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1. Introduction

Transition metal complexes are known to catalyze oxidation reactions of hydrocarbons (see reviews¹) and some other organic compounds, for example, alcohols (see reviews²) with molecular oxygen and peroxides, especially with hydrogen peroxide. Iron compounds are very often used as catalysts in the oxidation reactions.³ Much less is known about catalytic properties of compounds of osmium, which is an iron analog. Thus, osmium compounds catalyze dihydroxylations and cleavage of olefins,⁴ oxygenation reactions of saturated hydrocarbons and other C–H compounds by peroxides and NaIO₄,⁵ oxidation of alcohols.⁶

Continuing our studies of osmium-catalyzed oxidation reactions,^{7,8} in the present work we carried out an investigation of the oxidation of various organic substrates in acetonitrile by the very efficient " $H_2O_2/Os_3(CO)_{12}$ (compound 1)/pyridine" system. We describe here the application of this

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† For parts 1-3, see ref. 7a-c, respectively.

catalytic reagent to the oxidation of saturated and unsaturated hydrocarbons as well as alcohols including glycerol.



2. Results and discussion

2.1. Oxidation of alkanes

Oxidation reactions catalyzed by osmium compounds. Part 4.[†] Highly efficient oxidation of hydrocarbons and

alcohols including glycerol by the $H_2O_2/Os_3(CO)_{12}/$

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Triosmium dodecacarbonyl cluster $Os_3(CO)_{12}$ catalyzes oxidation of linear (*n*-heptane) and cyclic alkanes (cyclohexane, cyclooctane, methylcyclohexane, *cis*- and *trans*-1,2-dimethylcyclohexanes) to the corresponding cycloalkyl hydroperoxides by hydrogen peroxide in acetonitrile solution. Addition of pyridine leads to the acceleration of the process. Turnover numbers in the case of cyclooctane attain 60 000 and turnover frequencies are up to 24 000 h⁻¹. The alkyl hydroperoxide partly decomposes in the course of the reaction to afford cyclooctanone and cyclooctanol. Selectivity parameters obtained in oxidations of various linear

and branched alkanes as well as kinetic features of the reaction indicated that the alkane oxidation occurs

with the participation of hydroxyl radicals. A similar mechanism operates in transformation of benzene

into phenol and styrene into benzaldehyde. The system also oxidizes 1-phenylethanol to acetophenone.

Glycerol is oxidized to produce dihydroxyacetone, glycolic acid and hydroxypyruvic acid.

pyridine reagent[‡]

and Dalmo Mandelli^c

We studied the oxidation of alkanes in acetonitrile solution with hydrogen peroxide catalyzed by complex **1** in the presence of pyridine. The oxygenation of cyclohexane gives rise to the formation of the corresponding alkyl hydroperoxide as the main primary product. To demonstrate the formation of cyclohexyl hydroperoxide in this oxidation and to estimate its concentration in the course of the reaction we used a simple method developed earlier by Shul'pin.^{7b,8f;9} If an excess of solid PPh₃ is added to the sample of the reaction solution before GC analysis, the alkyl hydroperoxide present is completely reduced to the corresponding alcohol. In recent years, our method was employed by other chemists for the

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[‡] Electronic supplementary information (ESI) available: Fig. S1–S7, Tables S1 and S2. See DOI: 10.1039/c3ra41997e



Fig. 1 Oxidation of cyclooctane with H_2O_2 catalyzed by **1** in the presence of pyridine. Accumulation of cyclooctyl hydroperoxide, cyclooctanone, and cyclooctanol with time is shown. Conditions: [cyclooctane]₀ = 0.5 M, [py] = 0.1 M. Graph A: [**1**]₀ = 1 × 10⁻⁴ M, [H₂O₂]₀ = 1.5 M (70% aqueous). Graph B: [**1**]₀ = 5 × 10⁻⁶ M, [H₂O₂]₀ = 2.0 M; solvent MeCN, 60 °C. Concentrations of the three products (cyclooctyl hydroperoxide, cyclooctanol and cyclooctanone) were calculated comparing concentrations of cyclooctanol and cyclooctanone measured before and after reduction with PPh₃ (for this method, see ref. 7*b*, 8*f* and 9 and experimental section).

