

# Oxidative decarboxylation of cyclohexanecarbaldehyde in the presence of cyclooctane catalyzed by a binuclear manganese(IV) complex

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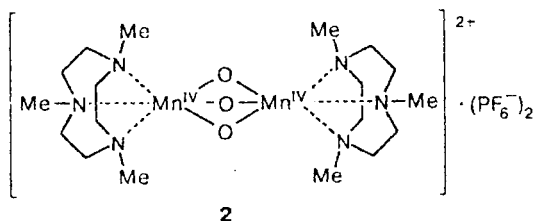
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On heating, a Mn<sup>IV</sup> complex initiates oxidation of cyclohexanecarbaldehyde with atmospheric oxygen in MeCN resulting in the formation of cyclohexanecarboxylic acid and considerable amounts of oxidative decarboxylation products (cyclohexane, cyclohexanol, and cyclohexanone). Cyclooctanol and cyclooctanone are also formed in the presence of cyclooctane.

**Key words:** alkanes, cyclooctane, aldehydes, oxidation, oxygen, activation of C—H bond, decarboxylation, radicals; manganese complexes, metallocatalysis.

Molecular oxygen and particularly air are promising oxidants for processing of inert saturated hydrocarbons into various chemicals. Such processes are often efficiently catalyzed by transition-metal complexes.<sup>1,2</sup> Joint oxidation of alkane and aldehyde with oxygen or air catalyzed by a metal complex is one of the reactions of this type. Though epoxidation of olefins by "aldehyde—oxygen—metal complex" systems has been studied in detail and used widely in practice,<sup>3</sup> only a small number of publications concerned with analogous conversions of saturated hydrocarbons is known.<sup>4–11</sup> In this work, catalytic oxidation of cyclohexanecarbaldehyde (**1**) with atmospheric oxygen was studied both in the presence and in the absence of saturated hydrocarbons. A binuclear manganese(IV) complex (**2**) with the 1,4,7-trimethyl-1,4,7-triazacyclononane macrocyclic ligand served as catalyst of oxidative transformations.



## Experimental

Oxidation of hydrocarbons was carried out with vigorous stirring in thermostatted glass cylindrical vessels equipped with reflux condensers. The volumes of the reaction solutions were 5 mL. In the course of the reactions, air was slowly

(1–5 mL min<sup>-1</sup>) bubbled through the solution of the substrates and the catalyst in MeCN.

The reaction mixture was analyzed by GLC using a PYE UNICAM PU 4500 ("Philips") chromatograph (an Alltech ECONO-CAP Carbowax column, 30 m × 0.25 mm; 0.25 μm; with helium as carrier gas). Quantitative analysis was performed after calibrating the chromatograms using solutions of the products with known concentrations.

Prior to use in the reactions, acetonitrile was purified by distilling over P<sub>2</sub>O<sub>5</sub> and cyclohexanecarbaldehyde ("Aldrich") was passed through an Al<sub>2</sub>O<sub>3</sub> layer in a nitrogen atmosphere to remove cyclohexanecarboxylic acid and other oxidation products (purity of the reagent obtained was monitored by GLC).

## Results and Discussion

In the studies of the oxidation of alkanes with atmospheric oxygen in the presence of cyclohexanecarbaldehyde we found that the expected process of oxidation of aldehyde **1** into cyclohexanecarboxylic acid (**3**) is accompanied by its intense decarboxylation. The formation of compound **3** (the major reaction product) on heating (60 °C) a solution of aldehyde **1** in MeCN in the presence of complex **2** in a low air flow is accompanied by accumulation of considerable amounts of cyclohexane, cyclohexanol, and cyclohexanone (Fig. 1). Four hours after the beginning of the reaction, the concentration of cyclohexane becomes somewhat lower, which is likely due to partial evaporation of this compound facilitated by constant air flow. In the initial period of the reaction (approximately to 5 h), accumulation of cyclohexanol and cyclohexanone occurs linearly; however, it is likely that oxidation of alcohol into ketone begins thereafter, since the rate of alcohol accumulation decreases somewhat, whereas the

