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Extremely Efficient Alkane Oxidation by a New Catalytic Reagent $H_2O_2/Os_3(CO)_{12}$/Pyridine

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Triosmium dodecacarbonyl catalyzes a very efficient oxidation of alkanes by H_2O_2 in MeCN to afford alkyl hydroperoxides (primary products) as well as alcohols and ketones (aldehydes) at 60 °C if pyridine is added in a low concentration. Turnover numbers attain 60 000, and turnover frequencies are up to 24 000 h^{-1}.

New methods of oxyfunctionalization of inert saturated hydrocarbons catalyzed by various transition-metal complexes have been developed in the last decades.[1] These oxidations give directly valuable products such as alkyl hydroperoxides, alcohols, ketones, and carboxylic acids under mild conditions. Only a few papers are known that describe alkane oxidations catalyzed by soluble osmium compounds.[2]

Here, we report a very efficient oxidation of alkanes with H_2O_2 in an acetonitrile solution catalyzed by triosmium dodecacarbonyl, $Os_3(CO)_{12}$ (**1**). Examples of the kinetic curves for the oxidation of cyclooctane and *n*-octane are shown in Figures 1 and 2 and Table S1 (see the Supporting Information, SI). Graphs a and c of Figure 1 demonstrate that oxidation affords predominantly cyclooctyl hydroperoxide as well as some amounts of cyclooctanol and cyclooctanone. In this case, quantification of the three products was performed by a simple method developed earlier by some of us.[1p,3] In accordance with this method, concentrations of cyclooctanol and cyclooctanone were determined twice: before and after reduction of the aliquots with solid PPh_3 (see Appendices 1 and 2 and Figures S1−S4 in the SI). We will operate in this paper with the initial rate of formation of cyclooctyl hydroperoxide, $W_0 = (d[ROOH]/dt)_0$, which is equal to the initial rate of oxygenate formation.

In the absence of additives, the reaction occurs with autoacceleration (Figure 1a) because of a relatively slow process of generation of a catalyst active form. If pyridine in a low concentration is added to the reaction solution (Figure 1b), the lag period disappears, which indicates that in the presence of pyridine the formation of the catalytically active species is fast. Acetonitrile and pyridine are known to replace CO ligands in **1**.[4a] It is interesting to mention that OsO_4 oxidizes tertiary silanes in the presence of an excess of pyridine.[4b] Figures 1b and 2a demonstrate that at a relatively high concentration of the precatalyst ($[\mathbf{1}]_0 > 5 \times 10^{-5}$ M) overoxidation occurs and the product concentration drops after 2 h. It is important to note that when precatalyst **1** is used in a very low concentration (5×10^{-6} and even 1×10^{-6} M; see Figures 1c and 2c, respectively), cyclooctyl hydroperoxide is formed as the sole product.

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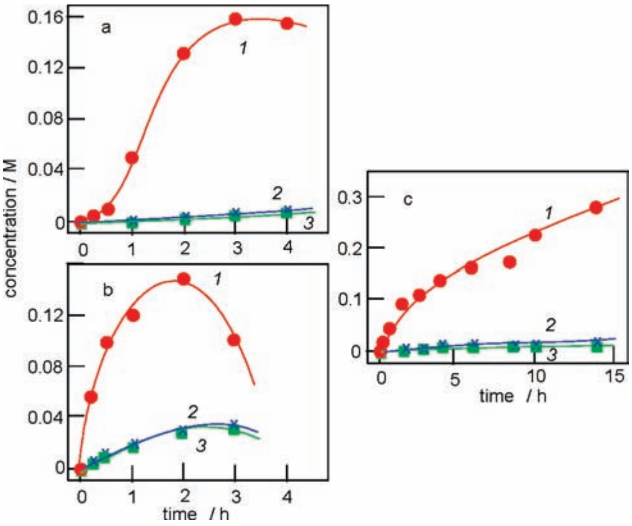

Figure 1. Kinetic curves of oxygenate accumulation (cyclooctyl hydroperoxide, curve 1; cyclooctanone, curve 2; cyclooctanol, curve 3) in cyclooctane (0.5 M) oxidation. Conditions: graphs a and b, $[\mathbf{1}]_0 = 1 \times 10^{-4}$ M, $[H_2O_2]_0 = 1.5$ M (70% aqueous); graph c, $[\mathbf{1}]_0 = 5 \times 10^{-6}$ M, $[H_2O_2]_0 = 2.0$ M; graphs b and c, in the presence of pyridine (0.1 M); MeCN up to 5 mL total volume; 60 °C. The concentrations of cyclooctanol and cyclooctanone were determined twice: before and after reduction of the aliquots with solid PPh_3 (for this method, see refs 1p and 3). In the experiment shown in graph c, TON (relative **1**) was 60 000 for the sum of oxygenates (cyclooctyl hydroperoxide + cyclooctanol + cycloooctanone) after 13 h.

