

Hydrogen Peroxide Oxidation of Alkanes Catalyzed by the Osmium Complex $\text{Os}_3(\text{CO})_{11}(\eta^2\text{-PhCOCH=CHCOPh})$

L. S. Shul'pina^a, A. R. Kudinov^a, E. A. Petrovskaya^a, T. V. Strelkova^a, and G. B. Shul'pin^{b, 1}

^a Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow, 119991 Russia

^b Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina 4, Moscow, 119991 Russia

¹ e-mail: gbsh@mail.ru

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Abstract—A very effective metal complex catalyst for the liquid-phase oxidation of saturated hydrocarbons with hydrogen peroxide in an acetonitrile medium is described for the first time. It is supposed that catalytically active species produced from the trinuclear osmium carbonyl olefin complex $\text{Os}_3(\text{CO})_{11}(\eta^2\text{-PhCOCH=CHCOPh})$ upon its interaction with hydrogen peroxide at 50–70°C efficiently generate hydroxyl radicals, which attack a dissolved alkane and, thus, lead to its oxidation. The turnover number reaches 2400.

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INTRODUCTION

The search for new effective alkane-oxidation catalysts based on soluble complexes of transition metals is a highly topical problem. In the last decades, new catalytic systems for the oxidation of inert alkanes under mild conditions have been described [1–12]. Very few works on the catalysis of oxidative transformations by soluble osmium derivatives have been reported. These studies concerned the oxidation of not only saturated hydrocarbons [13–15] but also olefins [16, 17] and alcohols [18, 19] by the action of hydrogen peroxide and other organic and inorganic reagents. In the present work, we reveal for the first time that the osmium(0) carbonyl π -olefin complex $\text{Os}_3(\text{CO})_{11}(\eta^2\text{-PhCOCH=CHCOPh})$ (compound **1**) exhibits a high catalytic activity in the oxidation of alkanes with hydrogen peroxide.

EXPERIMENTAL

The synthesis and the structure of complex **1** were described earlier [20]. Oxidation reactions of alkanes were performed in a glass cylindrical vessel surrounded by a jacket with water circulating through a thermostat. The volume of the solution was 2 ml. Samples of the reaction solution (0.2 ml) were taken at certain time intervals and analyzed by GLC before and after treatment (for 10–20 min) of the solution with an excess of solid triphenylphosphine. Upon the reduction of the solution by triphenylphosphine, alkylhydroperoxide was quantitatively converted into the corresponding alcohol, and a comparison of chromatograms of the sample before its treatment with triphenylphosphine and after the reduction made it possible to determine the amount of alkylhydroperoxide, as well as ketone and alcohol, produced in the solution [4, 8, 21–25]. The

GLC analysis was performed on an LKhM-80-6 chromatograph with 2-m columns packed with 5% Carbowax 1500-coated Inerton AW-HMDS (0.25–0.315 mm) and argon as a carrier gas, and on a 3700 chromatograph equipped with a 30 m \times 0.2 mm capillary column coated with a 0.3- μm layer of FFAP/OV-101 taken at a mass ratio of 20/80 (with helium as a carrier gas). Chromatograms were preliminarily calibrated with the authentic compounds, the alkane oxidation products. Since the cyanoacetic acid formed from 2-cyanoethanol was completely decarboxylated in the chromatograph injection port, the oxidation products of this alcohol were analyzed by the ¹H NMR technique (Bruker 400 MHz) using D₂O and nitromethane (as an internal standard).