analysis of reaction products and detection of alkyl hydroperoxides in various oxidations of C-H compounds by molecular oxygen, hydrogen peroxide and other peroxides.^{10,11} For more details, see ref. 7*b*, 8*f* and 9 and supplementary data.[‡]

Examples of the kinetic curves for the oxidation of cyclooctane are shown in Fig. 1. Graphs A and B demonstrate that the oxidation affords predominantly cyclooctyl hydroperoxide as well as some amounts of cyclooctanol and cyclooctanone. In the absence of pyridine the reaction occurs with autoacceleration (Fig. S1, ESI‡) due to a relatively slow process of the generation of a catalyst active form. If pyridine in a low concentration is added to the reaction solution (Fig. 1) the lag period disappears, which indicates that in the presence of pyridine the formation of the catalytically active species is fast. Fig. 1A demonstrates that at relatively high concentration of precatalyst ($[1]_0 > 5 \times 10^{-5}$ M) the over-oxidation occurs and the product concentration drops after 2 h. ¹H NMR spectra of the reaction solution indicate the formation of a complex mixture of various compounds in low concentrations. Alkyl hydroperoxides as well as ketones and alcohols decompose with C-C bond rupture to produce *inter alia* derivatives of linear short-chain alkanes. A remarkable peculiarity of the reaction is the possibility to use the catalyst in very low concentrations, which gives high turnover numbers (TONs up to 60 000; Fig. 1B) and turnover frequencies (TOFs up to 24 000 h⁻¹) (for TON and TOF, see below and ref. 12). Total yields of primary oxygenates (alkyl hydroperoxides, ketones and alcohols) were in some cases about 50%. It is important to note that when precatalyst 1 is used in a very low concentration (5 × 10⁻⁶ and 1 × 10⁻⁶ M, see, for example, Fig. 1B) cyclooctyl hydroperoxide is formed as a sole product.

We checked also the catalytic activity of some other amines (4-picoline, pyrazine, 2,2'-bipyridine, and imidazole). Only 4-picoline showed activity comparable with that of pyridine. All other amines are very poor cocatalysts (Table S1, ESI[‡]). Acetonitrile and pyridine are known to replace CO ligands in **1** (see experimental section).

Using cyclooctane as a model substrate we studied dependences of the initial reaction rate W_0 (based on the sum of cyclooctanol and cyclooctanone concentrations measured after reduction of the reaction sample with PPh₃) on the initial concentration of each reactant at fixed concentrations of all other components of the reaction solution. Further, in our kinetic analysis we will operate with the initial rate of the formation of cyclooctyl hydroperoxide, $W_0 = (d[ROOH]/dt)_0$, which is equal to the initial rate of the oxygenates formation. This initial rate W_0 was determined from the slope of a dotted straight line which is tangent to the kinetic curve (two examples are presented by the dotted lines in Fig. 1). A dotted line in Fig. S1, ESI‡ corresponds to the maximum initial rate in the case when the reaction proceeds with auto-acceleration.

The dependence of W_0 on the initial concentration of H_2O_2 (straight line) is shown in Fig. 2. In addition, Fig. S2, ESI‡ demonstrates the dependence of the yield of oxygenates after 4 and 8 h on initial concentration of hydrogen peroxide. Water does not dramatically affect the initial reaction rate (Fig. S3, ESI‡).

