates (after reduction of the samples with PPh_3) in the cyclohexane oxidation co-catalyzed by trifluoroacetic acid **6** (curve 1) and trichloroacetic acid **7** (curve 2).

acid (**8**) as a co-catalyst. In this case no autoacceleration was noticed (Fig. 3, curve 1) and the initial rate (which was equal to the maximum rate) was very high (8.3×10^{-6} M s^{-1}). In the initial period the oxidation gives almost exclusively cyclohexyl hydroperoxide (after 8 min concentrations of cyclohexanone and cyclohexanol were 1.8 mM before reduction with PPh_3 and 3.7 and 0.2 mM, respectively, after reduction with PPh_3).[1d,5a–h,8] Some amount of cyclohexanone was found after 65 min (concentrations of cyclohexanone and cyclohexanol were 2.4 mM and 10.4 mM, respectively, after reduction with PPh_3 whereas these concentrations have been found to be approximately equal without treatment with PPh_3). This testifies that cyclohexyl hydroperoxide partially decomposes in the course of the reaction to produce the more stable cyclohexanone and cyclohexanol.

Surprisingly, acid **8** turned out to be a unique co-catalyst, and carboxylic acids with similar composition and structure were less (as pyrazine-2-carboxylic acid, **9**, pyrazol-3,5-dicarboxylic acid, **10**, and anthranilic acid, **11**) or much less (as phthalic acid, **12**, pyridine-2,6-dicarboxylic acid, **13**, and picolinic acid, **14**) efficient (see Fig. 3 and/or Table 1) in the oxidation. Thus we assume that only an amino acid with a specific structure can interact with the catalyst reaction center enhancing its activity. The rate of the oxidation co-catalyzed by **8** is approximately 30% lower if the reaction is carried out in argon atmosphere and this testifies that atmospheric oxygen takes part in the process.

When comparing the pK_{HA} values in acetonitrile for different acids used in this work we can notice that there is no dependence of the oxidation rate on the pK_{HA} of a co-catalyst used. Indeed, the pK_{HA} parameters (first ionization) for acids **3**, **4**, and **5** increase in the sequence 14.5<15.3<19.2 whereas the W_{max} values are almost the same, ca. 1.4×10^{-6} M s^{-1} (see Table 1). Acid **12** (first pK_{HA}=14.3) is less efficient (W_{max}=0.5) than a weaker acid **5** (first pK_{HA}=19.2; W_{max}=1.4). Finally, an efficient co-catalyst **9** ($W_0=W_{max}$=2.6) is a relatively weak acid (pK_{HA}=18.7).

The oxidation in the presence of **8** occurs with highest initial rate, however, the final yield of products in this case is only one half of that obtained by using acids **6** and **7**. At the same time, oxidations co-catalyzed by **6** and especially by **7** proceed with a substantial induction period (Fig. 2). Combining two co-catalysts, i.e., using the combinations **8**+**7** or **8**+**6**, we were able to reduce the induction period (removing it completely in the latter case) and simultaneously enhance the final yield of oxygenates (Fig. 4). Turnover number (TON; based on **1**) attained 460 after 90 min and the turnover frequency parameter in the initial period was 24 min^{-1}.

Table 2 summarizes selectivity parameters for the alkane oxidations by the system based on complex **1** and one of three carboxylic acids (2,3-PDCA, acetic and oxalic acids) as well as, for comparison, oxygenations by some other systems. It can be seen that the regioselectivity parameters C(1):C(2):C(3):C(4) are close for the oxidations co-catalyzed by the three carboxylic acids (entries 1–3) and similar to those found for the oxidation by *meta*-chloroperoxybenzoic acid (*m*-CPBA; entry 4). At the same time these parameters (as well as the bond selectivity parameter 1°:2°:3° in the oxidation of 2,2,4-trimethylpentane) are noticeably higher than corresponding parameters measured for the oxidations by the systems operating with participation of hydroxyl radicals (entries 5–7). The oxidations of *cis*-dimethylcyclohexane catalyzed by combinations of **1** with acids **2**, **3**, and **8** occur stereoselectively. The trans/cis parameter is higher in the case of **8** (0.5) in comparison with the oxidation co-catalyzed by oxalic acid (0.1). Thus the co-catalysis by **8** leads to less pronounced retention of configuration.

