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Oxidations catalyzed by osmium compounds. Part 1: Efficient alkane oxidation with peroxides catalyzed by an olefin carbonyl osmium(0) complex

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Abstract

A carbonyl osmium(0) complex with π-coordinated olefin, (2,3-η-1,4-diphenylbut-2-en-1,4-dione)undecacarbonyl triangulotriosmium (**1**), efficiently catalyzes oxygenation of alkanes (cyclohexane, cyclooctane, *n*-heptane, isooctane, etc.) with hydrogen peroxide, as well as with *tert*-butyl hydroperoxide and *meta*-chloroperoxybenzoic acid in acetonitrile solution. Alkanes are oxidized to corresponding alcohols, ketones (aldehydes) and alkyl hydroperoxides. Thus, heating cyclooctane with the **1**–H_2O_2 combination at 70 °C gave products with turnover number as high as 2400 after 6 h. The maximum obtained yield of all products was equal to 20% based on cyclohexane and 30% based on H_2O_2. The oxidation of linear and branched alkanes exhibits very low regio- and bond-selectivity parameters and this testifies that the reaction proceeds via attack of hydroxyl radicals on C–H bonds of the alkane. The oxygenation products were not formed when the reaction was carried out under argon atmosphere and it can be thus concluded that the oxygenation occurs via the reaction between alkyl radicals and atmospheric oxygen. In summary, the Os(0) complex is much more powerful generator of hydroxyl radicals than any soluble derivative of iron (which is an analogue of osmium in the Periodic System).

Keywords: Alkanes; Homogeneous catalysis; Hydrogen peroxide; Organometallic compounds; Osmium complexes; Oxidation

1. Introduction

Saturated hydrocarbons, alkanes, are known to exhibit only very low reactivity in reactions with variety of normal reagents and in many cases the yields of the products are negligible. In last decades, new methods of alkane functionalization with participation of various transition metal complexes in solutions have been discovered and developed (see recent books and reviews [1–10]) and original publications [11–28]. Organometallic derivatives of transition metals very seldom exhibit high activity in alkane oxygenations [29,30]. A remarkable example is methyltrioxorhenium (MTO) [31,32] which efficiently oxidizes alkanes in the presence of pyrazin-2-carboxylic acid [33]. Metal-catalyzed alkane oxidations in solutions give directly valuable products such as alkyl hydroperoxides, alcohols, ketones, and carboxylic acids under mild conditions (see, for example, recent reviews [34,35]). It is interesting to note that although iron plays an extremely important role in oxidations occurring in living cells (e.g., cytochrome P450 [1,2,36] and methanemonooxygenase, MMO [1,2,37–39]) iron complexes and especially simple salts of this metal do not usually exhibit high activity in oxidations in vitro. Turnover numbers (TONs) in alkane oxidations are typically attain values only of 20–100 [34,35,40–45]. Thus, TONs in $FeCl_3$-catalyzed "Gif oxidations" (i.e., in the presence of pyridine) have been reported to equal values not higher than 1–20 [46]. Iron complexes (especially polynuclear derivatives) containing *N*-ligands are more powerful catalysts [40–45,47]. As for the classical Fenton reagent

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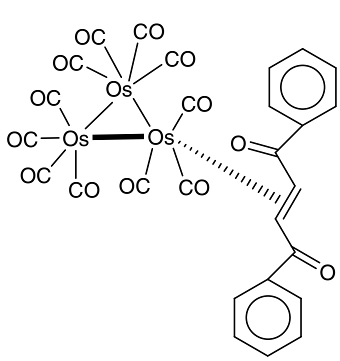
[48–55], i.e., the Fe(II)–H_2O_2 combination, is concerned, the efficiency of oxidation by this stoichiometric system is very low and usually the reaction proceeds non-selectively giving a variety of products (see also [47]). Catalytic system $FeCl_3$–H_2O_2 is also not efficient in alkane oxidation in acetonitrile [42]. All these processes proceed with formation of free hydroxyl radicals [48–62]. It should be also noted that oxidations of alkanes, RH, with participation of cytochrome P450 and MMO are believed to include in the crucial step an abstraction of a hydrogen atom to produce an alkyl radical, R$^{\bullet}$, which is involved into subsequent transformations. One cannot exclude that this radical adds (at least partly) molecular oxygen affording hydroperoxyl radical, ROO$^{\bullet}$.