The initial reaction rate W_0 (Fig. 3) does not practically depend on concentration of pyridine at its concentration > 0.04 M (for the dependence of yield of the products, see Fig. S4, ESI^{\ddagger}). The mode of the dependence of W_0 on the initial concentration of precatalyst 1 shown in Fig. 4 testifies that the order of the reaction rate relative to $Os_3(CO)_{12}$ is lower than first order. In accord with data of Fig. 4 the order in 1 determined as $\Delta \log W_0 / \Delta \log [\mathbf{1}]_0$ in the studied interval of concentrations is close to 0.65. The order value lower than unity apparently indicates that the catalytically active species contains less than three osmium atoms, that is in the process of active species generation starting complex $Os_3(CO)_{12}$ dissociates with the loss of one or two osmium atoms. Assuming that the order 0.65 corresponds to the true order of the reaction rate and that the extent of 1 dissociation is not high we will come to the conclusion that the catalytically active species "Os2" contains two Os atoms and is formed as a result of the following consecutive transformations:



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0.5 M, [py] = 0.1 M, $[\mathbf{1}]_0 = 1 \times 10^{-5}$ M, H_2O_2 , 70% aqueous, solvent MeCN, 60 °C. Concentration of water in the reaction was maintained constant $[H_2O] =$ const by adding necessary amounts of H_2O . The initial rate W_0 was determined from the slope of tangent to the kinetic curve of accumulation of the sum of cyclooctyl hydroperoxide, cyclooctanone, and cyclooctanol (concentration of the sum cyclooctanol + cyclooctanone was measured after reduction of the sample with PPh₃).





Fig. 3 Dependence of initial reaction rate W_0 on initial concentration of added pyridine in the cyclooctane oxidation. Conditions: $[cyclooctane]_0 = 0.5 \text{ M}, [1]_0 =$ 1 \times 10⁻⁵ M, [H₂O₂]₀ = 0.24 M, solvent MeCN, 60 °C. The initial rate W_0 was determined from the slop of tangent to the kinetic curve of accumulation of the sum of cyclooctyl hydroperoxide, cyclooctanone, and cyclooctanol (concentration of the sum cyclooctanol + cyclooctanone was measured after reduction of the sample with PPh₃).

Fig. 4 Oxidation of cyclooctane with H_2O_2 (2.0 M) in the presence of pyridine (0.1 M) ([cyclooctane]₀ = 0.5 M, solvent MeCN, 60 °C). Graph A: dependence of W_0 oxidation in on initial concentration of precatalyst **1**. Graph B: linearization of dependence shown in graph A using coordinates $\log[\mathbf{1}]_0 - \log W_0$.

$$Os_3(CO)_{12} = "Os_3" \xrightarrow{K_1} 3"Os_1"$$
(1)

$$2 \text{``Os}_1 \text{'`} \underbrace{\overset{K_2}{\longleftarrow}} \text{``Os}_2 \text{'`} \tag{2}$$

The analysis of this scheme in a quasi-equilibrium approximation gives rise to eqn (3).

$$["Os_2"] = K_2 (K_1 ["Os_3"])^{\frac{2}{3}}$$
(3)

Assuming that W_0 is proportional to ["Os₂"] we obtain the dependence:

$$W_0 \approx \omega ["Os_3"]^{\frac{2}{3}}$$
(4)

Here ω is a coefficient. The exponent $\frac{2}{3}$ at concentration ["Os₃"] is practically equal to the experimental value 0.65.

Decreasing the concentration of catalyst 1 we were able to significantly increase TONs (i.e., turnover numbers; mols of products per one mol of the catalyst; see ref. 12) and initial TOFs (i.e., turnover frequencies; mols of products per one mol of the catalyst obtained during the first hour of the reaction). It is necessary to note here that the very high turnover numbers attained by our system for the alkane oxidation are due to the order of the reaction in the catalyst 1, which is less than unity. Indeed, we can use a very low concentration of 1. Another reason why we can reach such high TONs is the remarkable stability of the catalytically active system during a long period of the reaction. Values TON and TOF for the cyclohexane oxidation by the $1/py/H_2O_2$ reagent in acetonitrile as well as by other most efficient catalytic systems are summarized in Table S2, ESI[‡] (see ref. 9a and 13-16). These data allow us to conclude that organometallic osmium complexes in the combination with pyridine oxidize alkanes with the highest TON and TOF values (entries 1 and 2). Very active mononuclear vanadate in the form of salt (n-Bu₄N)VO₃ in combination with pyrazine-2-carboxylic acid (PCA; for this reagent, see ref. 9a, 13b-d, 14 and 15) affords oxygenates with slightly lower TON = 20 000 and TOF = 2100 values (entries 3 and 4). It should be noted that when we decrease the catalyst concentration we can increase TON and TOF parameters; however, at least for relatively short reaction times the yield of oxygenates dramatically drops. It can be seen from the data of Table S2, ESI[‡] that other meal complex catalysts (entries 5-11) exhibit noticeably lower TONs and TOFs.

