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Oxidation of hydrocarbons with H_2O_2/O_2 catalyzed by osmium complexes containing *p*-cymene ligands in acetonitrile†

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The soluble osmium complexes containing *p*-cymene (π-*p*-cym) ligands, $[(\eta^6\text{-}p\text{-cym})OsCl_2]_2$ (**1**), $[(\eta^6\text{-}p\text{-cym})Os(bipy)Cl]PF_6$ (**2**), and $[(\eta^6\text{-}p\text{-cym})_2Os_2(\mu\text{-}H)_3]PF_6$ (**3**), are efficient catalysts for the oxidation of alkanes (cyclohexane, *n*-heptane, methylcyclohexane, isooctane, and *cis*- and *trans*-1,2-dimethylcyclohexane) with hydrogen peroxide in air to the corresponding alkyl hydroperoxides in acetonitrile solution if a small amount of pyridine is present in the solution. The binuclear complex **1** is the most active precatalyst in the oxidation whereas compound **2** containing the bipyridine ligand is much less efficient. The oxidation of cyclohexane at 60 °C and low concentration $[\mathbf{1}]_0 = 10^{-7}$ M gave a turnover number (TON) of 200 200 after 24 h. A study of the selectivity parameters in the oxidation of linear and branched alkanes and the kinetic peculiarities of the cyclohexane oxidation led to the conclusion that the main reaction mechanism includes the formation of hydroxyl radicals. The effective activation energy E_a for the cyclohexane oxidation catalyzed by complex **1** was 10 ± 2 kcal mol^{-1}. A kinetic analysis verified also that monomerization of complex **1** occurs before the oxidizing species is involved in the catalytic cycle. The **1**-catalyzed reaction of cyclohexane, $c\text{-}C_6H_{12}$, with $H_2{}^{16}O_2$ in an atmosphere of $^{18}O_2$ gave labeled cyclohexyl hydroperoxide, $c\text{-}C_6H_{11}\text{–}{}^{18}O\text{–}{}^{18}OH$. In addition, a small amount of "light" cyclohexanone, $c\text{-}C_6H_{10}{=}{}^{16}O$, is produced apparently *via* a mechanism which includes neither hydroxyl radicals nor incorporation of molecular oxygen from the atmosphere. The oxidation of benzene with $H_2{}^{16}O_2$ under $^{18}O_2$ gave phenol which did not contain the ^{18}O isotope. The reactions with cyclohexane and benzene were shown to proceed also *via* an alternative minor mechanism with oxo derivatives of high-valent osmium "Os=O" as key oxidizing species.

1. Introduction

In recent decades, many soluble derivatives of transition metals were reported as efficient catalysts for oxidation of organic compounds and particularly of hydrocarbons with molecular oxygen and peroxides.[1] In contrast to complexes of iron, manganese or copper, much fewer publications have been devoted to osmium compounds as catalysts. Although soluble osmium complexes are known to catalyze some organic reactions,[2a] for example, alkylation,[2b] dihydroxylation,[2c,d] oxyamination,[2e] hydrogenation,[2f] alcohol dehydrogenation,[2g] cyclization,[2h,i] oxidative cleavage of olefins,[2j] hydrophenylation of ethylene,[2k] carbonylation of methanol,[2l] and oxidation of C–H compounds with various oxidants,[2m–o] including photochemical coupling of arenes[2p] and oxygenation of alkanes catalyzed by osmium chlorides,[2q] only a few examples of hydrocarbon oxidation with peroxides have been reported.[2r,s]

Previously, some of us demonstrated that simple osmium salts ($OsCl_3$, Na_2OsCl_6) are good catalysts for the oxidation of alkanes and some other organic compounds with hydrogen peroxide.[3a,b] The oxidation of cycloheptane in MeCN with H_2O_2 in air in the presence of $OsCl_3$ (1.0×10^{-3} M) gave cycloheptanol and cycloheptanone, and the total turnover number (TON) after 3 h was 63. A comparison of the chromatograms of the reaction samples before and after their treatment with PPh_3 (see below, section 2.2) demonstrated that concentrations of alkyl hydroperoxides were very low. Thus, under these conditions all of the cycloheptyl hydroperoxide

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† Electronic supplementary information (ESI) is available: Additional details of results and discussion. Data on oxidations of linear, branched and cyclic alkanes: regio-, bond-, and stereo-selectivity parameters. Details of kinetic experiments. Details of chromato-mass experiments with $^{18}O_2$. See DOI: 10.1039/c4cy00492b

decomposed in the course of the oxidation reaction. Addition of a small amount of pyridine led to a noticeable increase in the yield and to the predominant formation of the ketone (after 90 min TON was 112). The $OsCl_3$ salt catalyzes the oxidation of alcohols. Thus, the oxidation of 2-cyanoethanol with hydrogen peroxide produces the corresponding aldehyde and acid in a yield of up to 90% and a TON of up to 1500.[3c,d] Introduction of a π-coordinated olefin to a carbonyl osmium(0) complex led to noticeable enhancement of activity: the olefin complex (2,3-η-1,4-diphenylbut-2-en-1,4-dione)undecacarbonyl triangulotriosmium efficiently catalyzed the alkane oxidation with hydrogen peroxide (TONs were up to 2400).[3e,f] It turned out that addition of pyridine improved the oxidation reactions. Thus, in the alkane oxidation osmium carbonyl $Os_3(CO)_{12}$ exhibited[3g,h] a very high TON (60 000). The carbonyl hydride $Os_3(CO)_{10}(\mu\text{-H})_2$ with a similar structure was less efficient (TON was 1400).[3i] A high activity calculated per one metal ion (TON = 51 000, TOF = 6000 h^{-1}) was shown by decamethylosmocene $Cp_2{}^*Os$ as the catalyst.[3j] In the present work, we studied some *p*-cymene osmium complexes and found that they are very efficient catalysts for hydrocarbon oxidation with hydrogen peroxide exhibiting TON values much higher than those reported so far for complexes of other metals (recently, high TONs have been reported for the metalloporphyrine-catalyzed cyclohexane oxidation with molecular oxygen,[3k] although this reaction probably proceeds at 155 °C *via* a classical radical chain mechanism). This publication is part 5 from the series "Oxidation reactions catalyzed by osmium compounds"; for part 4, see ref. 3*h*.

2. Experimental section

2.1. Synthesis of catalysts

The ^1H NMR spectra were recorded using a Bruker AMX-400 spectrometer (400.13 MHz) relative to residual signals of the solvent (for the spectra, see Fig. S1, S2†). Complex $[(\eta^6\text{-}p\text{-cym})_2Os_2(\mu\text{-H})_3]PF_6$ was prepared by a known procedure.[4a] Compounds $[(\eta^6\text{-}p\text{-cym})Os(bipy)Cl]PF_6$ (ref. 4*b*) and $[(\eta^6\text{-}p\text{-cym})OsCl_2]_2$ (ref. 4*c*,*d*) were synthesized by substantially modified methods.

$[(\eta^6\text{-}p\text{-cym})OsCl_2]_2$. A heavy-walled microwave vessel containing Na_2OsCl_6 (635 mg, 1.41 mmol), 3 mL of γ-terpinene, 8 mL of EtOH (96%) and a stirring bar was filled (bubbled through the solution) with argon, sealed and placed into a microwave reactor. The mixture was allowed to react for 4 h at 100 °C and a maximum power of 200 W. The reaction mixture was cooled to room temperature and left at ~20 °C overnight. The orange precipitate was filtered off and washed successively with EtOH, water, EtOH and diethyl ether. After drying in air the yield was 417 mg (75%) of the product as orange crystals. The reaction mixture after filtration and washing with EtOH (water washes were not added!) was evaporated under reduced pressure, and the residue was washed with diethyl ether and crystallized from EtOH/diethyl ether. That gave an additional 104 mg (19%) of the product.