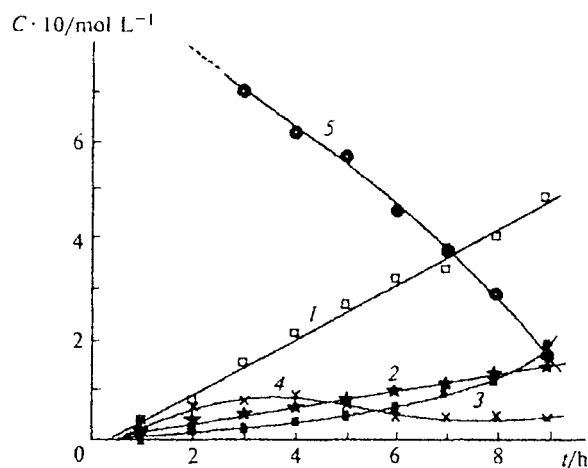


Fig. 1. Curves of the accumulation of cyclohexanecarboxylic acid (1), cyclohexanol (2), cyclohexanone (3), and cyclohexane (4) on oxidation of cyclohexanecarbaldehyde (at an initial concentration of 1.0 mol L<sup>-1</sup>) (5) in acetonitrile (60 °C) catalyzed by complex 2 (0.5 mmol L<sup>-1</sup>).

slope of the curve of ketone accumulation (see Fig. 1) increases. Oxidation of aldehyde 1 into acid 3 also occurs in the absence of catalyst 2 and is accompanied by decarboxylation; however, the rate of cyclohexanecarbaldehyde consumption and that of accumulation of

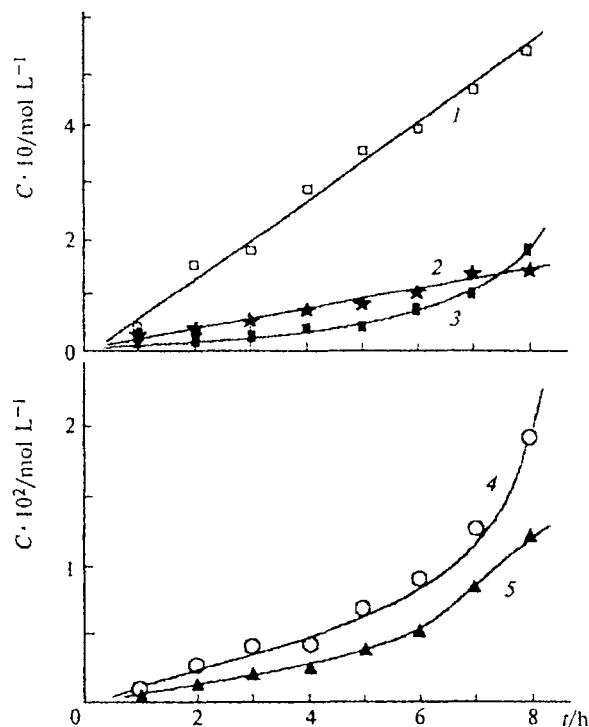
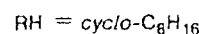
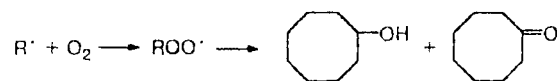
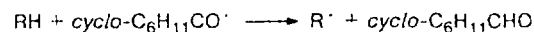
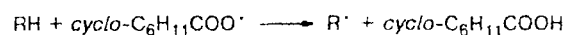
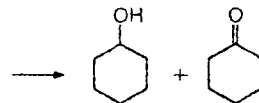
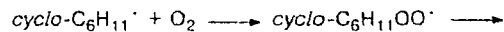
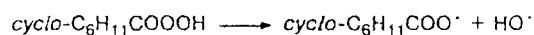
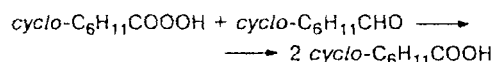
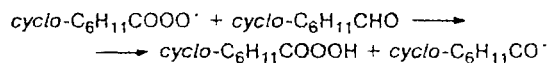
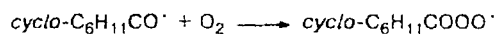
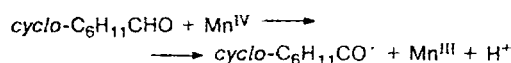


Fig. 2. Curves of the accumulation of cyclohexanecarboxylic acid (1), cyclohexanol (2), cyclohexanone (3), cyclooctanol (4), and cyclooctanone (5) on joint oxidation of cyclohexanecarbaldehyde (1.0 mol L<sup>-1</sup>) and cyclooctane (0.4 mol L<sup>-1</sup>) in acetonitrile (50 °C) catalyzed by complex 2 (0.5 mmol L<sup>-1</sup>).

all the products are approximately halved compared to those in the catalytic reaction.