RESULTS AND DISCUSSION

We found that the trinuclear Os(0) olefin carbonyl complex (2,3- η -1,4-diphenylbut-2-ene-1,4-dione)undecacarbonyltriangulotriosmium effectively catalyzed the oxidation of alkanes with hydrogen peroxide. Acetonitrile was used as a solvent, and reactions were performed in air at 50–70°C. Oxygenation of cyclic, linear, and branched alkanes (RH) leads to the formation of corresponding alkylhydroperoxides (ROOH), which gradually decompose during the reaction to give more stable ketones (aldehydes) and alcohols. In particular, the oxidation of cyclohexane (CyH) in acetonitrile at 60°C, a catalyst concentration of $[\mathbf{1}] = 2 \times 10^{-4} \text{ mol l}^{-1}$, $[\text{CyH}]_0 = 1.38 \text{ mol l}^{-1}$, and $[\text{H}_2\text{O}_2]_0 = 1.4 \text{ mol l}^{-1}$, gives products at as high a total concentration as 0.175 mol l⁻¹, which corresponds to yields of 20% and 30% in terms of cyclohexane and hydrogen peroxide, respectively (assuming that two H₂O₂ molecules are required to produce one peroxide molecule,

CyOOH). At a lower catalyst concentration ($[1] = 5 \times 10^{-5} \text{ mol l}^{-1}$) and a higher amount of cyclooctane (0.5 ml; in this case, the hydrocarbon was partially insoluble in the reaction mixture containing 0.4 ml 35% H_2O_2 and 0.8 ml acetonitrile), the maximum turnover number (TON) was attained (2400 within 6 h at 70°C). We also showed that efficient oxidation could be performed in the two-phase system in the absence of an organic solvent (1 ml cyclohexane and 1 ml 35% aqueous hydrogen peroxide solution). In this case, the TON reached 420 within 6 h at 70°C .

In the case of cyclooctane oxidation, the initial reaction rate was proportional to the concentration of catalyst **1**. The first order was also found for the dependence on the initial concentration of hydrogen peroxide. The plot of the initial rate versus the initial cyclooctane concentration reached a plateau at $[\text{cyclooctane}]_0 > 0.1 \text{ mol l}^{-1}$. The presence of the plateau may be explained by competition between cyclooctane and acetonitrile in their interaction with an oxidizing species, which can be the hydroxyl radical in this case [26, 27].

The oxidation of *n*-heptane (0.9 mol l^{-1}) in acetonitrile at 60°C ($[1] = 1 \times 10^{-4} \text{ mol l}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 1.2 \text{ mol l}^{-1}$, for 8 h) gave the following products (concentrations given in parentheses in mmol l^{-1} were determined after the reduction with triphenylphosphine of a sample of the reaction mixture): heptanal (0.65), heptanone-2 (2.60), heptanone-3 (2.50), heptanone-4 (1.10), heptanol-1 (0.40), heptanol-2 (1.80), heptanol-3 (1.60), heptanol-4 (0.74), and heptanoic acid (0.16). The normalized (with allowance for the number of hydrogen atoms on the carbon atom of a given type) regioselectivity parameter (the relative reactivity of hydrogen atoms in the 1, 2, 3, and 4 positions of the *n*-heptane chain) calculated from these data was $\text{C}(1) : \text{C}(2) : \text{C}(3) : \text{C}(4) = 1.0 : 5.5 : 5.0 : 4.6$. This value is very close to the data obtained earlier for the oxidation of *n*-heptane with hydrogen peroxide in acetonitrile upon irradiation with UV light (1 : 7 : 6 : 7) and by the reagent "H₂O₂-vanadate anion-pyrazine-2-carboxylic acid" (1 : 9 : 7 : 7) [1, 3, 4, 8, 27–29]. It is assumed that both systems oxidize alkanes via the mechanism involving free hydroxyl radicals [1, 27–29]. Note for comparison that oxidation of *n*-heptane with the system H_2O_2 -[(TMTACN)Mn^{IV}(O₃)Mn^{IV}(TMTACN)]²⁺-MeCO₂H (where TMTACN = 1,4,7-trimethyl-1,4,7-triazacyclononane), which does not generate hydroxyl radicals [3, 4, 8, 30–32], results in a noticeably higher regioselectivity (1 : 46 : 35 : 35). The oxidation of branched alkanes (3-methylhexane, methylcyclohexane, and 2,2,4-trimethylpentane) with the system **1**-H₂O₂ proceeds with low values of the bond selectivity typical of reactions involving reactive free radicals. The oxygenation of *cis*-decalin and *cis*-1,2-dimethylcyclohexane is not stereoselective, which is also consistent with the free-radical mechanism.

