*Tetrahedron*

**Electronic Supplementary Material (Figs. S1–S12)**

# Oxidations by the system 'hydrogen peroxide–$[Mn_2L_2O_3][PF_6]_2$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane)–carboxylic acid'. Part 10.☆ Co-catalytic effect of different carboxylic acids in the oxidation of cyclohexane, cyclohexanol and acetone

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## FIGURES:

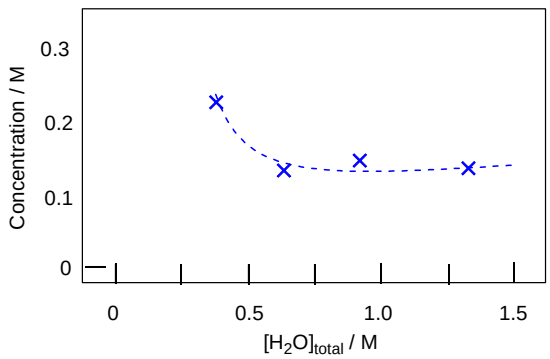


**Figure S1.** Dependence the yield of cyclohexanone after 8 h on total concentration of water in oxidation of cyclohexanol (0.25 M) with 70% aqueous $H_2O_2$ (0.50 M) catalyzed by **1** ($5 \times 10^{-5}$ M) in the presence of oxalic acid (0.11 M). The temperature was 25 ºC, and the solvent was acetonitrile.

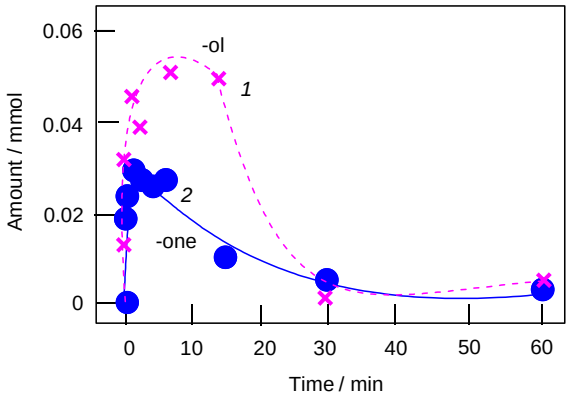


**Figure S2**. Accumulation of cyclohexanol (*1*) and cyclohexanone (*2*) in cyclohexane (9.2 mmol) oxidation with 70% aqueous $H_2O_2$ (2.1 mmol) catalyzed by complex **1** ($7.75 \times 10^{-4}$ mmol) in the presence of oxalic acid (0.28 mmol). The oxidant substrate:ratio was 1:0.23. Amounts of products were measured after reduction of the reaction mixture with $PPh_3$) with time is shown. The temperature was 25 ºC, no organic solvent was used.