It was interesting to compare catalytic activity of derivatives of ruthenium and osmium which are analogues of iron in the Periodic System. Surprisingly, although osmium-catalyzed oxidation reactions of olefins [63–73] and alcohols [74–78] have been reported and are used in organic synthesis, much less is known about catalysis of alkane transformations by soluble osmium compounds [79–82]. Oxide of high-valent osmium, OsO_4 [79], and osmium chlorides [80] have been used in alkane oxidations with hydrogen peroxide in organic solvents. Very recently, Mayer and co-workers described [81] stoichiometric and catalytic oxidations of alkanes with OsO_4. This osmium derivative has been used as a catalyst in oxidation of isobutane with $NaIO_4$ in aqueous solution (pH ≈ 4.3; 168 h at 85 °C), TON being only ca. 4. Cyclohexene was oxidized by molecular oxygen or *tert*-butyl hydroperoxide (TBHP) in the presence of osmium carbonyl clusters supported on polymer matrices [82].

2. Results and discussion

In this work, we have found that π-olefin osmium(0) complex, (2,3-η-1,4-diphenylbut-2-en-1,4-dione)undecacarbonyl triangulotriosmium (**1**), efficiently catalyses oxygenation of alkanes with hydrogen peroxide, as well as with *tert*-butyl hydroperoxide (TBHP) and *meta*-chloroperoxybenzoic acid (MCPBA). Complex **1** was synthesized as described previously [83] starting from $Os_3(CO)_{11}$-(MeCN) and *trans*-1,4-diphenylbut-2-ene-1,4-dione. The structure of **1** was determined by the X-ray method [83].



Complex **1**

Acetonitrile was used as a solvent and reactions were carried out in air at 50–70 °C. The oxygenation of cyclic, linear and branched alkanes, RH, gives rise to the formation of the corresponding alkyl hydroperoxides, ROOH, as the main primary products which further gradually decompose to yield more stable products, the ketones (aldehydes) and alcohols. The formation of alkyl hydroperoxides in addition to the corresponding alcohols and ketones was demonstrated employing a method previously used by us and which is based on the GC analysis [2,34,84–87]. 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. In our kinetic studies presented below, we measured the concentrations of the cyclohexanone and cyclohexanol only after the reduction with PPh_3 because in this case we obtained more precise values of the initial rates.

Kinetics of the cyclohexane, CyH, oxidation in homogeneous solution in acetonitrile are presented in Fig. 1. It can be seen that the corresponding alcohol, ketone and alkyl hydroperoxide are formed in comparable amounts. Turnover number under these conditions attains 550 (Table 1, entry 1). When catalyst **1** was used in higher concentration the TON became lower (entry 2) but in this case the maximum yield of all products was obtained: the concentration of oxygenates attained 0.175 mol dm^{-3} which corresponds to yield of 20% based on cyclohexane and of 30% based on H_2O_2 (assuming that two molecules of H_2O_2 are required to produce one molecule of CyOOH). The highest TON

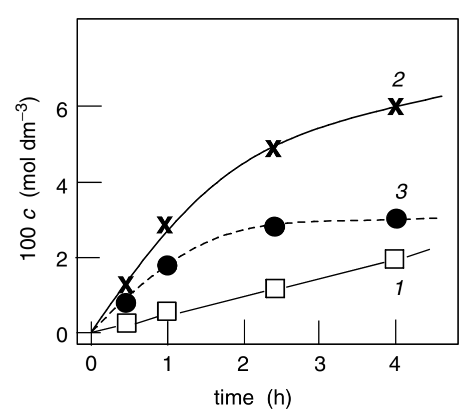


Fig. 1. Accumulation of oxygenates (concentrations, *c*, of cyclohexanone, curve 1; cyclohexanol, curve 2; cyclohexyl hydroperoxide, curve 3, are given) in the cyclohexane (initial concentration 1.38 mol dm^{-3}) oxidation with H_2O_2 (1.4 mol dm^{-3}) catalyzed by **1** (2×10^{-4} mol dm^{-3}). Conditions: solvent MeCN; homogeneous solution at 60 °C.