The complex under consideration catalyzes the oxidation of benzene into phenol and quinone, and ethylbenzene is oxidized into the corresponding alkylhydroperoxide, phenylethanol, and acetophenone. The latter reaction does not occur when the reaction solution is purged with argon, which removes oxygen from the vessel. Furthermore, the system H_2O_2 -**1** oxidizes alcohols into the corresponding carbonyl derivatives. In particular, we used this system for the conversion of 2-cyanoethanol $\text{NCCH}_2\text{CH}_2\text{OH}$, which is difficult to oxidize, into the corresponding aldehyde NCCH_2CHO . With the use of **1** at a concentration of $1 \times 10^{-4} \text{ mol l}^{-1}$, the conversion of the alcohol was only 17%. When **1** was introduced into the reaction at a higher concentration ($1 \times 10^{-3} \text{ mol l}^{-1}$) and 2,2'-bipyridyl ($5 \times 10^{-2} \text{ mol l}^{-1}$) was added as a co-catalyst, the oxidation of 0.1 ml cyanoethanol (0.2 ml H_2O_2 , 0.15 ml MeCN, at 60°C for 6 h) gave the aldehyde with a yield of 28%. It is interesting that the oxidation of isopropanol without the co-catalyst has a low selectivity (the yield of acetone is only 6%). Previous experiments showed that carbonylhydride $\text{H}_2\text{Os}_3(\text{CO})_{10}$, a related osmium derivative (see reference [33] on some transformations of this compound), exhibited a somewhat higher catalytic activity than complex **1** in the oxidation of alcohols. In particular, the oxidation of cyanoethanol (0.1 ml) in the presence of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ ($2 \times 10^{-4} \text{ mol l}^{-1}$), hydrogen peroxide (0.5 ml), and acetonitrile (0.3 ml) for 3 h at 50°C gave cyanoacetic aldehyde (28%) and cyanoacetic acid NCCH_2COOH (8%). In the analogous reaction of isopropanol (0.1 ml) under the same conditions, acetone was obtained with a yield of 58% in terms of isopropanol.

The data obtained in this work suggest that osmium complex **1** is a precursor of a catalytically active species (or several different species) that efficiently generates free hydroxyl radicals by interaction with hydrogen peroxide. The hydroxyl radicals attack molecules of the organic substrate with hydrogen atom abstraction from an alkane or alcohol. The alkane is converted into an alkyl radical, which, in turn, rapidly reacts with a molecule of atmospheric oxygen. A similar mechanism is supposed for the catalysis of the hydrogen peroxide oxidation of organic substrates by iron(III) ions [26]. However, it should be noted that the osmium complex described in this work is a much more effective generator of hydroxyl radicals in the presence of hydrogen peroxide than the known iron ions and complexes.