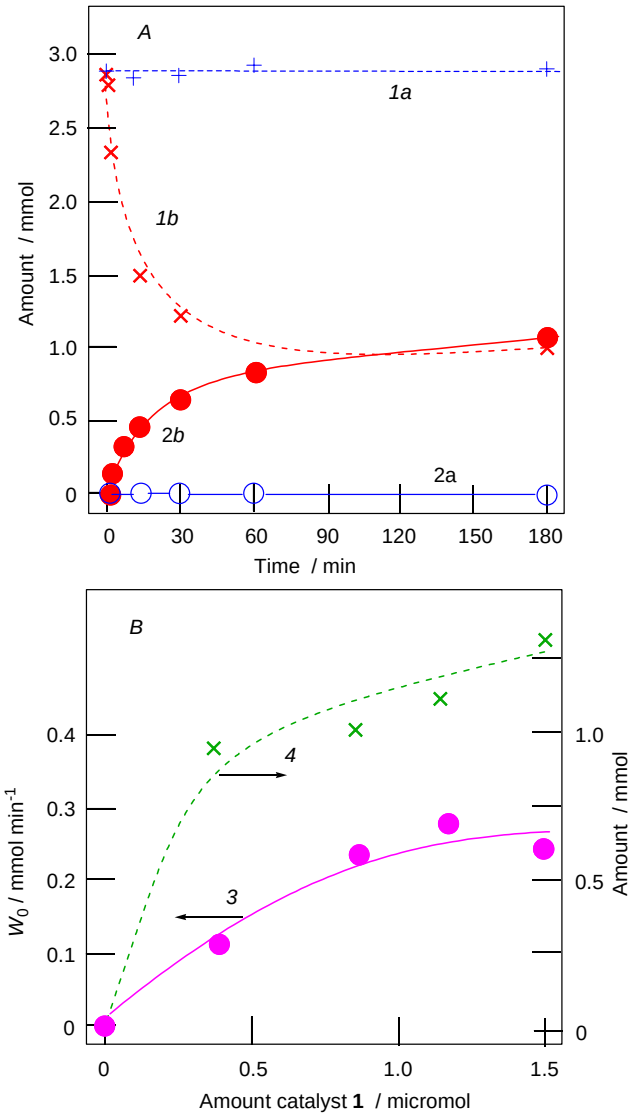


**Figure S3.** Cyclohexanol (2.8 mmol) oxidation at 25 ºC with $H_2O_2$ (8.1 mmol) catalyzed by complex **1** in the presence of oxalic acid (0.34 mmol). Graph A: consumption of cyclohexanol (curves *a*) and accumulation of cyclohexanone (curves *b*); amount of **1**: 0 (curves *1*) and 0.4 micromol (curves *2*). Graph B: dependences of initial reaction rate (curve *3*) and the amount (mmol) of cyclohexanone after 360 min (curve *4*) on amount of catalyst **1**.

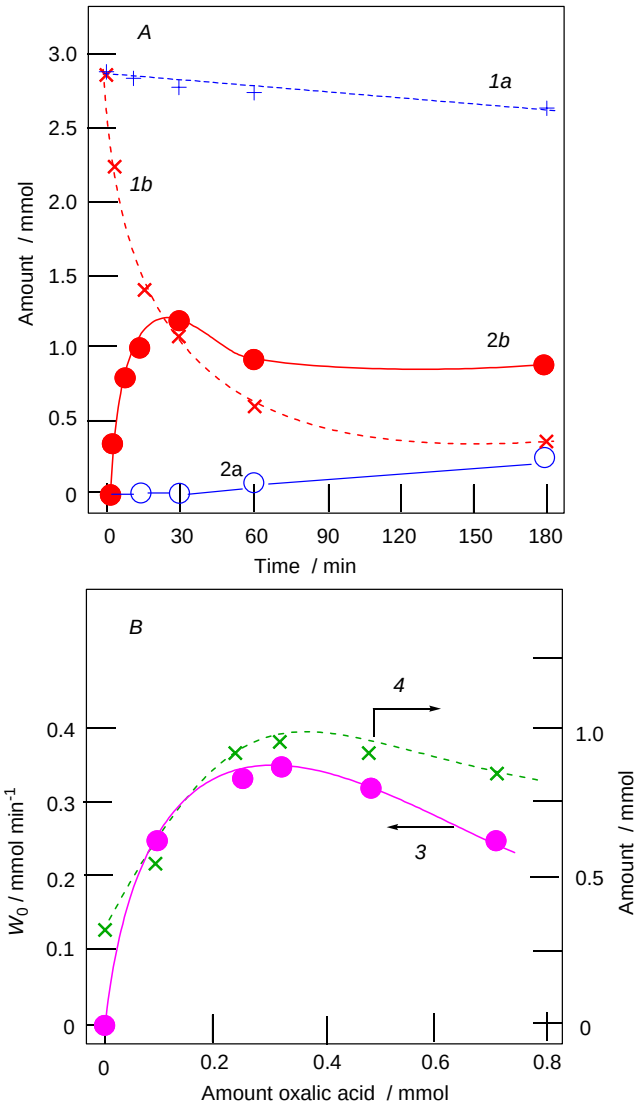


**Figure S4.** Cyclohexanol (2.8 mmol) oxidation at 25 ºC with $H_2O_2$ (8.1 mmol) catalyzed by complex **1** (0.8 micromol) in the presence of oxalic acid. Graph A: consumption of cyclohexanol (curves *a*) and accumulation of cyclohexanone (curves *b*); amount of oxalic acid: 0 (curves *1*) and 0.25 mmol (curves *2*). Graph B: dependences of initial reaction rate (curve *3*) and the amount (mmol) of cyclohexanone after 360 min (curve *4*) on amount of oxalic acid.