$[(\eta^6\text{-}p\text{-cym})Os(bipy)Cl]PF_6$. A solution of 2,2′-bipyridine (24 mg, 0.15 mmol) and $[(\eta^6\text{-}p\text{-cym})OsCl_2]_2$ (49.5 mg, 0.063 mmol) in 2 mL of methanol was stirred for 24 h at ambient temperature. Then a solution of KPF_6 (100 mg, 4.3 mol equiv.) in 10 mL of water was added. The reaction mixture was extracted with CH_2Cl_2, extracts were dried with anhydrous Na_2SO_4 and the solvent volume was reduced to ~3 mL under reduced pressure. After addition of diethyl ether to the CH_2Cl_2 solution the product precipitated as a yellow crystalline powder which was filtered off, washed with diethyl ether and dried. Yield: 79.5 mg (96%).

2.2. Oxidation experiments

The catalysts and the co-catalyst (pyridine) were used in the form of stock solutions in acetonitrile. (**CAUTION**: osmium derivatives are toxic and all experiments should be carried out in a hood.) Aliquots of these solutions were added to the reaction mixtures in the oxidations of alkanes. The oxidation reactions were typically carried out in air in thermostated Pyrex cylindrical vessels with vigorous stirring; the total volume of the reaction solution was 5 mL. (**CAUTION**: the combination of air or molecular oxygen and H_2O_2 with organic compounds at elevated temperatures may be explosive!). The reactions were stopped by cooling and analyzed twice, *i.e.*, before and after addition of an excess solid PPh_3. This method was developed and used previously by Shul'pin[3g,i,5] for the analysis of reaction mixtures obtained from various alkane oxidations and was used in recent years by other chemists.[6] In the meantime some scientists continue to measure concentrations of alcohols and ketones by injecting the samples directly to the chromatograph although this does not give any valuable information about the existence or non-existence of alkyl hydroperoxides in the reaction solution. Applying in the present work for the oxidation of cyclohexane the comparison of chromatograms before and after reduction with PPh_3 we demonstrate that the reaction affords predominantly cyclohexyl hydroperoxide as a primary product. The hydroperoxide only slowly decomposes to form cyclohexanol and cyclohexanone. In our kinetic studies for precise determination of oxygenate concentrations only the data obtained after reduction of the reaction sample with PPh_3 were used.

A Fisons Instruments GC 8000 series gas chromatograph with a capillary column (30 m × 0.32 mm × 25 μm, DB-WAX (J&W)) and a Perkin-Elmer Clarus 600 gas chromatograph, equipped with a Perkin-Elmer Clarus 600 C mass spectrometer (electron impact), with a BPX5 capillary column (SGE) (helium was the carrier gas; the internal standard was nitromethane) were used. In the kinetic experiments each oxidation was carried out at least twice and the average value is shown in the corresponding figure. The experimental error was 10%. The concentration of H_2O_2 in the course of the oxidation reactions was determined by the Ti(IV) reagent.

2.3. Experiments with $^{18}O_2$

A Perkin-Elmer Clarus 600 C mass spectrometer (electron impact) equipped with two capillary columns (SGE BPX5; 30 m × 0.32 mm × 25 μm), one with an EI-MS detector and the other one a FID detector, was used for analyses of the reaction mixtures. Helium was used as the carrier gas. All EI mass spectra were taken with 70 eV energy.

Labeled dioxygen (99% of ^{18}O) was purchased from CortecNet. Freshly prepared catalytic reaction mixtures contained in Schlenk flasks were frozen with liquid nitrogen, pumped and filled with N_2 a few times in order to remove air. Then the cooled mixtures were pumped again, the vacuum pump was turned off, and the evacuated mixtures were heated up to 20 °C and immediately filled with $^{18}O_2$ gas with a syringe through a septum. The mixtures were then heated up to 60 °C with a possibility of gas flow to compensate for excessive pressure. The ^{16}O and ^{18}O compositions of the oxygenated products were determined by the relative abundances of mass peaks at m/z = 57/59 (for cyclohexanol), 98/100 (for cyclohexanone) and 94/96 (for phenol), unless stated otherwise.

3. Results and discussion

In this work, we used for the first time *p*-cymene complexes of osmium, the binuclear **1** and **3** and the mononuclear complex **2** (Scheme 1).

3.1. Synthesis of catalysts

A few publications which describe the synthesis of the compound $[(\eta^6\text{-}p\text{-cym})OsCl_2]_2$ are known. All methods comprise interaction of α-phellandrene [2-methyl-5-(l-methylethyl)cyclohexa-1,3-diene] with $OsCl_3{\cdot}3H_2O$ (ref. 7) or Na_2OsCl_6 (ref. 4*c*) in ethanol. Reaction of Na_2OsCl_6 with α-phellandrene proceeds slowly and requires prolong refluxing (100 h). Very recently, the benzene analog $[(\eta^6\text{-benzene})OsCl_2]_2$ was synthesized from Na_2OsCl_6 in excellent yield and low reaction time using microwave oven heating.[4d] We applied this approach in the synthesis of the complex $[(\eta^6\text{-}p\text{-cym})OsCl_2]_2$. The reaction of Na_2OsCl_6 with γ-terpinene [2-methyl-5-(l-methylethyl)cyclohexa-1,4-diene] in ethanol solution and microwave heating allowed us to obtain complex **1** in 94% yield after only 4 h. Complex **2** was synthesized by a known method[4b] using a modified set up of the reaction mixture. This modification provides complex **2** in almost quantitative yield. Complex **3** was synthesized by a procedure described in ref. 4*a*.

3.2. Main features of alkane oxidation

We have found that the *p*-cymene compounds **1**, **2**, and **3** catalyze the oxidation of cyclohexane with H_2O_2/O_2 in acetonitrile at 60 °C. Addition of a small amount of pyridine improves the reaction. As demonstrated by a comparison of chromatograms obtained before and after the reduction of the samples with PPh_3 (for this method, see section 2.2 and ref. 3*g*,*i*,5), cyclohexyl hydroperoxide is the main primary product (the sole product at the initial period of the reaction) which only slowly decomposes partly in the course of the oxidation reaction to afford small amounts of cyclohexanol and cyclohexanone. For precise determination of oxygenate concentrations, we used only the data obtained after reduction of the reaction sample with PPh_3. Accumulation of products in the cyclohexane oxidation catalyzed by compounds **1**, **2**, and **3** is shown in Fig. 1. The maximum initial rates W_0 were measured from the slopes of tangents (dotted straight lines) to the kinetic curves of oxygenate accumulation. It can be

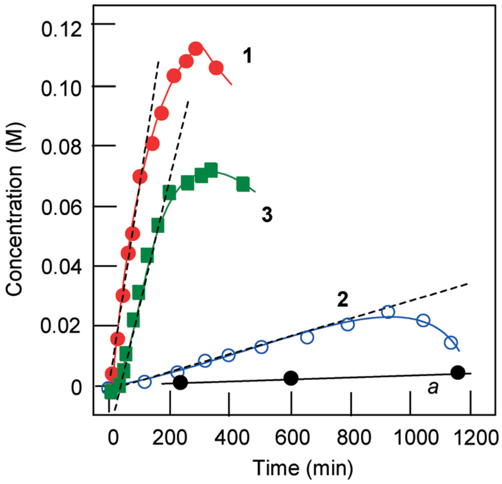
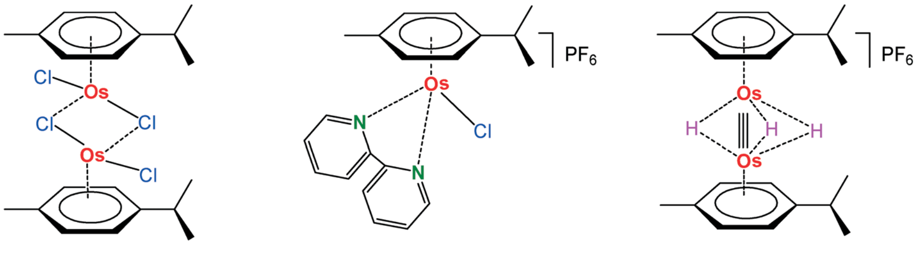


Fig. 1 Accumulation of the sum of oxygenates (predominantly cyclohexyl hydroperoxide) with time in the cyclohexane oxidation with H_2O_2 in air catalyzed by complexes **1**, **2** and **3** in the presence of pyridine in acetonitrile. Curve *a*: in the absence of any catalyst. The maximum initial rates W_0 were measured from the slopes of tangents (dotted straight lines) to the kinetic curves of oxygenate accumulation. Conditions: $[\text{catalyst}]_0 = 1 \times 10^{-5}$ M, [py] = 0.05 M, $[\text{cyclohexane}]_0$ = 0.46 M, $[H_2O_2]_0$ = 2.2 M, $[H_2O]_{\text{total}}$ = 4.15 M, 60 °C. The concentrations were measured as a sum of cyclohexanol and cyclohexanone after reduction of the reaction sample with PPh_3.