We measured the selectivity parameters in oxidations of certain alkanes (Table S3, ESI,‡ entries 1 and 2) in order to determine the nature of the alkane oxidizing species. Parameters determined previously^{9*a*,13-17} for other systems are also given in Table S3, ESI.‡ It can be seen that these parameters are close to the selectivities determined previously for the systems generating free hydroxyl radicals (entries 3–24) and noticeably lower than parameters determined for the systems oxidizing either without the participation of reactive hydroxyl radicals or in narrow cages (entries 25–31).

Approaching "a plateau" in the dependence of W_0 on initial concentration of cyclooctane, [RH]₀ (Fig. 5A), indicates that there is a competition between RH and another component of the reaction mixture for a transient oxidizing species.^{14a,16d,17b} Indeed, at high concentration of the hydrocarbon all oxidizing species are accepted by RH and the maximum possible oxidation rate is attained. This rate does not depend on [RH]₀ in the interval 0.25 < [RH]₀ < 0.5 M. Three components of the reaction solution which can compete with cyclooctane are pyridine, hydrogen peroxide and solvent acetonitrile. The concurrence can be described by the following kinetic scheme:

$$H_2O_2 + \text{catalyst} \rightarrow X \text{ (rate } W_i \text{)}$$
 (5)

$$X + RH \rightarrow \text{products (constant } k_1)$$
 (6)

$$X + py \rightarrow products (constant k_2)$$
 (7)

 $X + H_2O_2 \rightarrow \text{products (constant } k_3)$ (8)

$$X + MeCN \rightarrow products (constant k_4)$$
(9)



Fig. 5 Oxidation of cyclooctane with H_2O_2 (2.0 M) in the presence of pyridine (0.1 M), $[\mathbf{1}]_0 = 5 \times 10^{-5}$ M, solvent MeCN, 60 °C. Graph A: dependence of W_0 oxidation in on initial concentration of cyclooctane. Graph B: linearization of dependence shown in graph a using coordinates $1/[cyclooctane]_0 - 1/W_0$.

where W_i is the rate of generation of oxidizing species X. The analysis of this scheme in a quasi-stationary approximation relative to species X leads to eqn (10).

$$W_0 = \frac{d[\text{ROOH}]}{dt} = \frac{W_i}{1 + \frac{k_2[\text{py}] + k_3[\text{H}_2\text{O}_2] + k_4[\text{MeCN}]}{k_1[\text{RH}]}}$$
(10)

In accord with eqn (10) we can see the linear dependence of the experimentally measured reciprocal parameter $1/W_0$ on reciprocal concentration $1/[\text{RH}]_0$ (Fig. 5B). The tangent of this straight line slope angle corresponds to the value $(k_2[\text{py}] + k_3[\text{H}_2\text{O}_2] + k_4[\text{MeCN}])/k_1W_i$. The segment which is cut off by the line on Y-axis is equal to $1/W_i$. Using these data we can calculate the following value:

$$\frac{k_2[py] + k_3[H_2O_2] + k_4[MeCN]}{k_1} = 0.14$$
 (11)