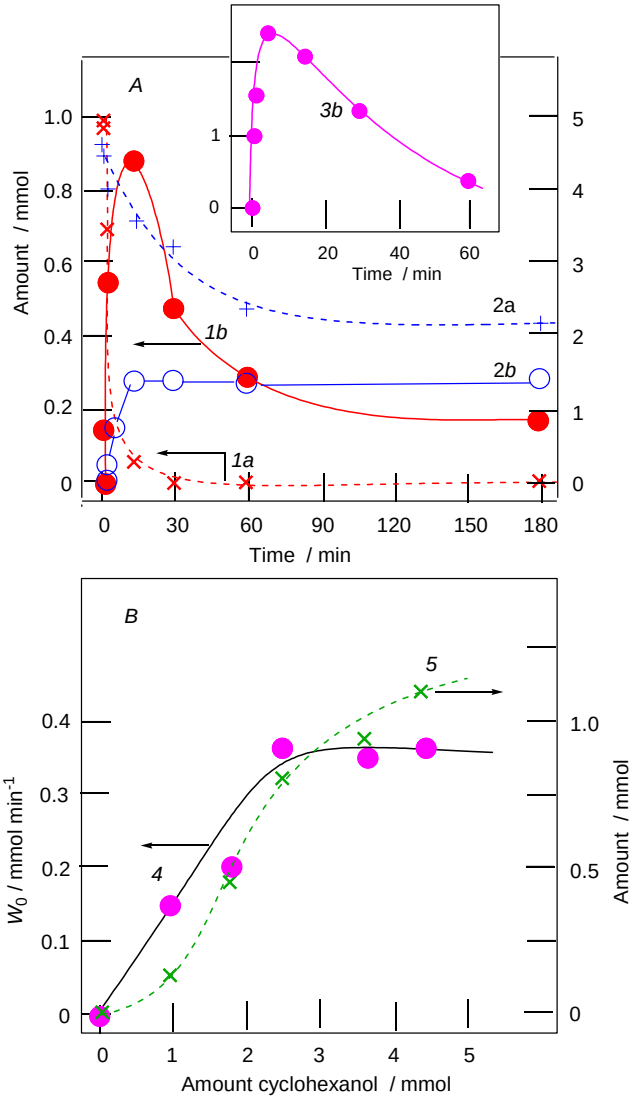


**Figure S5.** Cyclohexanol oxidation at 25 ºC with $H_2O_2$ (8.1 mmol) catalyzed by complex **1** (0.8 micromol) in the presence of oxalic acid (0.34 mmol). Graph A: consumption of cyclohexanol (curves *a*) and accumulation (and consequent over-oxidation) of cyclohexanone (curves *b*); amount of cyclohexanol: 0.94 (curves *1*; yield of cyclohexanone is 94% based on starting cyclohexanol) and 4.7 mmol (curves *2*). Curve *3b*: cyclohexanol, 2.8 mmol; $H_2O_2$, 13.5 mmol (yield of cyclohexanone is 87% based on starting cyclohexanol). Graph B: dependences of initial reaction rate (curve *4*) and the amount (mmol) of cyclohexanone after 360 min (curve *5*) on the initial amount of cyclohexanol.