1 **2** **3**

Scheme 1 Complexes used as catalysts.

clearly seen that complex **1** exhibits the highest oxidation rate and highest yield of products. Compound **3** is insignificantly less efficient whereas the activity of complex **2** is noticeably lower. In almost all further experiments we used the most active compound **1** as the catalyst.

As shown in Fig. 2 at $[\text{cyclohexane}]_0$ = 0.46 M and $[H_2O_2]_0$ = 0.35 M the oxidation stops after 500 min. Nevertheless, when new portions of the alkane and hydrogen peroxide are added the reaction begins again with the same rate (curve 1). A similar situation was noticed when only a new portion of H_2O_2 (without cyclohexane) was introduced into the reaction solution (curve 2). This clearly testifies that an Os-containing catalytically active species is not destroyed during the oxidation reaction.

We have also studied the dependences of the initial oxidation rates on initial concentrations of the reactants: catalyst **1** (Fig. 3A), pyridine (Fig. 4A), hydrogen peroxide (Fig. 5), water (Fig. 6), and cyclohexane (Fig. 7A). Kinetic analysis of these data (see below, section 3.5) led to the results shown in insets B for the figures. We also measured the initial reaction rates at different temperatures and evaluated the effective activation energy E_a = 10 ± 2 kcal mol^{-1} (see Fig. S8; see also Fig. S9† for original kinetic curves).

We found that benzene can also be oxidized to phenol with H_2O_2 if complex **1** and pyridine are used as components of the catalytic system (Fig. 8, curve 3). It turned surprisingly out that addition of benzene to the solution containing cyclohexane does not affect the rate of cyclohexane oxidation (compare curves 1 and 2 in Fig. 8; see also Fig. S10;† a discussion of this phenomenon is presented below, in section 3.5).

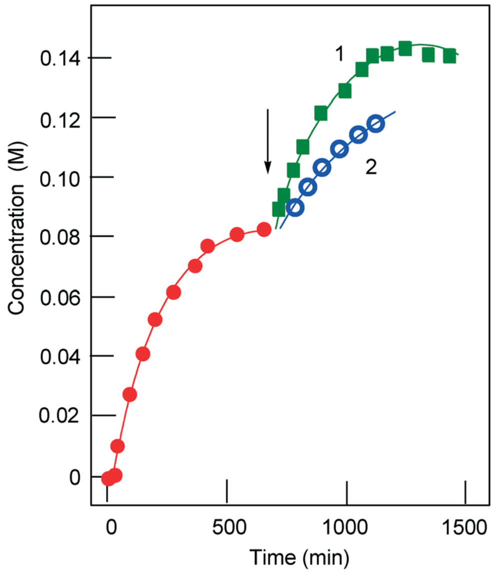


Fig. 2 Accumulation of the sum of oxygenates (predominantly cyclohexyl hydroperoxide) with time in the cyclohexane oxidation with H_2O_2 catalyzed by complex **1** in acetonitrile in air. Conditions: $[\text{catalyst}]_0 = 5 \times 10^{-5}$ M, [py] = 0.1 M, $[\text{cyclohexane}]_0$ = 0.46 M, $[H_2O_2]_0$ = 0.35 M, $[H_2O]_{\text{total}}$ = 0.67 M, 60 °C. At the time denoted by an arrow, new portions of cyclohexane (0.46 M) and H_2O_2 (0.35 M) were simultaneously added to the reaction mixture (curve 1) or a new portion of only hydrogen peroxide was added (curve 2). The concentrations were measured as the sum of cyclohexanol and cyclohexanone after reduction of the reaction sample with PPh_3.

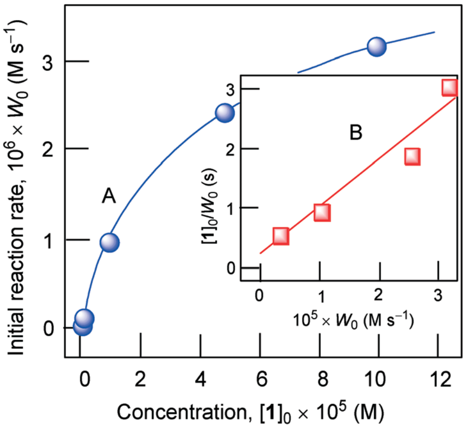


Fig. 3 Graph A: dependence of initial rate W_0 of the cyclohexane oxidation with H_2O_2/O_2 catalyzed by complex **1** on its concentration. Conditions: [py] = 0.05 M, $[\text{cyclohexane}]_0$ = 0.46 M, $[H_2O_2]_0$ = 2.2 M, $[H_2O]_{\text{total}}$ = 4.15 M, 60 °C. For the original kinetic curves obtained at various concentrations of **1**, see Fig. S3.† Graph B: dependence of $[\mathbf{1}]_0/W_0$ on W_0 which is a straight line in accordance with eqn (11).

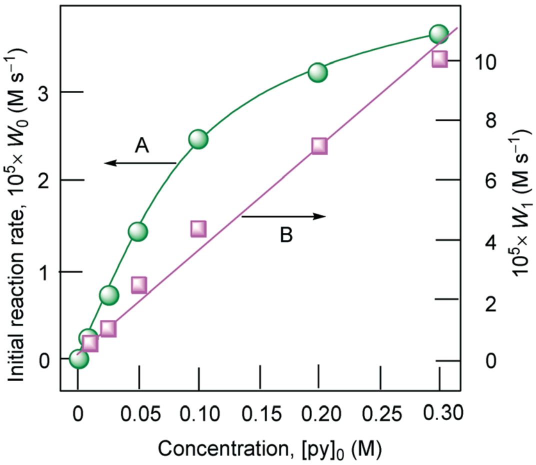


Fig. 4 Curve A: dependence of initial rate W_0 of the cyclohexane oxidation with H_2O_2/O_2 catalyzed by complex **1** on concentration of added pyridine. Conditions: $[\mathbf{1}]_0 = 5 \times 10^{-5}$ M, $[\text{cyclohexane}]_0$ = 0.46 M, $[H_2O_2]_0$ = 1.1 M, $[H_2O]_{\text{total}}$ = 2.1 M, 60 °C. For the original kinetic curves obtained at various concentrations of pyridine, see Fig. S4.† Line B: dependence of W_1 on $[\text{py}]_0$ calculated by taking into account the "inhibiting" effect of pyridine in accordance with eqn (5) and (6).