Table 1
Efficiency of cycloalkane oxidation with H_2O_2 catalyzed by **1**

Entry	Alkane	Media	**1**	Temperature (°C)	Time (h)	TON[a]
1	Cyclohexane	MeCN	2×10^{-4} mol dm^{-3}	60	4	550
2	Cyclohexane	MeCN	5×10^{-4} mol dm^{-3}	60	14	350
3	Cyclohexane	MeCN	5×10^{-5} mol dm^{-3}	60	2	900
4	Cyclooctane	MeCN–H_2O[b]	5×10^{-5} mol dm^{-3}	70	6	2400
5	Cyclooctane	H_2O[c]	2×10^{-5} mmol	70	6	420

[a] TON, turnover number, i.e., total moles of products produced per one mole of a catalyst.
[b] Cyclooctane (0.5 mL) was partly insoluble in the reaction solution containing 0.4 mL 35% H_2O_2 and 0.8 mL MeCN.
[c] The reaction was carried out in a two-phase system, volume of aqueous solution was 1 mL, volume of cyclooctane was 1 mL.

(2400) was attained when low concentration of **1** and large amount of cyclooctane was used (entry 4). We have also found that the efficient oxidation occurs in a biphasic system in the absence of any organic solvent (entry 5).

We have studied dependences of the initial rates in the cyclooctane oxidation on the concentrations of reactants. The initial rate is proportional to the concentration of **1** (Fig. 2) and first order has been also found for hydrogen peroxide (Fig. 3). The dependence of the initial hydrocarbon oxidation rate on the initial cyclooctane concentration (Fig. 4) exhibits a plateau when $[\text{cyclooctane}]_0 > 0.1$ mol dm^{-3}. Such behaviour has been earlier explained [42] by competition between cycloalkane and acetonitrile for the interaction with an active oxidizing species (which is most probably hydroxyl radical; see below). Generally speaking, acetonitrile is not completely inert solvent in this reaction and can be transformed into certain products with low yields [88,89].

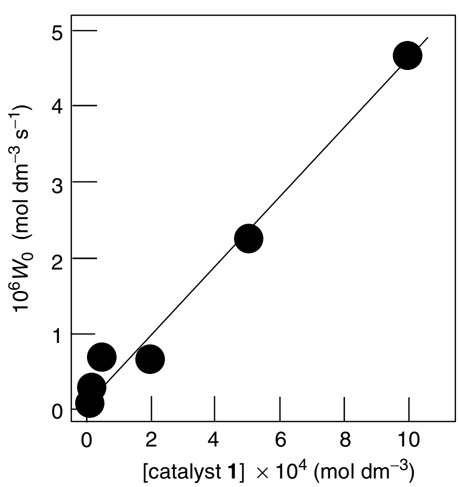


Fig. 2. Dependence of the initial rate of cyclooctane oxidation on the initial concentration of **1**. Conditions: cyclooctane, 0.35 mol dm^{-3}; H_2O_2, 0.6 mol dm^{-3}; solvent MeCN; 70 °C.

In order to get a mechanistic understanding of this oxidation process, we studied the oxidation of some linear and branched alkanes. The results are summarized in Tables 2 and 3. Table 2 demonstrates concentrations of all products formed in the oxidation of normal heptane and gives also the regioselectivity parameters C(1):C(2):C(3):C(4) for different times of the reaction. In addition to these parameters for *n*-hexane and *n*-heptane, bond selectivity parameters, 1°:2°:3°, are given in Table 3 for the oxidation of some branched alkanes (3-methylhexane, methylcyclohexane and 2,2,4-trimethylpentane). Normalized parameters in Table 3 have been calculated based only on concentrations of isomeric alcohols obtained after reduction of the reaction mixture with triphenylphosphine. This table contains also stereoselectivity parameters *trans/cis* obtained for the oxidation of disubstituted cyclohexanes (*cis*-1,2-dimethylcyclohexane and *cis*-decalin).