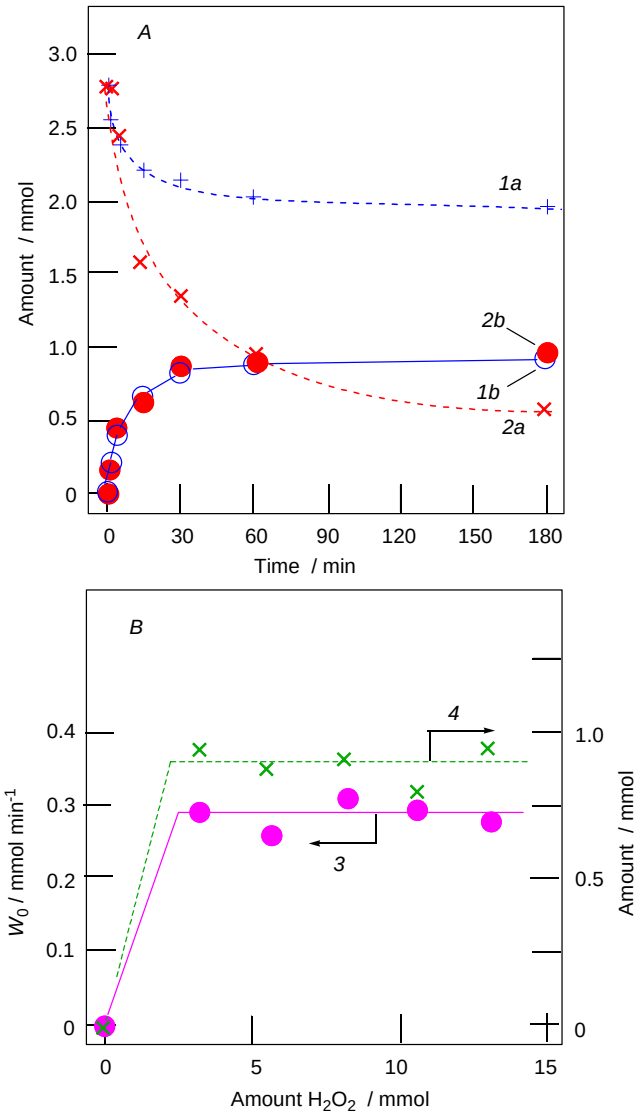


**Figure S6.** Cyclohexanol (2.8 mmol) oxidation at 25 ºC with $H_2O_2$ catalyzed by complex **1** (0.8 micromol) in the presence of oxalic acid (0.34 mmol). Graph A: consumption of cyclohexanol (curves *a*) and accumulation of cyclohexanone (curves *b*); amount of $H_2O_2$: 2.7 (curves *1*) and 10.8 mmol (curves *2*). Graph B: dependences of initial reaction rate (curve *3*) and the amount (mmol) of cyclohexanone after 360 min (curve *4*) on the initial amount of $H_2O_2$.