3.3. Turnover numbers in the oxidation catalyzed by Os complexes

Under similar conditions (concentration of the catalyst was 5×10^{-5} M) the TON[8] values for compounds **1**, **2**, and **3** after 5.5 h were 11 100, 980, and 7500, respectively. At a very low concentration of the catalyst **1** (1×10^{-7} M; entry 1 in Table S1;† see also Fig. 9) the TON (after subtracting the concentration of products formed in the reaction in the absence of **1**) was 200 200. The reaction catalyzed by **1** proceeds in 24% yield based on starting cyclohexane (see Fig. 1, curve for

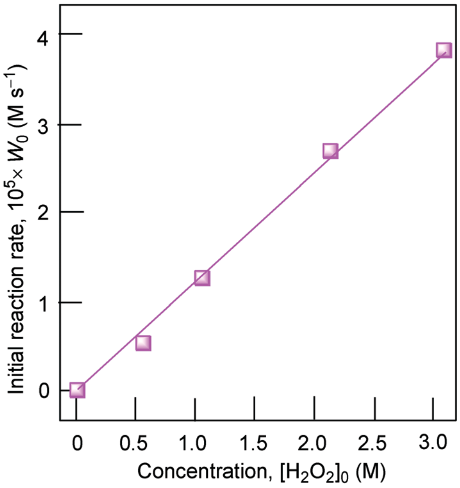


Fig. 5 Dependence of initial rate W_0 of the cyclohexane oxidation with H_2O_2/O_2 catalyzed by complex **1** on initial concentration of H_2O_2. Conditions: $[\mathbf{1}]_0 = 5 \times 10^{-5}$ M, [py] = 0.05 M, $[\text{cyclohexane}]_0 = 0.46$ M, $[H_2O]_{\text{total}}$ = const = 5.9 M, 60 °C. For the original kinetic curves obtained at various concentrations of pyridine, see Fig. S5.†

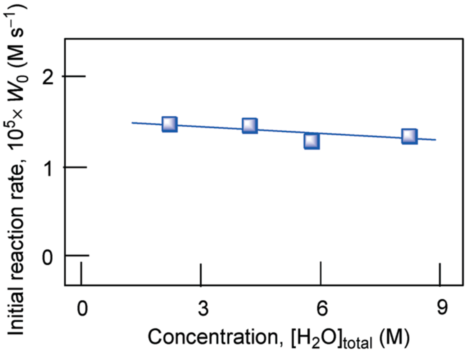


Fig. 6 Dependence of initial rate W_0 of the cyclohexane oxidation with H_2O_2/O_2 catalyzed by complex **1** on total concentration of water. Conditions: $[\mathbf{1}]_0 = 5 \times 10^{-5}$ M, [py] = 0.05 M, $[H_2O_2]_0 = 1.1$ M, $[\text{cyclohexane}]_0 = 0.46$ M, 60 °C. For the original kinetic curves obtained at various concentrations of pyridine, see Fig. S6.†

complex 1). Fig. S1b† shows that the concentration of oxygenates after 3 h reaches 0.14 M. It means that under the conditions ($[\mathbf{1}]_0 = 5 \times 10^{-5}$ M, [py] = 0.05 M, $[\text{cyclohexane}]_0 = 0.46$ M, $[H_2O_2]_0 = 2.2$ M, $[H_2O]_{\text{total}} = 4.15$ M, 60 °C.) the yield of products was 30%. It follows from Fig. 2 that the yield of oxygenates after 700 min equals 23% based on hydrogen peroxide taken in concentrations lower than the concentration of cyclohexane. Table S1† (entries 1–3) shows that osmium complexes **1**, $Os_3(CO)_{12}$ and decamethylosmocene bearing different ligands catalyze the alkane oxygenation with comparable initial reaction rates. Thus, we can conclude that the nature of ligands surrounding the osmium ion does not dramatically affect the catalyst's power. It follows also from Table S1† that the parameters of initial reaction rates W_0 per one catalytic center (calculated as TONs per one hour) attained in our studies on catalysis by osmium complexes are comparable with the parameters measured for the alkane oxidations catalyzed by various enzymes.[9]

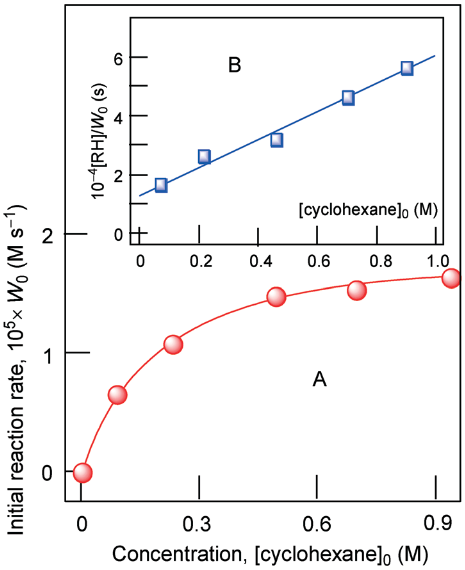


Fig. 7 Graph A: dependence of initial rate W_0 of the cyclohexane oxidation with H_2O_2/O_2 catalyzed by complex **1** on initial concentration of cyclohexane. Conditions: $[\mathbf{1}]_0 = 5 \times 10^{-5}$ M, [py] = 0.05 M, $[H_2O_2]_0 = 1.1$ M, $[H_2O]_{\text{total}} = 2.1$ M, 60 °C. For the original kinetic curves obtained at various concentrations of pyridine, see Fig. S7.† Graph B: the simulation of curve from graph A in accordance with eqn (6).

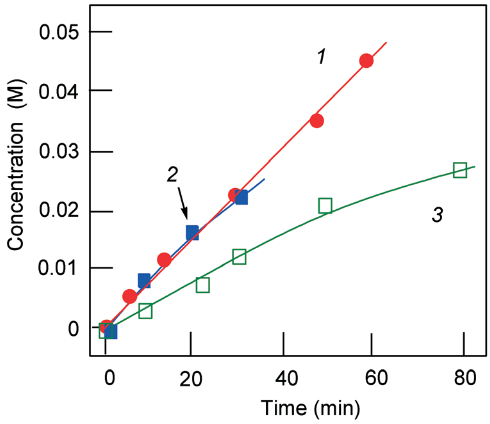


Fig. 8 Accumulation of the sum of oxygenates (cycohexanol + cyclohexanone after reduction with PPh_3) with time in the cyclohexane oxidation with H_2O_2/O_2 catalyzed by complex **1** in acetonitrile in the absence (curve 1) and in the presence of benzene (0.02 M; curve 2). Conditions: $[\mathbf{1}]_0 = 5 \times 10^{-5}$ M, [py] = 0.05 M, $[H_2O_2]_0 = 1.1$ M, $[H_2O]_{\text{total}} = 2.1$ M, $[\text{cyclohexane}]_0 = 0.46$ M, 60 °C. Curve 3: accumulation of phenol with time in benzene (0.46 M) oxidation with H_2O_2 catalyzed by complex **1** in acetonitrile under the experimental conditions shown by curves 1 and 2.

3.4. Selectivity parameters of alkane oxidation

In order to get an insight into the mechanism of oxygenation of alkane C–H bonds with H_2O_2/O_2 catalyzed by the osmium complexes we studied the oxidation of some assay alkanes in the presence of compound **1** and pyridine. The value of the regioselectivity parameter for *n*-octane oxidation with the **1**/py/H_2O_2 system was based on the distribution of isomeric alcohols. The oxidation gave (after reduction with PPh_3) the

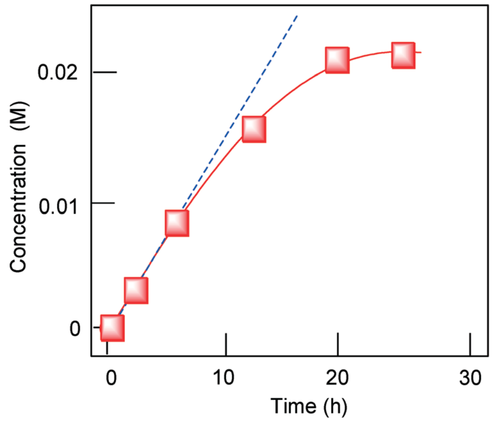


Fig. 9 Accumulation of the sum of oxygenates (predominantly cyclohexyl hydroperoxide) with time in the cyclohexane oxidation with H_2O_2/O_2 catalyzed by complex **1** in acetonitrile. The maximum initial rate was measured from the slopes of tangents of dotted straight lines to the kinetic curves of oxygenate accumulation. Conditions: $[\mathbf{1}]_0 = 1 \times 10^{-7}$ M, [py] = 0.05 M, $[\text{cyclohexane}]_0 = 0.97$ M, $[H_2O_2]_0 = 2.2$ M, $[H_2O]_{\text{total}} = 4.15$ M, 60 °C. The concentrations were measured as a sum of cyclohexanol and cyclohexanone after reduction of the reaction sample with PPh_3.