To compare selectivity parameters, the corresponding data for some other systems are also given in Table 3. Thus, it is believed that the alkane oxidation by reagent

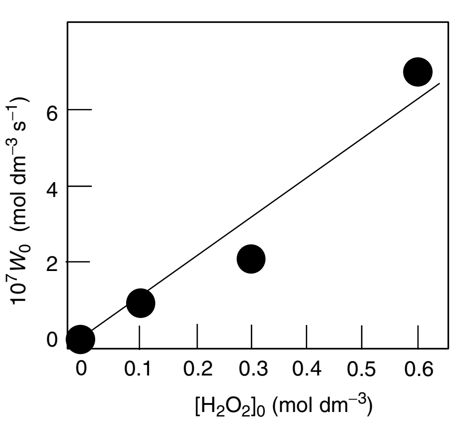


Fig. 3. Dependence of the initial rate of cyclooctane oxidation on the initial concentration of hydrogen peroxide. Conditions: cyclooctane, 0.35 mol dm^{-3}; **1**, 2×10^{-4} mol dm^{-3}; solvent MeCN; 70 °C.

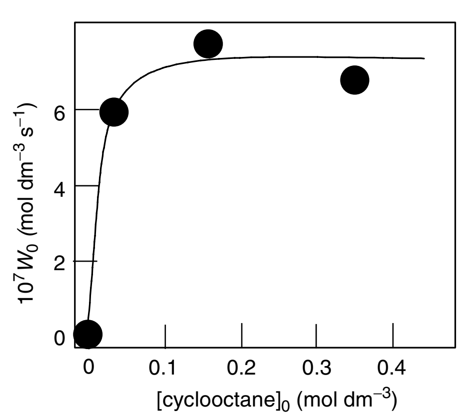


Fig. 4. Dependence of the initial rate of cyclooctane oxidation on the initial concentration of cyclooctane. Conditions: H_2O_2, 0.6 mol dm^{-3}; **1**, 2×10^{-4} mol dm^{-3}; solvent MeCN; 70 °C.

Table 2
Oxidation of *n*-heptane with H_2O_2 catalyzed by **1**[a]

Time (h)	Concentration (mmol dm^{-3})									Regioselectivity[b]
	al	one-2	one-3	one-4	ol-1	ol-2	ol-3	ol-4	Heptanoic acid	
0.5	0.04	0.22	0.17	0.09	0.10	0.15	0.16	0.06	0.05	1.0:3.0:2.6:2.4
1.0	0.15	0.25	0.22	0.11	0.20	0.20	0.20	0.08	0.05	1.0:1.7:1.6:1.4
3.0	0.70	0.50	0.44	0.20	0.23	0.20	0.17	0.10	0.10	1.0:1.0:0.9:0.9
8.0	0.65	2.60	2.50	1.10	0.40	1.80	1.60	0.74	0.16	1.0:5.5:5.0:4.6

[a] Reaction conditions: *n*-heptane, 0.9 mol dm^{-3}; H_2O_2, 1.2 mol dm^{-3}; **1**, 1×10^{-4} mol dm^{-3}; solvent MeCN; homogeneous solution at 60 °C.
[b] Relative reactivities of hydrogen atoms at carbons 1, 2, 3 and 4, C(1):C(2):C(3):C(4), of the *n*-heptane chain. The parameters were normalized, i.e., calculated taking into account the number of hydrogen atoms at each carbon.

"H_2O_2–VO_3^-–pyrazine-2-carboxylic acid" (see [1,2,10,34,35,90–93]) proceeds via the formation of hydroxyl radicals which attack C–H bonds of the alkane. Oxidations with H_2O_2 induced by irons salts $Fe(ClO_4)_3$ and $FeSO_4$ as well as the reaction stimulated by UV irradiation also occur with the formation of $HO^{\bullet}$ radicals. On the contrary, alkane oxygenation by the "H_2O_2–[(TMTACN)$Mn^{IV}(O_3)$-Mn^{IV}(TMTACN)]$^{2+}$–CH_3COOH" system (see [2,10,34,35,94–98]) apparently involves the interaction of the C–H bonds with $Mn^{V}{=}O$ species. It follows from Tables 2 and 3 that the oxidations by the "H_2O_2–**1**" system exhibit very low selectivities for linear and branched alkanes and the reaction with *cis*-decalin is not stereoselective. For example, regioselectivity in the *n*-heptane oxygenation by this system in MeCN (ca. 1:5:5:5; compare with the value for the photoinduced reaction, 1:7:6:7) is noticeably lower than the corresponding parameter (1:46:35:35) for the "H_2O_2–[(TMTACN)$Mn^{IV}(O_3)Mn^{IV}$(TMTACN)]$^{2+}$–CH_3COOH" system. These data testify clearly that **1**-catalyzed alkane oxygenation proceeds mainly with participation of free hydroxyl radicals.