The kinetic curves of accumulation of the products of oxidation of aldehyde 1 in the presence of cyclooctane are shown in Fig. 2. As in the absence of saturated hydrocarbon, acid 3 is the major product in this case. In addition, decarboxylation of compound 1 results in its conversion into cyclohexanone and cyclohexanol. Oxidation of aldehyde 1 is also accompanied by cyclooctane oxidation and the formation of cyclooctanol and cyclooctanone whose overall concentration after 8 h approximates 3 · 10<sup>-2</sup> mol L<sup>-1</sup>.

When discussing the mechanism of transformations described, it can be assumed that in addition to conversion of aldehyde 1 into acid 3 the former undergoes decarboxylation with the participation of a manganese complex under the reaction conditions. The cyclohexyl radical formed in this case can react either with the donors of hydrogen atoms (e.g., with aldehyde 1 and cyclooctane) to give cyclohexane or with an oxygen molecule to give cyclohexanol and cyclohexanone. The radical species present in the system are also capable of abstracting a hydrogen atom from cyclooctane to give (after several transformations) cyclooctanol and cyclooctanone. Several stages of the process are shown below (see, e.g., Refs. 13–20).



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### References

1. A. E. Shilov and G. B. Shul'pin, *Aktivatsiya and kataliticheskie reaktsii uglevodorodov* [Activation and Catalytic Reactions of Hydrocarbons], Nauka, Moscow, 1995, 400 pp. (in Russian).
2. A. E. Shilov and G. B. Shul'pin, *Chem. Rev.*, 1997, **97**, 2879.
3. T. Mukaiyama and T. Yamada, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 17.
4. S.-I. Murahashi, Y. Oda, and T. Naota, *J. Am. Chem. Soc.*, 1992, **114**, 7913.
5. S.-I. Murahashi, Y. Oda, T. Naota, and N. Komiya, *J. Chem. Soc., Chem. Commun.*, 1993, 139.
6. S.-I. Murahashi, T. Naota, and N. Komiya, *Tetrahedron Lett.*, 1995, **36**, 8059.
7. T. Punniyamurthy, S. J. S. Lalra, and J. Iqbal, *Tetrahedron Lett.*, 1995, **36**, 8497.
8. N. Komiya, T. Naota, and S.-I. Murahashi, *Tetrahedron Lett.*, 1996, **37**, 1633.
9. P. Battioni, R. Iwanejko, D. Mansuy, T. Mlodnicka, J. Poltowicz, and F. Sanchez, *J. Mol. Catal., A: Chem.*, 1996, **109**, 91.
10. G. Pozzi, M. Cavazzini, S. Quici, and S. Fontana, *Tetrahedron Lett.*, 1997, **38**, 7605.
11. D. K. Chand, and P. K. Bharadwaj, *Inorg. Chem.*, 1997, **36**, 5658.
12. N. M. Emanuel', E. T. Denisov, and Z. K. Maizus, *Tsepnye reaktsii okisleniya uglevodorodov v zhidkoi faze* [Chain Reactions of Liquid-Phase Oxidation of Hydrocarbons], Nauka, Moscow, 1965, 176 (in Russian).
13. A. S. Dneprovskii and T. I. Temnikova, *Teoreticheskie osnovy organicheskoi khimii* [Theoretical Foundations of Organic Chemistry], Khimiya, Leningrad, 1979, 444 (in Russian).
14. C. Chatgililoglu and M. Lucarini, *Tetrahedron Lett.*, 1995, **36**, 1299.
15. J. Wang, H. Itoh, M. Tsuchiya, K. Tokumaru, and H. Sakuragi, *Tetrahedron*, 1995, **51**, 11967.
16. N. Anoune, P. Lanteri, R. Longaray, and C. Arnaud, *Tetrahedron Lett.*, 1995, **36**, 6679.
17. C. B. Castellani, O. Carugo, M. Giusti, C. Leopizzi, A. Perotti, A. G. Invernizzi, and G. Vidari, *Tetrahedron*, 1996, **52**, 11045.
18. W. Nam, S. J. Baek, K. A. Lee, B. T. Ahn, J. Mueller, C. J. Burrows, and J. S. Valentine, *Inorg. Chem.*, 1996, **35**, 6632.
19. Y. I. Kim and Y. H. Kim, *Tetrahedron Lett.*, 1998, **39**, 639.
20. A. P. Darmanyany, D. D. Gregory, Y. Guo, W. S. Jenks, L. Burel, D. Eloy, and P. Jardon, *J. Am. Chem. Soc.*, 1998, **120**, 396.

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