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REFERENCES

1. R. Z. Khaliulin, A. T. Bell, and M. Head-Gordon, *J. Phys. Chem.*, B **109**, 17984 (2005).
2. G. B. Shul'pin, C. C. Golfeto, G. Süss-Fink, et al., *Tetrahedron Lett.* **46**, 4563 (2005).
3. G. B. Shul'pin, in *Transition Metals for Organic Synthesis*, Ed. by M. Beller and C. Bolm (Wiley-VCH, Weinheim, 2004), Vol. 2, p. 215.
4. G. B. Shul'pin, *C. R. Acad. Sci., Ser. 2* **6**, 163 (2003).
5. A. I. Nekhaev, R. S. Borisov, V. G. Zaikin, and E. I. Bagrii, *Pet. Chem.* **42**, 418 (2002).
6. A. I. Nekhaev, R. S. Borisov, V. G. Zaikin, and E. I. Bagrii, *Pet. Chem.* **42**, 238 (2002).
7. M. V. Avdeev, E. I. Bagrii, G. B. Maravin, and Yu. M. Korablev, *Kinet. Catal.* **43**, 38 (2002).
8. A. E. Shilov and G. B. Shul'pin, *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes* (Kluwer Academic, Dordrecht, 2000), Chap. X.
9. M. V. Avdeev, E. I. Bagrii, G. B. Maravin, et al., *Pet. Chem.* **40**, 391 (2000).
10. G. B. Maravin, M. V. Avdeev, and E. I. Bagrii, *Neftekhimiya* **40**, 3 (2000) [*Pet. Chem.* **40**, 1 (2000)].
11. A. E. Shilov and G. B. Shul'pin, *Chem. Rev.* **97**, 2879 (1997).
12. E. I. Bagrii and A. I. Nekhaev, *Zh. Vses. Khim. O-va im. D.I. Mendeleeva* **34**, 634 (1989).
13. G. B. Shul'pin, G. Süss-Fink, and L. S. Shul'pina, *Chem. Commun.*, 1131 (2000).
14. S. N. Kholuiskaya, A. D. Pomogailo, N. M. Bravaya, et al., *Kinet. Katal.* **44**, 831 (2003).
15. B. C. Bales, P. Brown, A. Dehestani, and J. M. Mayer, *J. Am. Chem. Soc.* **127**, 2832 (2005).
16. K. Lee, Y.-H. Kim, S. B. Han, et al., *J. Am. Chem. Soc.* **125**, 6844 (2003).
17. P. P. Pescarmona, A. F. Masters, J. C. Van der Waal, and T. Maschmeyer, *J. Mol. Catal., A: Chem.* **220**, 37 (2004).
18. C. Döbler, G. M. Mehlretter, U. Sundermeier, et al., *Tetrahedron Lett.* **42**, 8447 (2001).
19. A. M. Khenkin, L. J. W. Shimon, and R. Neumann, *Inorg. Chem.* **42**, 3331 (2003).
20. L. V. Rybin, E. A. Petrovskaya, M. I. Rybinskaya, et al., *Metalloorg. Khim.* **5**, 684 (1992).
21. G. B. Shul'pin, *J. Mol. Catal., A: Chem.* **189**, 39 (2002).
22. G. B. Shul'pin and A. N. Druzhinina, *React. Kinet. Catal. Lett.* **47**, 207 (1992).
23. G. B. Shul'pin and G. V. Nizova, *React. Kinet. Catal. Lett.* **48**, 333 (1992).
24. G. B. Shul'pin, M. M. Bochkova, and G. V. Nizova, *J. Chem. Soc., Perkin Trans. 2*, 1465 (1995).
25. G. B. Shul'pin, G. V. Nizova, and Y. N. Kozlov, *New J. Chem.* **20**, 1243 (1996).
26. G. B. Shul'pin, G. V. Nizova, Y. N. Kozlov, et al., *Adv. Synth. Catal.* **346**, 317 (2004).
27. Y. N. Kozlov, G. V. Nizova, and G. B. Shul'pin, *J. Mol. Catal., A: Chem.* **227**, 247 (2005).
28. G. B. Shul'pin, D. Attanasio, and L. Suber, *J. Catal.* **142**, 147 (1993).
29. G. B. Shul'pin, Y. N. Kozlov, G. V. Nizova, et al., *J. Chem. Soc., Perkin Trans. 2*, 1351 (2001).
30. G. B. Shul'pin, G. V. Nizova, Y. N. Kozlov, and I. G. Pechenkina, *New J. Chem.* **26**, 1238 (2002).
31. C. B. Woitiski, Y. N. Kozlov, D. Mandelli, et al., *J. Mol. Catal., A: Chem.* **222**, 103 (2004).
32. G. B. Shul'pin, G. V. Nizova, Y. N. Kozlov, et al., *J. Organomet. Chem.* **9690**, 4498 (2005).
33. S.-G. Ang, X. Zhong, and H.-G. Ang, *J. Organomet. Chem.* **665**, 218 (2003).