The "**1**–H_2O_2" system oxidizes also benzene in acetonitrile solution at 60 °C. Phenol (TON = 500) and quinone (TON = 300) were detected in the reaction mixture after 3 h. Ethylbenzene was oxidized under similar conditions mainly to a mixture of ethylbenzene hydroperoxide, 1-phenylethanol and acetophenone. It is important to note that experiments on ethylbenzene oxidations at 70 °C in atmosphere of either argon or air gave absolutely different results. Only traces of oxygenates have been found in the reaction mixture after heating in an argon atmosphere. On the contrary, when a slow stream of air was passed through the reaction solution ethylbenzene reacted with high conversion. As the reaction does not proceed in an argon atmosphere it can be concluded that catalyst **1** does not induce a substantial decomposition of hydrogen peroxide to yield dioxygen.

One can assume that a key step of the oxidation is generation of hydroxyl radicals in the reaction between hydrogen peroxide and a 'low-valent' osmium derivative, similar with formation of hydroxyl radicals in the Fenton reagent:

$$Os(II) + H_2O_2 \rightarrow Os(III) + HO^{\bullet} + HO^-$$

A 'high-valent' derivative thus formed can be reduced with a new molecule of H_2O_2 back to Os(II):

$$Os(III) + H_2O_2 \rightarrow Os(II) + HOO^{\bullet} + H^+$$

Other Os(n)–Os(n+1) pairs can also operate in such type cycles, for example, the Os(III)–Os(IV) pair. Hydroxyl radicals attack C–H bonds in accordance with equation:

$$RH + HO^{\bullet} = R^{\bullet} + H_2O$$

Alkyl radicals add rapidly molecular oxygen from atmosphere:

$$R^{\bullet} + O_2 = ROO^{\bullet}$$

Peroxyl radicals can be reduced with a 'low-valent' osmium species, for example:

$$ROO^{\bullet} + Os(II) = ROO^- + Os(III)$$

and after addition of a proton are transformed into the primary reaction product, alkyl hydroperoxide:

$$ROO^- + H^+ = ROOH$$

Aqueous solution of TBHP can be also used as an oxidant instead of hydrogen peroxide. The reaction with cyclohexane affords mainly cyclohexanol and less amounts of cyclohexanone and cyclohexyl hydroperoxide (Fig. 5). TON attains in this case 20. The initial reaction rate does not depend on concentration of **1** when [**1**] > 1×10^{-3} mol dm^{-3} (Fig. 6). Selectivity parameters in the TBHP oxidations have been found to be higher than those for the H_2O_2 oxidations. For example, bond selectivity for the oxidation of methylcyclohexane was 1°:2°:3° = 1:5.4:66. This value is less than the corresponding parameter for the oxidation with the "H_2O_2–[(TMTACN)$Mn^{IV}(O_3)Mn^{IV}$(TMTACN)]$^{2+}$–CH_3COOH" system (1:26:200). It is known that the radical *tert*-$Me_3CO^{\bullet}$ abstracts a hydrogen atom from branched alkanes to give the 1°:2°:3° = 1:10:40 ratio [99]. The 1°:3° ratio in the oxidation of isooctane with participation of this radical was found to equal 1:41 [100]. The oxidation by the TBHP–**1** system exhibits low stereoselectivity. Thus, for oxidations of *cis*- and *trans*-1,2-dimethylcyclohexanes *trans*/*cis* parameters were 0.85 and 0.6, respectively. All these data allow us to propose that in the TBHP oxidations the key step is the attack of relatively weak voluminous *tert*-butoxyl radical, *tert*-$Me_3CO^{\bullet}$, on C–H bonds of hydrocarbon substrates.