following alcohols (*M*): octanol-1 (0.0005), octanol-2 (0.0014), octanol-3 (0.0014), and octanol-4 (0.0013). This corresponds to the selectivity parameter C(1) : C(2) : C(3) : C(4) = 1 : 2.8 : 2.8 : 2.6. This parameter is low and comparable with the corresponding values for some other systems[10] which oxidize with hydroxyl radicals: the oxidation by hydrogen peroxide in air under UV irradiation or in the presence of an Fe(II) salt (the Fenton's reagent) and the oxidation by the H_2O_2/VO_3^-/PCA and the $H_2O_2/VO_3^-/H^+$ systems. A chromatogram obtained for the products of the methylcyclohexane oxidation is shown in Fig. S11.† The selectivity parameter based on concentrations of alcohols 1° : 2° : 3° equals 1 : 5.2 : 13.8 which is typical for the oxidation with hydroxyl radicals. The oxidation with the $\mathbf{1}/H_2O_2$ system of *cis*-1,2-DMCH and *trans*-1,2-DMCH (where DMCH is dimethylcyclohexane) proceeds non-stereoselectively. Parameter *trans*/*cis* for the oxidation of *cis*-1,2-DMCH was 0.84 and for *trans*-1,2-DMCH it was 0.88. Thus, we can conclude that selectivity parameters testify that in the main pathway alkanes are oxidized by the system under discussion with hydroxyl radicals.

3.5. Kinetic analysis of the alkane oxidation

The kinetic analysis of the liquid-phase alkane (RH) oxidation initiated with such reactive radicals as hydroxyl or alkoxyl at low temperatures shows that this process is possible to some extent *via* a classical radical-chain mechanism only in the case of RH having weak C–H bonds (for example, tetralin, decalin, cumene). This mechanism involves the reaction $RH + ROO^{\cdot} \rightarrow R^{\cdot} + ROOH$ as a key step. Indeed, if the 10% conversion time at 100 °C for tetralin and cumene is only 0.2 h, the same parameter for cyclohexane and methane is 6.5 and 30 days, respectively. The time necessary for 10% methane conversion at 30 °C with involvement solely of a radical-chain mechanism has been estimated to be 22 000 years.

The data described in section 3.4 are in good agreement with an assumption that the main route of the alkane oxidation proceeds with the formation of hydroxyl radicals. Additional support is obtained from the measurement of the kinetic isotope effect (KIE = k_H/k_D = 1.25 for **1** at 60 °C) and experiments with addition of CCl_3Br (in this case bromocyclohexane was found after reduction with PPh_3 instead of cyclohexanol and cyclohexanone).

This reaction pathway is also in agreement with the kinetic data obtained in the present study. Thus, we have found that addition of cyclohexane, CyH or RH, into the reaction solution does not affect the hydrogen peroxide decomposition rate, whereas the rate $W_0 = d[ROOH]/dt$ of cyclohexyl hydroperoxide, ROOH, formation increases with increasing $[CyH]_0$ (Fig. 7A). This testifies that: (i) cyclohexane does not affect the catalyst reactivity, because it does not, *inter alia*, form any adduct with the catalytically active species; (ii) the oxidation of CyH is induced by an intermediate species X of the oxidative nature which is generated in the process of hydrogen peroxide decomposition; and (iii) the interaction between CyH and X is only one of a few pathways leading to the consumption of species X (contribution of this canal grows with growing the initial concentration of hydrocarbon RH). Based on this statement we can consider the following kinetic scheme of the competitive interaction of RH with species X:

$$\text{Reactants} \rightarrow \text{X} \tag{1}$$

$$\text{X} + \text{RH} \rightarrow \text{R}^{\cdot} \xrightarrow{O_2, e^-, /H^+} \text{ROOH} \tag{2}$$

$$\text{X} + \text{L}_i \rightarrow \ldots \rightarrow \text{products} \tag{3}$$

Here reaction (1) is a stage of the oxidative species X generation in the catalytic process of H_2O_2 decomposition with rate W_1; (2) is the sequence of transformations of RH into ROOH with the rate limiting step of interaction between X and RH (this step is characterized by a bimolecular rate constant k_2); (3) is the interaction of species X with various reactants present in the reaction mixture L_i. Reactants L_i compete with hydrocarbon RH for the oxidizing species X, and the limiting steps of these competitions are characterized by bimolecular rate constants $k_3(L_i)$.

Using the method of quasi-stationary concentrations relative to the intermediate X_i we can deduce the following expression:

$$W_1 = \left(k_2[\text{RH}]_0 + \sum_i k_3(\text{L}_i)[\text{L}_i] \right)[\text{X}] \tag{4}$$

where $\sum_i k_3(\text{L}_i)[\text{L}_i][\text{X}]$ is the sum of all possible reactions of the X consumption excluding the interaction of X with RH.

In this case we come to the following equation:

$$-\frac{\mathrm{d}[\mathrm{RH}]}{\mathrm{d}t}=\frac{\mathrm{d}[\mathrm{ROOH}]}{\mathrm{d}t}=\frac{W_1 k_2[\mathrm{RH}]_0}{k_2[\mathrm{RH}]_0+\sum_i k_3(\mathrm{L}_i)[\mathrm{L}_i]} \tag{5}$$

This equation can be presented in the form:

$$\frac{[\mathrm{RH}]_0}{\frac{\mathrm{d}[\mathrm{ROOH}]}{\mathrm{d}t}}=\frac{1}{W_1}\left\{[\mathrm{RH}]_0+\frac{1}{k_2}\sum_i k_3(\mathrm{L_i})[\mathrm{L}_i]\right\} \tag{6}$$

The experimental data given in Fig. 7 are in agreement with eqn (6). Indeed, the value $[\mathrm{RH}]_0/(\mathrm{d}[\mathrm{ROOH}]/\mathrm{d}t)$ linearly depends on $[\mathrm{RH}]_0$ as shown in Fig. 7B. In accordance with eqn (6) the reciprocal tangent of the slope of the straight line in Fig. 7B corresponds to the X generation rate W_1. The ratio of a segment that is cut off on the *y*-axis to the slope tangent corresponds to the value Ψ

$$\psi=\frac{1}{k_2}\sum_i k_3(\mathrm{L}_i)[\mathrm{L}_i].$$

Under the experimental conditions presented in Fig. 7 we have

$$W_i = 2.1 \times 10^{-5}\,\mathrm{M\ s^{-1}}$$

and the parameter Ψ

$$\psi=\frac{1}{k_2}\sum_i k_3(\mathrm{L}_i)[\mathrm{L}_i]=0.27\ \mathrm{M}.$$

The latter value Ψ = 0.27 M is higher than the average values (0.15 M) obtained previously from the data for the alkane oxidation by other systems which are believed to operate with hydroxyl radicals.[10a,11a] In previously studied systems the solvent acetonitrile played the role of a competitor to RH for the hydroxyl radical. The enhanced value of parameter Ψ measured in the present work reflects the fact that pyridine in addition to acetonitrile is an efficient rival for the hydroxyl radical. In summary, we have:

$$\frac{k_3(\mathrm{MeCN})[\mathrm{MeCN}]+k_3(\mathrm{py})[\mathrm{py}]}{k_2}=0.27\ \mathrm{M}$$

and in accordance with the parameters listed in ref. 11:

$$\frac{k_3(\mathrm{MeCN})[\mathrm{MeCN}]}{k_2}=0.15\ \mathrm{M}$$

It means that at [MeCN] = 18 M and [py] = 0.05 M under the experimental conditions shown in Fig. 7 we have

$$\frac{k_3(\mathrm{py})[\mathrm{py}]}{k_2}=0.12\ \mathrm{M},\ \text{that is}\ \frac{k_3(\mathrm{py})}{k_2}=2.4$$

and

$$\frac{k_3(\mathrm{MeCN})[\mathrm{MeCN}]}{k_3(\mathrm{py})[\mathrm{py}]}=\frac{0.15\ \mathrm{M}}{0.12\ \mathrm{M}}=1.25,$$

$$\text{that is}\ \frac{k_3(\mathrm{py})}{k_3(\mathrm{MeCN})}=290$$

Both results are in satisfactory agreement with our assumption that the oxidizing species is the hydroxyl radical for which the rate constants are known from radiation-chemical, photochemical and chemical experiments (see ref. 3*g*,10*a*,11) where $k_3(\mathrm{py})/k_3(\mathrm{MeCN}) \approx 300$.