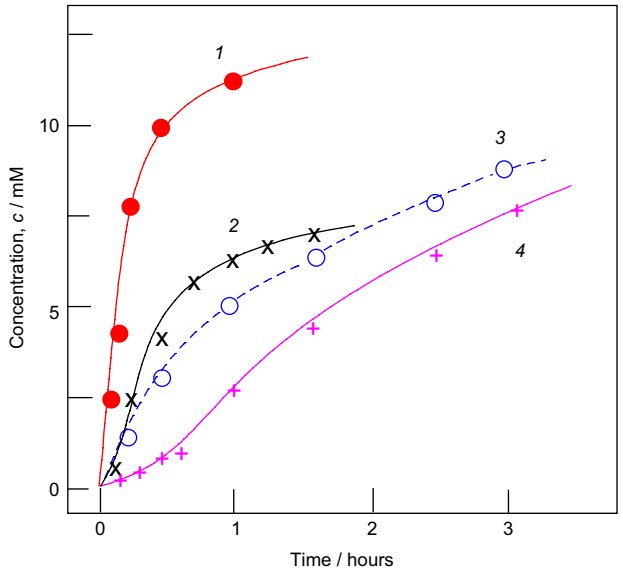


Figure 3. Accumulation of sum of oxygenates (after reduction of the samples with PPh_3) in the cyclohexane oxidation co-catalyzed by pyrazine-2,3-dicarboxylic acid **8** (curve 1), pyrazine-2-carboxylic acid **9** (curve 2), pyrazol-3,5-dicarboxylic acid **10** (curve 3), and anthranilic acid **11** (curve 4).

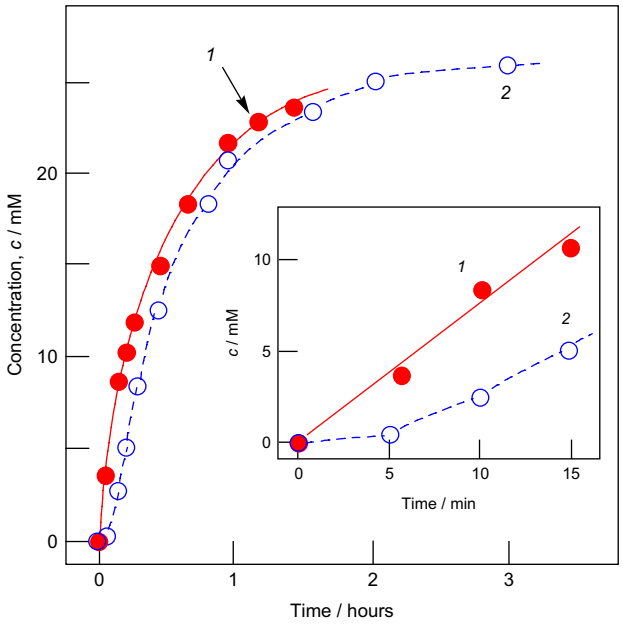


Figure 4. Accumulation of sum of oxygenates (after reduction of the samples with PPh_3) in the cyclohexane oxidation co-catalyzed by combinations **8**+**6** (curve 1) and **8**+**7** (curve 2). Concentration of each acid was 50×10^{-5} M.