Complex **1** catalyzes also alkane oxidation with MCPBA in acetonitrile at room temperature (for iron-catalyzed alkane oxidations with MCPBA, see our recent paper [44]). Total yield of oxygenates (ketone, alcohol and alkyl

Table 3
Selectivity parameters in oxidation of alkanes[a]

Entry	System	C(1):C(2):C(3):C(4)[b]		1°:2°:3°[c]			*trans*/*cis*[d]	
		n-Hexane	*n*-Heptane	3-Methylhexane	Methylcyclohexane	2,2,4-Trimethylpentane	*cis*-DMCH[e]	*cis*-Decalin
1	**1**–H_2O_2 (MeCN, 60 °C)	1.0:6.2:7.1	1.0:5.5:5.0:4.6	1:6:19	1:4: 10	1:5:8.5	0.9	2.9
2	**1**–H_2O_2 (H_2O, 70 °C)		1:9.5:9:9	1:4:11		1:2:14	0.7	1.3
3	**1**–MCPBA (MeCN, 25 °C)	1:34:29			1:11:260		0.5	0.55
4	MCPBA (MeCN, 25 °C)	1:36:36.5		1:89:750	1:20:520		0.65	
5	$OsCl_3$–H_2O_2 (MeCN, 80 °C)[f]		1:12:10:3.5	1:3:58		1:2:9		1.2
6	$FeCl_3$–H_2O_2 (MeCN, 20 °C)					1:7:57		1.0
7	$Fe(ClO_4)_3$–H_2O_2 (MeCN, 20 °C)	1:9:9		1:4:30	1:7:43	1:5:13		
8	$FeSO_4$–H_2O_2 (MeCN, 20 °C)		1:5:5:4.5			1:3:6	1.3	3.5
9	hν–H_2O_2 (MeCN, 20 °C)	1:10:7	1:7:6:7	1:4:12		1:2:6	0.9	1.3
10	*n*-Bu_4NVO_3–PCA–H_2O_2 (MeCN, 40 °C)[g]	1:8:7	1:9:7:7	1:6:22	1:6:18	1:4:9	0.75	2.1
11	$[L_2Mn_2O_3]^{2+}$–$MeCO_2H$–H_2O_2 (MeCN, 20 °C)[h]		1:46:35:35	1:22:200	1:26:200	1:5:50	0.34	0.12

[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. Reaction conditions for the oxidations catalyzed by **1** are similar to those described in Table. 1.

[b] Parameters C(1):C(2):C(3):C(4) are relative 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 unbranched alkanes.

[c] Parameters 1°:2°:3° are relative 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 *cis*-disubstituted cyclohexanes.

[e] *cis*-DMCH is *cis*-1,2-dimethylcyclohexane.

[f] See [80].

[g] PCA is pyrazine-2-carboxylic acid; for this system, which is believed to oxidize substrates via formation of hydroxyl radicals, see [1,2,10,34,35,90–93].

[h] L is 1,4,7-trimethyl-1,4,7-triazacyclononane; for this system which is believed to oxidize substrates without participation of free radicals (though the formation of radicals in the course of the reaction is assumed), see [2,10,34,35,94–98].

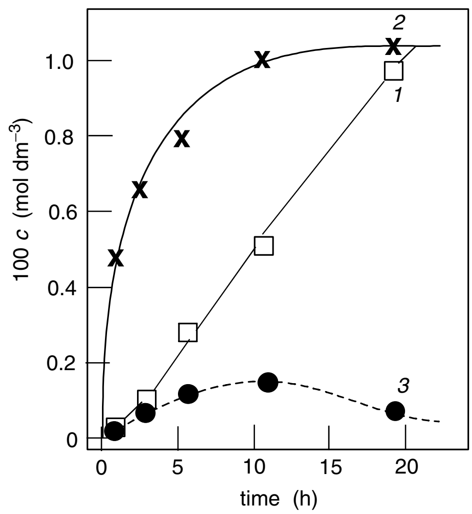


Fig. 5. Accumulation of oxygenates (concentrations, *c*, of cyclohexanone, curve 1; cyclohexanol, curve 2; cyclohexyl hydroperoxide, curve 3, are given) in the cyclohexane (initial concentration 0.92 mol dm^{-3}) oxidation with TBHP (0.78 mol dm^{-3}) catalyzed by **1** (1×10^{-3} mol dm^{-3}). Conditions: solvent MeCN; homogeneous solution at 60 °C.