As the selectivity parameters summarized in Table 2 indicate that the oxidizing species X is hydroxyl radical it is reasonable to use known from the literature rate constants of the interaction between HO[•] and pyridine, hydrogen peroxide, and acetonitrile. The comparison of the term values in the numerator of the fraction given above (11) can evaluate the

Table 1 Oxidation of benzene with H_2O_2 catalyzed by $Os_3(CO)_{12}$ in the presence of pyridine^a

Entry	Os ₃ (CO) ₁₂ (M)	Time (h)	Phenol (M)	TON
1	5×10^{-5}	1	0.025	500
2		3	0.050	1000
3^b		5	0.058	1160
4		8	0.049	980
5	1×10^{-5}	1	0.03	3000
6 ^{<i>c</i>}		3	0.08	8000

^{*a*} Conditions: $[benzene]_0 = 0.5 \text{ M}; [H_2O_2 (50\%)]_0 = 2.0 \text{ M}; [py] = 0.05 \text{ M}; 40 °C. ^{$ *b*} Maximum yield of phenol was 12% based on benzene (conversion of benzene was 48%). ^{*c*} Maximum yield of phenol was 16% based on benzene (conversion of benzene was 35%).

dominating reaction which competes with the alkane oxidation.

The constant values for reactions (7), (8), and (9) ($X = HO^{-}$) are known (M⁻¹ s⁻¹): $k_2 = 2.3 \times 10^9$ or 4.5×10^9 ; $k_3 = (4.5 \pm$ 1.4) \times 10⁷; $k_4 = 3.6 \times 10^6$ or 2.2 \times 10⁷ (see ref. 14*a*, 16*d* and 17b). Taking into account that under conditions of the experiments presented in Fig. 5 concentrations [py] = 0.1 M, $[H_2O_2] = 2.0$ M, and $[MeCN] \approx 18$ M we can calculate the following parameters (s⁻¹): k_2 [py] = 2.3 × 10⁸ or 4.5 × 10⁸; k_3 [H₂O₂] = (9 ± 2.8) × 10⁷, and k_4 [MeCN] = 6.4 × 10⁷ or 3.9 × 10⁸. This estimation shows that the most probable competitors of cyclooctane for hydroxyl radicals are pyridine and acetonitrile. The rate constant k_1 (M⁻¹ s⁻¹) for reaction (6) can be calculated using eqn (11) and given above values k_2 [py] and k_2 [MeCN]. The minimum value of constant k_1 equals to 1.4 \times 10^9 and maximum value is 5.0 \times 10^9 M⁻¹ s⁻¹. Taking into account the experimental errors in determination of rate constants we can see that the minimum value of k_1 is typical for the reactions of hydroxyl radicals with alkanes (see ref. 16*d*): $k_1 = 1.2 \times 10^9$ for cyclopentane, $k_1 = 1.3 \times 10^9$ for cyclohexane, and $k_1 = 1.6 \times 10^9 \text{ M}^{-1} \text{ s}$ for cycloheptane in aqueous solution. Therefore, the experimentally found competition is in good agreement with the assumption that the oxidizing species in our system is hydroxyl radical. Radical HO' attacks the hydrocarbon RH to generate alkyl radical R' which very rapidly reacts with molecular oxygen. Produced peroxyl radical, ROO', can be reduced in the presence of H⁺ by a low-valent form of Os-containing species to lead to the formation of the first product alkyl hydroperoxide. The nature

Table 2 Oxidation of styrene with $\rm H_2O_2$ catalyzed by $\rm Os_3(CO)_{12}$ in the presence of pyridine^a

Entry	$Os_3(CO)_{12}$ (M)	Time (h)	Benzaldehyde (M)	TON
1	5×10^{-5}	1	0.028	560
2		3	0.039	780
3		5	0.046	920
4		8	0.040	800
5	1×10^{-5}	1	0.027	2700
6		3	0.066	6600

 a Conditions: [styrene]_0 = 0.5 M; [H_2O_2 (50%)]_0 = 2.0 M; [py] = 0.05 M; 40 $^\circ \rm C.$