Table 2. Selectivity parameters in oxidation of linear, branched, and cyclic alkanes[a]

Entry	System	C(1):C(2):C(3):C(4)[b]			1°:2°:3°[c]	trans/cis[d]	
		n-Hexane	*n*-Heptane	*n*-Octane	2,2,4-Trimethylpentane	*cis*-DMCH	*trans*-DMCH
1	**1**–**8**–H_2O_2 (MeCN, 20 °C)	1:32:32	1:63:62:47	1:43:38:20	1:3:30	0.5	0.9
2	**1**–**2**–H_2O_2 (MeCN, 20 °C)		1:46:35:35	1:30:30:25	1:8:40	0.34	4.1
3	**1**–**3**–H_2O_2 (MeCN, 20 °C)		1:46:35:34	1:27:28:18	1:2:130	0.1	0.64
4	*m*-CPBA (MeCN, 25 °C)	1:36:36.5				0.65	
5	*hν*–H_2O_2 (MeCN, 20 °C)	1:10:7	1:7:6:7		1:2:6	0.9	1.0
6	$FeSO_4$–H_2O_2 (MeCN, 20 °C)		1:5:5:4.5		1:3:6	1.3	1.2
7	*n*-Bu_4NVO_3–PCA–H_2O_2 (MeCN, 40 °C)[e]	1:6.9:7.0	1:5.7:7.2 :5.0	1:6.7:7.5:5.3	1:1.5:10	0.75	0.8

[a] All parameters were measured after reduction of the reaction mixtures with triphenylphosphine before GC analysis and calculated based on the ratios of isomeric alcohols.
[b] Parameters C(1):C(2):C(3):C(4) are relative and normalized (i.e., calculated taking into account the number of hydrogen atoms at each carbon) reactivities of hydrogen atoms at carbons 1, 2, 3, and 4, of the chain of linear alkanes.
[c] Parameters 1°:2°:3° are relative and normalized reactivities of hydrogen atoms at primary, secondary, and tertiary carbons of branched alkanes.
[d] Parameter trans/cis is the ratio of trans- and cis-isomers of *tert*-alcohols formed in the oxidation of dimethylcyclohexanes (*cis*-DMCH and *trans*-DMCH).
[e] For this system, which is believed to oxidize substrates via formation of hydroxyl radicals, see Refs. 1a,d,g,8c,10.

We can conclude that the oxidations in the presence of 'simple' carboxylic acids (acetic and oxalic) and of the amino acid **8** proceed via the same mechanism, which does not include the formation of active free radicals like hydroxyl radicals. Since the co-catalytic activities of some carboxylic acids (e.g., phthalic) and amino acids (e.g., picolinic) are negligible it is clear that the unique activity of 2,3-PDCA is due to the possibility of this compound to coordinate to the reaction center in a special mode, probably with participation of both nitrogen atoms.

3. Conclusions

We discovered in this work a remarkable accelerating effect of pyrazine-2,3-dicarboxylic acid used as a co-catalyst. Picolinic acid which has a very similar structure was almost inactive in this oxidation. The highest rate was attained using 2,3-PDCA in combination with trifluoroacetic acid.

4. Experimental section

The oxidations of hydrocarbons were carried out in acetonitrile in air in thermostated (25 °C) Pyrex cylindrical vessels with vigorous stirring. The total volume of the reaction solution was 2 mL. Initially, a portion of H_2O_2 (35% aqueous; concentration in the reaction solution was 0.1 M) was added to a solution of the catalyst **1** (concentration in the reaction solution was 5×10^{-5} M), co-catalyst (50×10^{-5} M), and cyclohexane (0.46 M). After certain time intervals samples (about 0.2 mL) were taken. In order to determine the concentration of a sum of cyclohexane oxidation products the sample of the reaction solution was typically treated with PPh_3 (see Refs. 1d,5a–h,8) and analyzed by GC (LKhM-80-6, columns 2 m with 5% Carbowax 1500 on 0.25–0.315 mm Inerton AW-HMDS; carrier gas was argon). Other saturated hydrocarbons were oxidized under analogous conditions.

Acknowledgements

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