Taking into account the results discussed above we can easily find a correlation between initial rates of the ROOH formation and initial rates of the active oxidizing species generation W_1 in the decomposition of H_2O_2, as it is reflected by eqn (5) and (6). For the conditions under which we studied the dependence of $(\mathrm{d}[\mathrm{ROOH}]/\mathrm{d}t)_0$ on initial concentration of catalyst $[\mathbf{1}]_0$, $W_1 = 1.5(\mathrm{d}[\mathrm{ROOH}]/\mathrm{d}t)_0$ and W_1 does not depend on $[\mathbf{1}]_0$. Thus, dependence of W_1 on $[\mathbf{1}]_0$ is analogous to the experimental dependence shown in Fig. 3, taking, however, into account that rate values on the *Y* axis should be multiplied by 1.5. The data in Fig. 3 testify that the oxidation reaction order in pre-catalyst **1** is lower than the first order. At high $[\mathbf{1}]_0$ the reaction order is close to 0.5. Such a type of dependence of $W_0 = (\mathrm{d}[\mathrm{ROOH}]/\mathrm{d}t)_0$ (and, consequently, also of W_1) on $[\mathbf{1}]_0$ allows us to assume that a catalytically active species is a monomeric form of the osmium compound (**M**) which is produced by the dissociation of the starting dimeric form of pre-catalyst **1**:

$$\mathbf{1} \rightleftarrows 2\mathbf{M} \tag{7}$$

The dissociation constant is small and at a high value of [**1**] the degree of its dissociation is not high. Let us assume that *K* is the concentration constant of this equilibrium and *k* is the effective rate constant of the oxidizing species generation. The latter reaction is pseudo-first order for **M**. To describe the experimental dependence shown in Fig. 4A we have:

$$W_1 = k[\mathbf{M}];\ K[\mathbf{1}] = [\mathbf{M}]^2 \text{ and } [\mathbf{1}]_0 = [\mathbf{1}] + [\mathbf{M}]/2 \tag{8}$$

The following equation can be deduced from these expressions:

$$[\mathbf{1}]_0=\frac{W_1^2}{k^2K}+\frac{W_1}{2k} \tag{9}$$

Eqn (9) can be transformed into eqn (10) which is more convenient for treating the experimental results.

$$\frac{[\mathbf{1}]_0}{W_1}=\frac{W}{k^2K}+\frac{1}{2k} \tag{10}$$

Taking into account that $W_1 = 1.5W_0$ we come to eqn (11):

$$\frac{[\mathbf{1}]_0}{W_0} = \frac{2.25}{k^2K}W_0 + \frac{0.75}{k} \tag{11}$$

Treating the data shown in Fig. 3A by the least-square method applying eqn (11) leads to the conclusion that our experimental results are satisfactorily described by eqn (11) which is demonstrated by Fig. 3B. In accordance with these results we can calculate $2.25/k^2K$ to be 0.77×10^5 and $0.75/k$ to be 0.29 s. Consequently, for the conditions of our experiments $K = 4.3 \times 10^{-6}$ M and $k = 2.6$ s^{-1}.

In the reaction under consideration pyridine plays a double role. First, addition of pyridine substantially enhances the reaction rate which in its absence is very low. This effect can be due to the facilitation of the **1** monomerization that is pyridine shifts the equilibrium (7) to the reactive monomer **M**. Besides, binding the monomer with pyridine can enhance the reactivity of the monomer. We cannot exclude the simultaneous effect of both factors. Second, pyridine is a competitor of the alkane and acetonitrile for hydroxyl radicals leading, by this way, to the decrease of the RH oxidation rate (for the oxidation of acetonitrile by this system, see below, section 3.6 and Fig. S14 and S15†). The relationship of these factors governs the experimental dependence of W_0 on [py] (Fig. 4A): at low [py] this linear dependence reflects mainly the activating effect of pyridine; whereas the decrease of the reaction order at relatively high concentrations of pyridine is due to the decrease of the fraction (relative to the total amount) of hydroxyl radicals which react with RH in agreement with eqn (5). If we take into account the "inhibiting" effect of pyridine in accordance with eqn (5) and (6) it is possible to calculate the activating effect of pyridine at its different concentrations using the data in Fig. 4. This analysis shown in Fig. 4B demonstrates that in all of the studied intervals of [py] values there is a linear dependence of pyridine activation on the rate of hydroxyl radical generation.

The proposed mechanism of the cyclohexyl hydroperoxide formation is a radical one but it is not a radical-chain mechanism. Radical chain mechanism is typical for the autoxidation of alkanes.[11b]

It is well known that benzene is an efficient acceptor of hydroxyl radicals and due to this the phenol formation in the catalytic system under discussion is not surprising (Fig. 8, curve 3). The rate of phenol accumulation is low in comparison with the rate of the ROOH formation in RH oxidation. This can be explained if we assume that for the transformation of benzene to phenol the system requires two oxidative equivalents produced by the system (for example two hydroxyl radicals) whereas in the RH oxidation hydroxyl radicals provide one oxidative equivalent and the subsequent transformations of radical R$^\bullet$ occur with the participation of molecular oxygen from the atmosphere. This assumption is supported by our experiments with labeled dioxygen: molecular oxygen from the atmosphere is incorporated into ROOH but not into C_6H_5OH (see below, section 3.6).

We expected that addition of benzene as competing for the hydroxyl radical reagent would decrease the rate of RH → ROOH transformation. Surprisingly, the experimental data have demonstrated that the ROOH formation rate does not practically depend on the presence or absence of added benzene (see Fig. 8, curve 2 and Fig. 9). It is possible to assume that this unexpected result reflects the fact that radicals generated in the interaction between benzene and hydroxyl radicals react efficiently further with the alkane RH to produce radicals R$^\bullet$ which under an O_2 atmosphere are transformed into ROOH. We realize that an additional special study is required to get an insight into this intriguing phenomenon.

3.6. The oxidation under an $^{18}O_2$ atmosphere: incorporation of $^{18}O_2$ into produced cyclohexyl hydroperoxide and not into phenol

The interaction of alkyl radical with molecular oxygen is a principal step in the mechanism of oxygenation of both saturated and aromatic hydrocarbons with the participation of hydroxyl radicals ($R'R''CH^\bullet + O_2 \rightarrow R'R''CH{-}O{-}O^\bullet$). When atmospheric air in the reaction vessel is partly (some air is still present in the solution) replaced with a stream of argon the rate of oxygenate formation decreases (an example is shown in Fig. S4,† graph f, curve *A*), and this indicates that molecular oxygen takes part in the oxygenation reaction. The experiments with isotopically labeled $^{18}O_2$ are a useful mechanistic probe to test the involvement and the mode of involvement of molecular oxygen into the radical reactions. It has previously been shown that the cyclodecane oxidation under Gif conditions (Fe^{III}/Pyridine/CH_3COOH/H_2O_2) under an $^{18}O_2$ atmosphere results in a *ca.* 50% degree of ^{18}O incorporation in the cyclodecanone where the yield of ketone was *ca.* 15%. However, the yield of the corresponding alcohol (as well as some important reaction conditions) was not reported.[12a] That results clearly led to an involvement (reduction) of air/oxygen in open-air reactions and inspired us to investigate the process of such a type in more detail using the catalytic system based on osmium complex **1**.