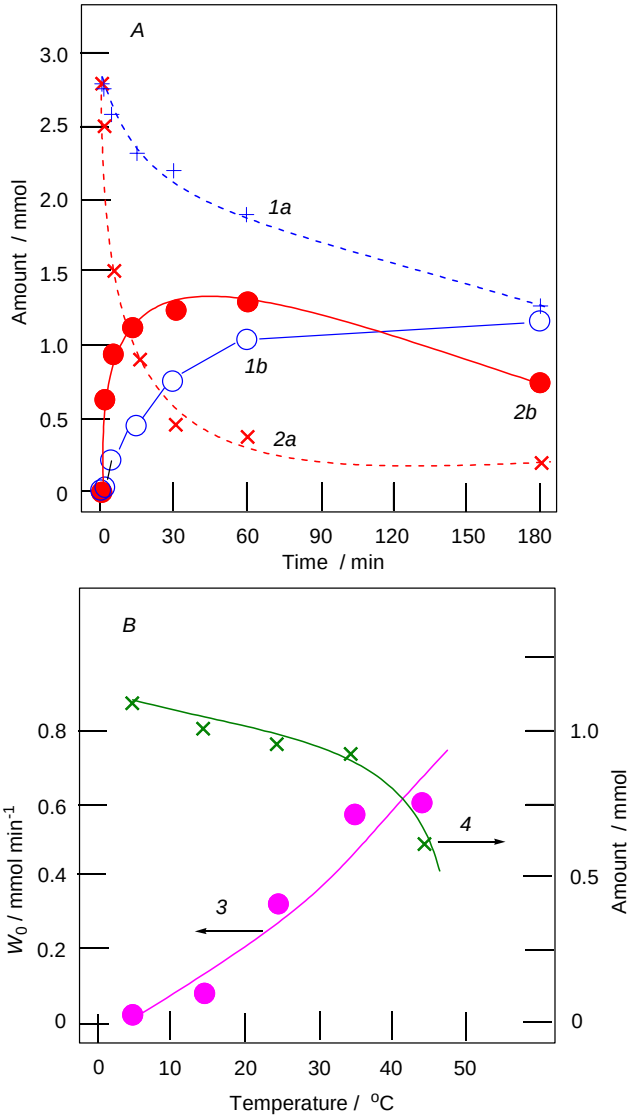


**Figure S7.** Cyclohexanol (2.8 mmol) oxidation with $H_2O_2$ (8.1 mmol) catalyzed by complex **1** (0.8 micromol) in the presence of oxalic acid (0.34 mmol). Graph A: consumption of cyclohexanol (curves *a*) and accumulation of cyclohexanone (curves *b*) at different temperatures: 5 (curves *1*) and 45 ºC (curves *2*). Graph B: dependences of initial reaction rate (curve *3*) and the amount (mmol) of cyclohexanone after 360 min (curve *4*) on the temperature of the reaction.

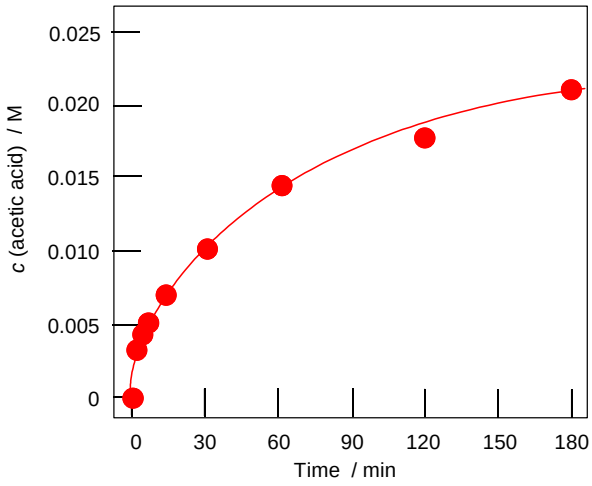


**Figure S8.** Accumulation of acetic acid with time in the acetone oxidation at 40 ºC with 70% aqueous $H_2O_2$ (0.54 M) catalyzed by complex **1** ($5 \times 10^{-5}$ M) in the presence of oxalic acid (0.125 M) and acetonitrile (1.0 mL). Total volume of the reaction solution was 5 mL.

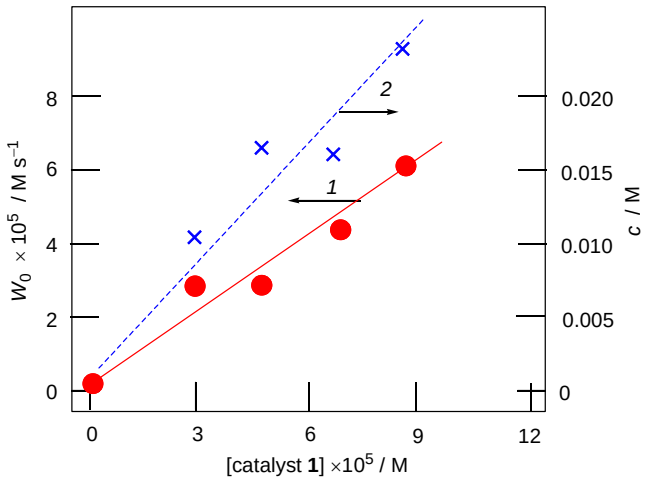


**Figure S9.** Oxidation of acetone with hydrogen peroxide (70% aqueous; 0.54 M) catalyzed by **1** and oxalic acid (0.05 M) in the presence of MeCN (1 mL) at 40 °C. Total volume of the reaction solution was 5 mL. Dependences of the initial rate of formation of acetic acid $W_0$ (curve *1*) and the total yield of acetic acid after 3 h *c* (curve *2*) on initial concentration of catalyst **1** are shown.