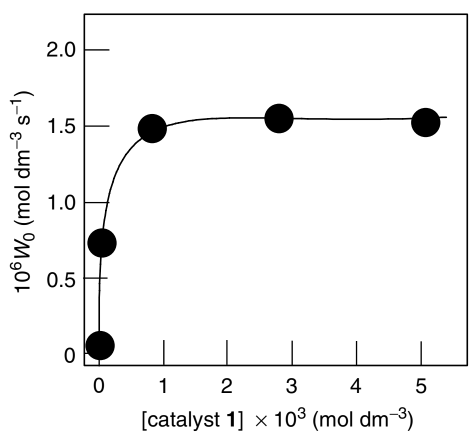


Fig. 6. Dependence of the initial rate of cyclohexane oxidation with TBHP on the initial concentration of **1**. Conditions: cyclohexane, 0.925 mol dm^{-3}; TBHP, 0.78 mol dm^{-3}; solvent MeCN; 60 °C.

hydroperoxide) in the cyclohexane (0.46 mol dm^{-3}) oxidation (MCPBA, 1.16 mol dm^{-3}, **1**, 1×10^{-3} mol dm^{-3}; MeCN; 25 °C) attained 0.037 mol dm^{-3} after 72 h which corresponds to TON = 37. The oxidation under the same conditions in the absence of **1** gave only 0.0017 mol dm^{-3} products. The TON can be enhanced (up to 80 after 48 h) using lower concentration of **1** (1×10^{-4} mol dm^{-3}). The initial rate of oxygenate accumulation is proportional to the concentration of catalyst **1** (Fig. 7). It is interesting that order of the reaction in respect to MCPBA is higher than unity (Fig. 8). First order has been found for substrate at $[\text{cyclohexane}]_0 < 0.5$ mol dm^{-3}, whereas the initial reaction rate does not depend on the hydrocarbon concentration at its higher concentration (Fig. 9).

Selectivity parameters in the Os-catalyzed oxidation with MCPBA are much higher (Table 3, entry 3) than those

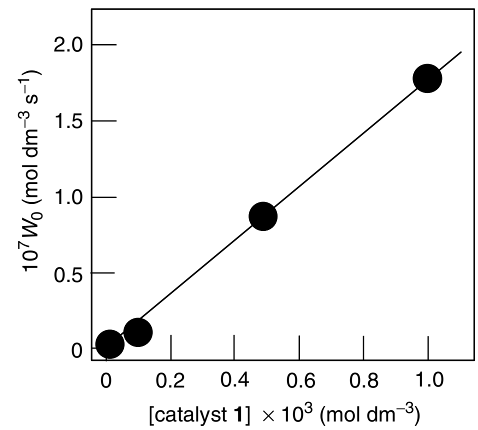


Fig. 7. Dependence of the initial rate of cyclohexane oxidation with MCPBA on the initial concentration of **1**. Conditions: cyclohexane, 0.46 mol dm^{-3}; MCPBA, 1.74 mol dm^{-3}; solvent MeCN; 25 °C.

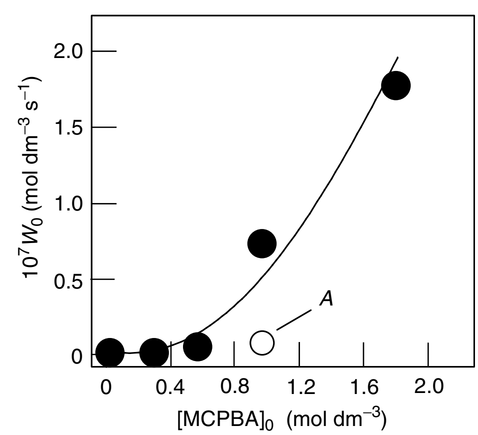


Fig. 8. Dependence of the initial rate of cyclohexane oxidation with MCPBA on the initial concentration of MCPBA. Conditions: cyclohexane, 0.46 mol dm^{-3}; **1**, 1×10^{-3} mol dm^{-3}; solvent MeCN; 25 °C. *A*: an experiment without **1**.