The accumulation of labeled oxygenated products with time was studied for conditions $[\mathbf{1}]_0 = 5 \times 10^{-5}$ M and 60 °C under the atmosphere of $^{18}O_2$. The yields and isotopic abundances were measured typically after reduction of the reaction samples with PPh_3. The highest degree (66%) of ^{18}O incorporation into cyclohexanol was observed at the beginning of reaction (Fig. 10, graph A). The percentage of labeled alcohol decreases with reaction time reaching 53% of Cy–^{18}OH after 6 h. This effect can be explained by a weak catalase activity of the catalytic system which produces unlabeled oxygen $^{16}O_2$ from the hydrogen peroxide $H_2{}^{16}O_2$. One may expect the incorporation of the ^{18}O isotope into the formed triphenylphosphine oxide ($O{=}PPh_3$) *via* the following reaction scheme where the alkyl hydroperoxide is reduced to alcohol by phosphine:

$$\mathrm{Cy{-}^{18}O^{18}OH + PPh_3 \rightarrow Cy{-}^{18}OH + {}^{18}O{=}PPh_3} \tag{12}$$

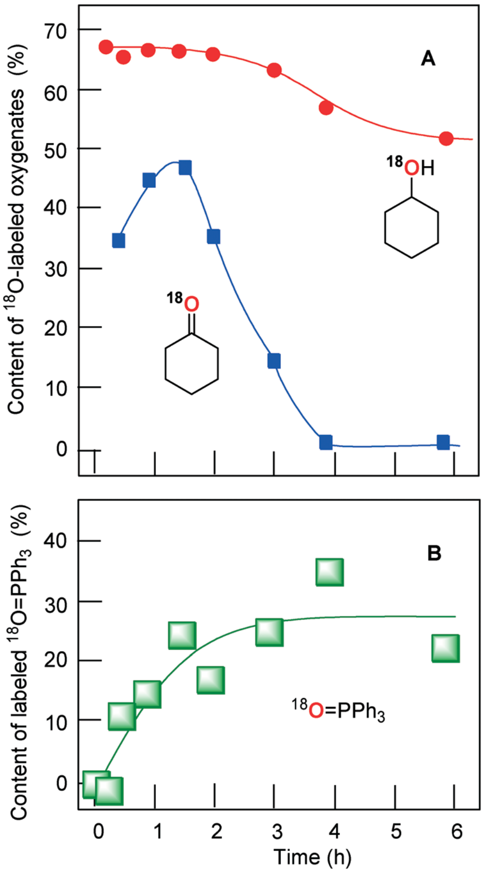


Fig. 10 Incorporation of the labeled oxygen into cyclohexanol and cyclohexanone (graph A) and triphenylphosphine oxide (graph B; squares are experimental data, solid line is an exponential fit) in the course of the cyclohexane oxidations. Conditions: $[\mathbf{1}]_0 = 5 \times 10^{-5}$ M; [py] = 0.05 M; $[H_2O_2]_0 = 1.1$ M; $[H_2O]_{total} = 2.1$ M; $[\text{cyclohexane}]_0 = 0.46$ M; 60 °C; $^{18}O_2$, 1 bar. The yields and isotopic abundances were measured after reduction of the reaction samples with PPh_3.

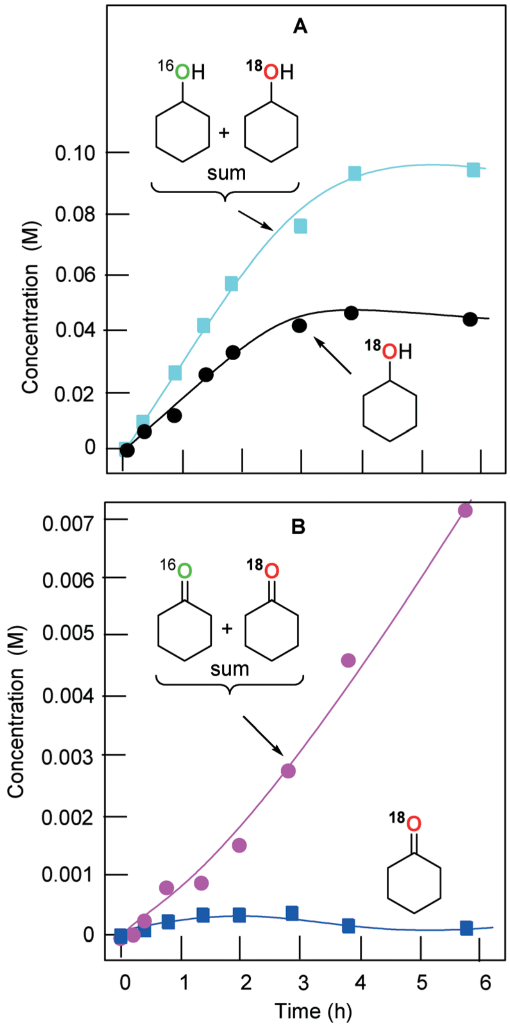
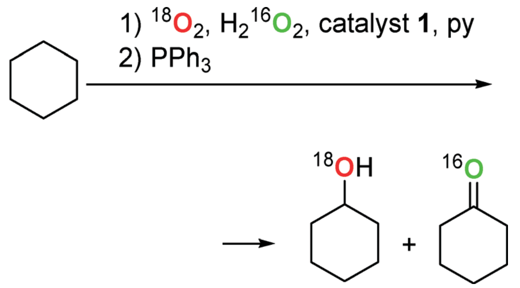


Fig. 11 Kinetic curves of accumulation with time of cyclohexanol (graph A) and cyclohexanone (graph B) containing both partially labeled (^{16}O + ^{18}O) and completely ^{18}O-labeled oxygenates. The yields and isotopic abundances were measured after reduction of the reaction samples with PPh_3.

The analysis of spectral patterns of O═PPh$_3$ which represent overlapped sets of peaks[12b] of $[M]^{\bullet+}$ and $[M\text{–}H]^{\bullet+}$ reveals the highest degree of ^{18}O incorporation that is equal to *ca.* 30% (Fig. 10, graph B). The mode of the experimental data resulted in the curve shown in Fig. 10, graph B, which resembles the overall dependence of product accumulation (Fig. 11, graph A). These results can be expected taking into account the reaction scheme reflected by eqn (12).

Dependence of the ^{18}O incorporation into cyclohexanone drastically differs from that obtained for the alcohol (Fig. 11). Maximum concentration of the ^{18}O-labeled ketone does not exceed 5×10^{-4} M (yield is 0.1% based on cyclohexane). We can clearly see in Fig. 11B that the yield of cyclohexanone–^{16}O is much higher than that of labeled cyclohexanone. It is necessary to emphasize that the yield of a ketone *after* reduction with PPh_3 is equal to the real yield of this compound in the reaction. Unlabeled ketone cannot be formed from the unlabeled peroxide Cy–^{16}O–^{16}OH. Indeed, the labeled hydroperoxide Cy–^{18}O–^{18}OH is present in the reaction solution and its decomposition would lead to the formation of cyclohexanone–^{18}O in addition to cyclohexanol–^{16}O. Thus, as some amount of cyclohexanone which is really present in the reaction mixture (the amount observed after reduction of CyOOH by PPh_3) does not contain ^{18}O we can conclude that this portion of cyclohexanone is formed *not* from CyOOH. It is reasonable to assume that this unlabeled cyclohexanone is produced in an alternative pathway which apparently does not involve either hydroxyl radicals or ROOH. Molecular oxygen from the atmosphere is not incorporated into the product in this route.

A summary of two competitive routes is depicted by eqn (13). The second route apparently involves the direct oxygenation of the alkane by a high-valent osmium-containing species. Although such a mechanism leads to a sufficiently lower amount of the product (concentration of cyclohexanone is *ca.* 15 times lower than the concentration of the corresponding alcohol) this pathway is of significant interest because it does not involve the formation of free radicals. Possibly, our observations are relevant to the studies made by Mayer and co-workers who reported the data on oxidations (which require the presence of pyridine) of alkanes, silanes, alkenes and H_2 with OsO_4 "consistent with a concerted [3 + 2] mechanism".[2m,13a–c] It should also be noted that our recent kinetic study[3i] of the alcohol oxidation with H_2O_2 catalyzed by the trinuclear carbonyl hydride cluster, $Os_3(CO)_{10}(\mu\text{-}H)_2$, led to the conclusion that oxidation of alcohols does not involve hydroxyl radicals as main oxidizing species and apparently proceeds with the participation of osmyl species, 'Os═O'. Periana and co-workers[13d] established "the viability of using *cis*-dioxo metal compounds, such as OsO_4, as reagents for the facile, selective functionalization of nucleophilic metal alkyl species *via* a low energy (2 + 3) transition state".