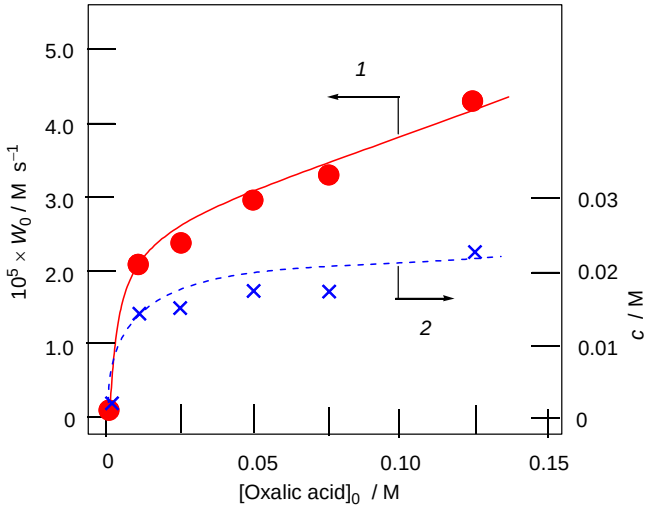


**Figure S10.** Oxidation of acetone with hydrogen peroxide (0.54 M) catalyzed by **1** ($5 \times 10^{-5}$ M) and oxalic acid at 40 °C. Total volume of the reaction solution (containing 1 mL MeCN) was 5 mL. Dependences of the initial rate of acetic acid formation $W_0$ (curve *1*) and the yield of acetic acid after 3 h *c* (curve *2*) on initial concentration of oxalic acid are shown.

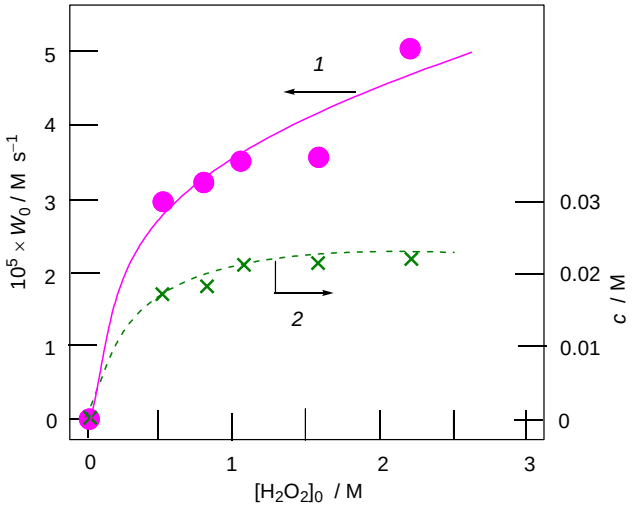


**Figure S11.** Oxidation of acetone with hydrogen peroxide (0.54 M) catalyzed by **1** ($5 \times 10^{-5}$ M) and oxalic acid at 40 °C. Total volume of the reaction solution (containing 1 mL MeCN) was 5 mL. Dependences of the initial rate of acetic acid formation $W_0$ (curve *1*) and the yield of acetic acid after 3 h *c* (curve *2*) on initial concentration of hydrogen peroxide are shown.

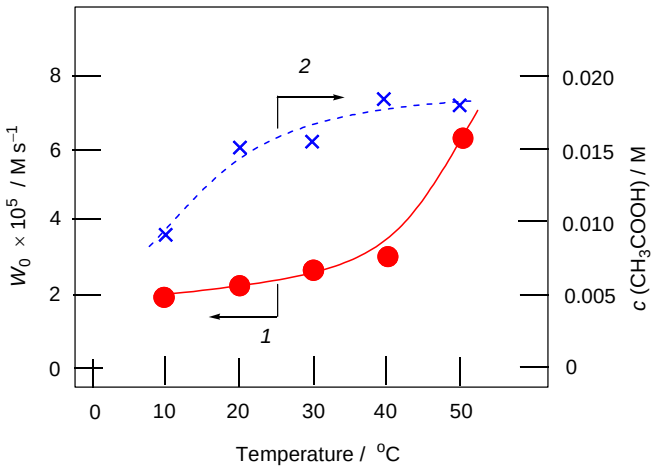


**Figure S12.** Oxidation of acetone with hydrogen peroxide (0.54 M) catalyzed by **1** ($5 \times 10^{-5}$ M) and oxalic acid (0.05 M) at various temperatures. Total volume of the reaction solution (containing 1 mL MeCN) was 5 mL. Dependences of initial reaction rate (curve *1*) and the yield (M) of acetic acid after 180 min (curve *2*) on the temperature of the reaction are shown.