Fig. 6 Graph A: oxidation of cyclooctane (accumulation of a sum of oxygenates) at different temperatures. Conditions: $[1]_0 = 1 \times 10^{-5}$ M, [py] = 0.1 M, $[H_2O_2]_0 = 0.24$ M, $[cyclooctane]_0 = 0.5$ M. Graph B: The Arrhenius plot based on data is presented in Graph A.

of the catalytically active Os-containing species which are involved into the alkane oxygenation with H_2O_2 is at present unknown. We can, however, assume that manifold $Os^{III}-Os^{II}$ operates in this system,^{7*a*} which is analogous to the pairs Fe^{III}– Fe^{II} and V^V–V^{IV} (ref. 14 and 15). In this case the catalytic cycle of the alkane hydroperoxidation can involve the following steps:

$$Os^{III} + H_2O_2 \rightarrow Os^{II} + HOO' + H^+$$
(12)

$$Os^{III} + HOO^{\bullet} \rightarrow Os^{II} + H^{+} + O_{2}$$
(13)

$$Os^{II} + H_2O_2 \rightarrow Os^{III} + HO^- + HO^{\bullet}$$
(14)

$$RH + HO' \rightarrow R' + H_2O \tag{15}$$

$$R' + O_2 \rightarrow ROO'$$
 (16)

$$\text{ROO}^{\bullet} + \text{Os}^{\text{II}} \rightarrow \text{ROO}^{-} + \text{Os}^{\text{III}}$$
 (17)

$$\text{ROO}^- + \text{H}^+ \rightarrow \text{ROOH}$$
 (18)

 $\text{ROO}' + \text{HOO}' \rightarrow \text{ROOH} + \text{O}_2$ (19)

In the sequence (15)–(19), stage (15) is the reaction limiting the rate of alkyl hydroperoxide formation. We carried out the oxidation of cyclooctane at different temperatures (Fig. 6). Estimated effective activation energy is 12 ± 3 kcal mol⁻¹.

2.2. Oxidation of benzene

A very important chemical product phenol is utilized in the fabrication of polycarbonates and epoxy resins with more than 90% produced via the cumene process.^{18a} One of the alternative methods used for the preparation of phenols from arenes is the oxidation of arenes with H₂O₂ catalyzed by metal complexes.^{18b} Unlike the cumene peroxidation route,^{18c} direct oxidation of benzene with hydrogen peroxide does not produce co-products such as acetone. However, usually the vields of phenol are not high. For example, in the oxidation of benzene with H₂O₂ catalyzed by Tp*Cu(NCMe), where Tp* is hydrotris(3,5-dimethylpyrazolylborate), phenol was detected as the major product in the reaction mixture, with some 1,4benzoquinone as the sole byproduct, as a consequence of overoxidation of the phenol produced.^{18d} Benzene conversion was between 15 and 21% and selectivity to phenol was between 73 and 81%. Catalysis by molybdovanadophosphoric heteropoly acid H₅PMo₁₀V₂O₄₀ gave^{18e} phenol with conversion of 34%, the benzene oxidation^{18f} catalyzed by $V(acac)_3$ gave a mixture of phenol and quinone with conversion to phenol from 2.7 to 9.0% and the phenol content in this mixture from 76 to 84%, the oxidation with the Fenton-like system^{18g} and vanadium silicalite zeolite catalysts^{18h} produced phenol in yields 12% and 11%, respectively.

Our Os-based system oxidizes efficiently benzene to phenol with maximum attained TON = 8000 (Table 1). The oxidation of benzene at different temperatures (Fig. 7). evaluated effective activation energy equal to 9 ± 2 kcal mol⁻¹.