(13)

The chromatogram of a sample taken after 1.2 h and injected without addition of PPh_3 revealed almost equal amounts of the alcohol and ketone produced *via* decomposition of CyOOH in the injector (see above, sections 2.2, 3.2, and ref. 3*g*,*i*,5) heated up to 200 °C. Both products were found to be half-labeled (55 and 66% of ^{18}O in cyclohexanol and cyclohexanone, respectively) confirming that these products originated from the 66% labeled cycloalkyl hydroperoxide. A detailed description and discussion of over-oxidation products is given in the ESI† (Appendix. Products of the cyclohexane over-oxidation with the $H_2{}^{16}O_2/{}^{18}O_2$ system; see also ref. 14 in the ESI†).

The accumulation of labeled phenol in the oxidation of benzene by the **1**/py/H_2O_2 system was studied using the same reaction conditions and procedures as for cyclohexane oxidation. The GC-MS spectra of the samples taken from the reaction mixture clearly showed that both phenol (main product) and benzenediols (byproducts) are free from ^{18}O at any reaction time. These results are in agreement with the earlier studied mechanism of benzene interaction with hydroxyl radical[13e] which proceeds in a substantially different manner compared to the case of saturated hydrocarbons as shown in Scheme 2, eqn (15) (for eqn (14), see the ESI†). Alternatively, the mechanism analogous to those assumed for the reaction by cytochrome P450 with the participation of an osmium–oxo species affords phenol *via* the intermediate epoxide (with the possible NIH shift; see ref. 1*d*, page 471) as depicted by eqn (16) in Scheme 2. Both routes lead to the formation of unlabeled phenol.

3.7. On the mechanisms of alkane and benzene oxygenation

Based on the results and discussions presented in the previous sections we can propose a simplified scheme of the oxidative hydrocarbon transformations. Initially, a starting osmium complex is transformed under the action of H_2O_2 (and also possibly pyridine) into catalytically active species. This could be a derivative of Os(II) which in the catalytic cycle can be oxidized to Os(III). In the Fenton-like mechanism the Os(III)–Os(II) manifold will further operate:

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

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

Hydroxyl radicals thus formed are the key oxidizing species which attack either the alkane RH

$$RH + HO^{\bullet} \rightarrow R^{\bullet} + HOH$$

or benzene

$$C_6H_6 + HO^{\bullet} \rightarrow HOC_6H_6{}^{\bullet}$$

Under the action of molecular oxygen these radical species are transformed into oxygenates *via* different mechanisms:

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \rightarrow \rightarrow ROOH$$

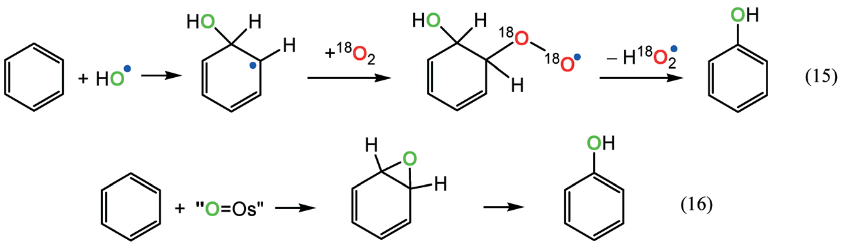
$$HOC_6H_6{}^{\bullet} + O_2 \rightarrow \rightarrow HOC_6H_5$$

Primary products (alkyl hydroperoxide or phenol) can be further transformed into more stable products (alcohol and ketone or quinone, *etc.*).

In a minor pathway, the interaction between complex **1** and $H_2{}^{16}O_2$ leads to the formation of an oxo–osmium derivative $Os{=}{}^{16}O$ which reacts with the alkane, RH, to produce cyclohexanol–^{16}O with further oxidation to cyclohexanone–^{16}O. Direct formation of cyclohexanone–^{16}O from $Os{=}{}^{16}O$ and CyH is also possible *via* the insertion of ^{16}O into the C–H bond. Similarly, the interaction between the $Os{=}{}^{16}O$ species and benzene can afford phenol C_6H_5–^{16}OH at least in one of the possible pathways.

4. Conclusions

Osmium complexes containing η^6-coordinated *p*-cymene ligands are efficient robust catalysts for the oxidation of alkanes and benzene with H_2O_2/O_2 to afford alkyl hydroperoxide or phenol, respectively. The catalytic studies reveal that the complex **1** is the most efficient precatalyst, showing high turnover numbers (TON) of 2×10^5 and 15.6×10^3 h^{-1}. As far as we are aware, these parameters are the highest ones observed for catalytic oxidation of alkanes, and even comparable to enzymatic oxidation of alkanes. The yield of cyclohexyl hydroperoxide, based on cyclohexane, is up to 30%, which is also among the highest reported.



Scheme 2 Proposed mechanisms for the benzene hydroxylation to phenol under the action of hydroxyl radical/molecular oxygen or the osmyl species "O═Os" or "O═Os═O".

The selectivity tests, as well as the kinetic studies and theoretical fitting of the kinetic data, show that the main route of the reaction involves the generation of hydroxyl radicals. The theoretical modeling allowed us to study the formation of the catalytically active species in detail and estimate the respective reaction rate constants. Particularly, it is shown that the monomeric form of the osmium complex **1** is the catalytically active species.

For the most active compound **1** the kinetic tests under the atmosphere of isotopically labeled $^{18}O_2$ have been performed, in order to understand the peculiarities of the catalytic mechanisms. While the incorporation of ^{18}O into cyclohexanol, formed from cyclohexyl hydroperoxide, was found to be at *ca.* 60% level, most of cyclohexanone was found to be ^{18}O-free. The formation of unlabeled cyclohexanone is fully unexpected and contrasts with the hydroxyl radical pathway, proposed as the main oxidation mechanism. We assume that unlabeled cyclohexanone is formed not from CyOOH but is produced in an alternative route which apparently does not involve hydroxyl radicals and ROOH. These observations were confirmed by studying the incorporation of ^{18}O into the main by-products (cyclohexanediols and hydroxycyclohexanones), where ketones were suggested to not contain labeled oxygen. Possibly, the minor amounts of the oxygenates, such as ketones, can be assumed to be formed *via* the interaction of an osmyl species (O═Os or O═Os═O) with an alkane or benzene, which is in agreement with the absence of ^{18}O in the respective products.

The present work combines the comprehensive catalytic studies of the osmium complexes, where a wide range of kinetic, isotopic and theoretical methods are applied together toward precise identification of the peculiarities of the catalytic systems. The unique results of ^{18}O experiments (particularly, for the first time studied ^{18}O incorporation into $Ph_3P{=}O$) provide a strong background for deep understanding of oxidative catalytic processes and the experiments deserve to be extended to a wide range of catalytic conditions. Finally, the present work contributes not only to catalysis but also to mass spectroscopy of valuable organic products. The results of comparative interpretation of EI-MS spectra of pure, ^{18}O- and D-labeled hydroxycyclohexanones allow us the practical use of the obtained data in the isotopic labeling experiments. The obtained data provide directions toward the preparation of new highly efficient catalysts.

Our Os-based system is efficient for the transformation of various CH compounds and in principle can be used in industry. The system uses relatively expensive H_2O_2 and also very small amounts of Os complexes and, naturally, it is expensive for the industrial oxidation of cyclohexane. However it could be considered for the oxidation of valuable CH compounds such as natural products, terpenes, steroids, *etc.* Cyclohexane is an excellent model compound for these studies.

Acknowledgements

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