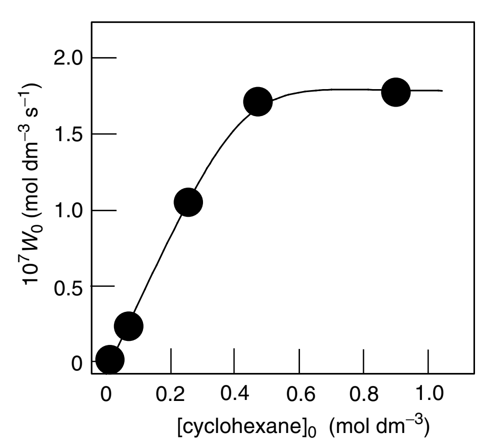


Fig. 9. Dependence of the initial rate of cyclohexane oxidation with MCPBA on the initial concentration of cyclohexane. Conditions: MCPBA, 1.74 mol dm^{-3}; **1**, 10^{-3} mol dm^{-3}; solvent MeCN; 25 °C.

for the oxidations with H_2O_2 and TBHP. These parameters are very close to the parameters obtained (Table 3, entry 4) for much less efficient (see Fig. 8) non-catalyzed oxidation with MCPBA. The catalyzed oxidation of disubstituted cyclohexanes occurs with partial retention of configuration (the *trans*/*cis* parameter was found to equal 0.5; see Table 3). It is clear that in the case of MCPBA the oxidation does not include free radicals as reactive intermediates.

3. Conclusions

In this work, we describe for the first time that a low-valent organometallic osmium complex is a very powerful generator of hydroxyl radicals from hydrogen peroxide and can be used as a catalyst in H_2O_2-oxygenations of saturated and aromatic hydrocarbons. This catalyst is much more efficient than any derivative of iron (an analogue of osmium in the Periodic System).

4. Experimental

The oxidations of hydrocarbons were carried out in MeCN in air in thermostated 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), TBHP (70% aqueous) or MCPBA (“Fluka”) was added to the solution of the catalyst and substrate. After certain time intervals samples (about 0.2 mL) were taken. In order to determine concentrations of all cycloalkane (cyclohexane or cyclooctane) oxidation products the samples of reaction solutions were analyzed twice (before and after their treatment with PPh_3) by GC (Chromatograph-3700, fused silica capillary column FFAP/OV-101 20/80 w/w, 30 m × 0.2 mm × 0.3 μm; helium as a carrier gas) measuring concentrations of cycloalkanol and cycloalkanone. Oxidations of other hydrocarbons were carried out analogously. Authentic samples of all oxygenated products were used to attribute the peaks in chromatograms (comparison of retention times was carried out for different regimes of GC-analysis). The reaction of MeCN with water in the presence of osmium derivatives can give some amount of acetamide [101]. Concentrations of products obtained in the oxidation of benzene and ethylbenzene were measured using ^1H NMR method (solutions in acetone-d_6; “Bruker AMX-400” instrument, 400 MHz). To demonstrate the role of atmospheric oxygen in the process, two experiments on the oxidation of ethylbenzene were carried out under identical conditions but in different atmospheres. In the first experiment, a slow stream of argon was passed through the reaction solution during 1 h prior addition of hydrogen peroxide and heating the solution at 70 °C. In the parallel experiment, a stream of air was used instead of argon. In both cases, the reaction mixtures were treated with sodium boron hydride and the products were determined by ^1H NMR method. It turned out that in the experiment under air ethylbenzene was converted mainly into 1-phenylethanol with conversion ca. 40%. Only traces of 1-phenyl alcohol were found in the experiment under argon atmosphere.

Complex **1** was prepared in accordance with the method described previously [83]. Carbonyl cluster containing acetonitrile ligand, $Os_3(CO)_{11}(MeCN)$ (**2**) was synthesized [102] starting from $Os_3(CO)_{12}$ (0.407 g, 0.45 mmol). A solution of **2** and *trans*-1,4-diphenylbut-2-en-1,4-dione (0.953 g, 0.40 mmol) in hexane (150 mL) was heated under reflux during 22 h. After evaporation of the solvent in vacuum and chromatography (silica gel, eluent hexane–chloroform 1:1), complex **1** was isolated (yield 0.374 g, 81%) as a yellow solid, m.p. 160 °C (with decomposition). The compound was characterized by elemental analysis, ^1H and ^{13}C NMR, IR spectra and X-ray analysis [83].

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