2.3. Oxidation of styrene

The oxidation of styrene with H_2O_2 catalyzed by metal complexes leads usually to the formation of styrene oxide, benzaldehyde and benzoic acid in relatively low yields. Thus, catalysis by [Cu(hmbmz)₂] (hmbmz is 2-(α -hydroxymethyl) benzimidazole) gave these products with selectivity of 16, 65 and 10%, respectively, and with conversion of 42% in addition to 9% of other products.^{19*a*} The oxidation of styrene with the reagent "H₂O₂–*n*Bu₄NVO₃–pyrazinecarboxylic acid" gave after 3 h at 60 °C benzaldehyde in 28% yield.^{19*b*} Our Os-system under consideration oxidizes styrene to produce benzaldehyde with TON attained 6600 (Table 2).

2.4. Oxidation of 1-phenylethanol

We checked the possibility of oxidation by our system of easily oxidizable alcohols. The first one is 1-phenylethanol which is effectively oxidized to acetophenone (Fig. 8). Effective activation energy was estimated: $11 \pm 3 \text{ kcal mol}^{-1}$.

2.5. Oxidation of glycerol

The second easily oxidizable alcohol checked here is glycerol. Glycerol is a by-product from biodiesel manufacturing. It is also a co-product in the production of fatty acids, alcohols and soap using fats and oils as a feedstock. Oxidative transformations of glycerol are especially important from the practical



Fig. 7 Graph A: accumulation of phenol in the oxidation of benzene at different temperatures. Conditions: [benzene]₀ = 0.5 M, $[H_2O_2]_0 = 1.0$ M, $[Os_3(CO)_{12}] = 5 \times 10^{-5}$ M, [py] = 0.05 M. Initial reaction rates were calculated from slops of the dotted lines. Graph B: The Arrhenius plot based on data presented in Graph A.

point of view.²⁰ For example, dihydroxyacetone (DHA) is a very valuable and important compound (it is widely used in cosmetics as a safe skin coloring agent as well as a nutritional supplement), being the first product in the chain of consecutive glycerol oxidation reactions. Glycolic acid that is formed from glycerol *via* C–C bond rupture finds applications in skin care products.

As glycerol is a very reactive compound, its oxidation typically gives rise to the formation of several compounds. Due to the high reactivity of both glycerol and its oxidation products, the oxidation of glycerol usually affords desirable products in low yield and selectivity. Recently we reported on two first systems which allow us to oxidize glycerol in homogeneous solution. These catalytic systems are based on complexes of manganese^{21a} and copper.^{21b} In the present work, glycerol was oxidized by the $H_2O_2/1/py$ system to DHA, glycolic acid and hydroxypyruvic acid (Scheme 1). Concentrations (determined by ¹H NMR; an example of the typical spectrum is shown in Fig. S5, ESI‡) and yields of these products are summarized in Table 3. The best result was



Fig. 8 Graph A: accumulation of acetophenone in the oxidation of 1-phenylethanol at different temperatures. Conditions: [1-phenylethanol]₀ = 0.5 M, $[H_2O_2]_0 = 1.0 \text{ M}$, $[Os_3(CO)_{12}] = 5 \times 10^{-5} \text{ M}$, [py] = 0.05 M. Initial reaction rates were calculated from slops of the dotted lines. Graph B: the Arrhenius plot based on data presented in Graph A.



Scheme 1 Products of glycerol oxidation.

obtained at 60 °C after 13 h. In this experiment (entry 6) glycerol conversion was 32%.

3. Conclusions

In the present work, the most efficient homogeneous metalcomplex reagent exhibiting very high TON (60 000) and TOF (24 000 h^{-1}) values was used for the oxidation of saturated, aromatic and olefinic hydrocarbons and alcohols, including glycerol. This system represents one of the first examples of homogeneous systems for the oxidation of glycerol. In the glycerol oxidation the system operates under mild conditions and shows good selectivity.

Experimental

4.1. Reagents

Hydrogen peroxide was used as 70% solution in H_2O in the oxidation of alkanes and 50% solution in H_2O in the oxidation of benzene, styrene and alcohols including glycerol.

Triosmium dodecacarbonyl, $Os_3(CO)_{12}$ (precatalyst 1; Aldrich) is insoluble in cold acetonitrile. The precatalyst was introduced into the reaction solution in the form of a stock solution which was prepared by the following method. Typically, $Os_3(CO)_{12}$ (9.2 mg) was suspended in CH₃CN (40 mL). The mixture was stirred at 60 °C for 1 h. This procedure led to replacing CO ligands by MeCN and gave a homogeneous bright yellow stock solution which was used in the oxidations (typically, concentration [1]₀ in the stock solution was from 5 × 10⁻⁵ to 2.5 × 10⁻⁴ M). A new weak peak at 2106 cm⁻¹ appeared in the IR spectrum of the stock solution (compare Fig. S6A and S6B, ESI‡) which indicates the formation of complex Os₃(CO)₁₁(MeCN).²² The stock solution is stable and can be stored either at room temperature or in a refrigerator without loss of activity in alkane oxidation (Fig. S7, ESI‡).

4.2. Oxidation of alkanes

The reactions of alkanes were typically carried out in air in thermostated Pyrex cylindrical vessels with vigorous stirring and using MeCN as solvent. Typically, precatalyst 1 ("Aldrich"; used as received) and the cocatalyst (pyridine) were introduced into the reaction mixture in the form of stock solutions in acetonitrile. The substrate (hydrocarbon or alcohol) was then added and the reaction started when hydrogen peroxide was introduced in one portion. (CAUTION. Compound 1 is toxic by absorption through the skin and should therefore be handled with care. All reactions should be carried out in a fume hood. The combination of air or molecular oxygen and H₂O₂ with organic compounds at elevated temperatures may be explosive!). The reactions were stopped by cooling and after addition of nitromethane as a standard compound analyzed by GC (instrument 'HP 5890-Serie-II'; fused silica capillary columns column Hewlett-Packard; the stationary phase was polyethyleneglycol: INNOWAX with parameters 25 m \times 0.2 mm \times 0.4 µm; carrier gas was N₂ with column pressure of 15 psi). Attribution of peaks was made by comparison with

Entry	Temperature °C	Time h	Glycerol conversion (%)	Products, conce	b)	
	remperature C	THIC II		DHA	Glycolic, acid	Hydroxo-pyruvic acid
1	17	24	5	0.007 (4.3)	0 (0)	0 (0)
2		72	10	0.010 (5.0)	0.005 (2.5)	0.006 (3.0)
3		144	18	0.011(5.5)	0.010 (5.0)	0.006 (3.0)
4	60	0.5	4	0.0008(0.4)	0 (0)	0 (0)
5		5	15	0.017 (8.3)	0.006 (4.0)	0.005 (2.7)
6		13	32	0.015 (7.5)	0.016 (8.0)	0.003 (1.5)

^{*a*} Conditions. Solvent was acetonitrile, $[glycerol]_0 = 0.2 \text{ M}$, $[H_2O_2]_0 = 0.3 \text{ M}$, $[Os_3(CO)_{12}]_0 = 5 \times 10^{-5} \text{ M}$, [py] = 0.05 M, total volume of the reaction solution was 2.5 mL. Yields (%) in parentheses are based on starting glycerol.

chromatograms of authentic samples. Blank experiments with cyclooctane showed that in the absence of catalyst **1** no products were formed. The quantification of alkyl hydroperoxides and ketones (aldehydes) and alcohols present in the reaction solution was performed using developed previously by Shul'pin^{7b,8f,9} simple GC method with reduction of the reaction samples with tryphenylphosphine.

4.3. Oxidation of benzene, styrene, 1-phenylethanol and glycerol

Oxidation reactions of benzene, styrene, 1-phenylethanol and glycerol were carried out as the reactions with alkanes. In these experiments concentration of the products was measured using ¹H NMR NMR method using instruments "Bruker AMX-400" and "Bruker AV-300". Solutions were in CD₃CN; signals were integrated using added 1,4-dinitrobenzene in acetone- d_6 as a standard.

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