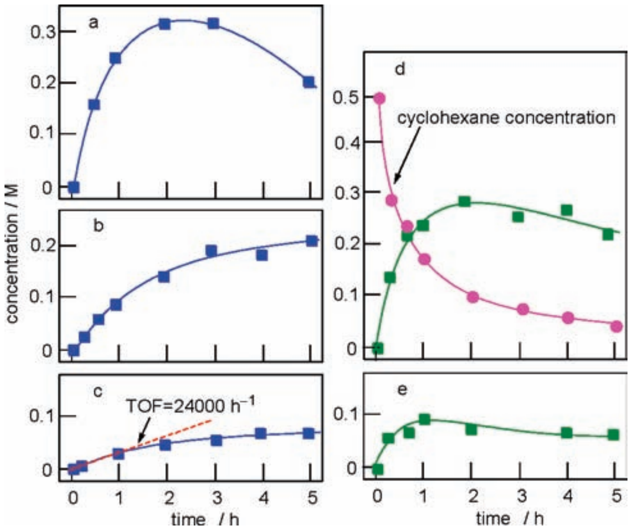

Figure 2. Kinetic curves of primary oxygenate accumulation (measured as the sum of cycloalkanol + cycloalkanone after reduction with PPh_3). Graphs a−c: cyclooctane (0.5 M) oxidation with H_2O_2 (2.0 M) in the presence of pyridine (0.1 M) at different concentrations of precatalyst **1** (graph a, 5×10^{-5}; graph b, 1×10^{-5}; graph c, 1×10^{-6} M). Graphs d and e: cyclohexane (0.5 M) oxidation with H_2O_2 (2.0 M, graph d) and $H_2O_2\cdot$urea (2.0 M, graph e) in the presence of precatalyst **1** (5×10^{-5} M) and pyridine (0.2 M). The solvent was MeCN and the temperature 60 °C.

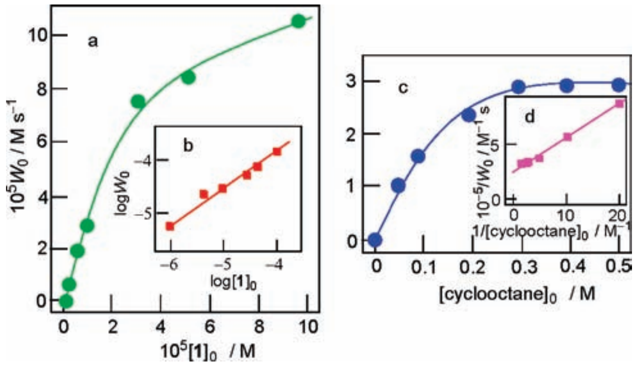

Figure 3. Oxidation of cyclooctane with H_2O_2 (2 M) in the presence of pyridine (0.1 M) (MeCN, 60 °C). The concentrations of cyclooctanol and cyclooctanone were determined after reduction of the aliquots with solid PPh_3. Graph a: dependence of W_0 oxidation on the initial concentration of precatalyst **1** ($[\text{cyclooctane}]_0 = 0.5$ M). Graph b: linearization of the dependence shown in graph a using coordinates log W_0 − log $[\mathbf{1}]_0$. Graph c: dependence of W_0 on the initial concentration of cyclooctane ($[\mathbf{1}]_0 = 5 \times 10^{-5}$ M). Graph d: linearization of the dependence shown in graph a using coordinates $1/W_0 - 1/[\text{cyclooctane}]_0$.

A remarkable peculiarity of the reaction is the possibility of using the catalyst at very low concentrations, which gives high turnover numbers (TONs up to 60 000; Figure 1c) and turnover frequencies (TOFs up to 24 000 h^{-1}; Figure 2c). The total yields of primary oxygenates (alkyl hydroperoxides, ketones, and alcohols) determined by gas chromatography (GC; Figure 2a) and NMR (Figures S6−S8 in the SI) were in some cases $>50\%$. It should be noted that, in very recent publications, yields up to 93% in metal-catalyzed alkane carboxylation under the action of the radical initiator potassium persulfate[5a,b] and up to 70% in cyclohexane oxygenation in the presence of hydrogen peroxide[5c] have been reported (see Appendix 3 in the SI).

The mode of the dependence of W_0 on the initial concentration of precatalyst **1** (Figure 3b) allows us to assume that a catalytically active species contains two osmium ions (see Appendix 4 in the SI).

To determine the nature of the alkane-oxidizing species, we measured the selectivity parameters in oxidations of certain alkanes (Table 1, entries 1 and 2). It can be seen that these parameters are close to the selectivities determined previously for the systems generating hydroxyl radicals (entries 3−7) and noticeably lower than parameters determined for the systems oxidizing without the participation of reactive radicals (entries 8 and 9).

A plateau in the dependence of W_0 on the initial concentration of cyclooctane, [RH] (Figure 3c), indicates that there is a competition between RH and another component of the reaction mixture for a transient oxidizing species. Indeed, at a

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Table 1. Selectivity Parameters in H_2O_2 Oxidations of Alkanes by Certain Catalytic Systems[a]

entry	catalytic system	C(1):C(2):C(3):C(4)	1°:2°:3°	trans/cis
1	**1**/py	1:4:4:4	1:5:11	0.85
2	**1**	1:5:5:5	1:6:14	
3	$h\nu$[b]	1:10:7:6	1:2:6	0.9
4	$FeSO_4$[b]	1:5:5:4.5		1.3
5	VO_3^-/PCA[c]	1:7:7:5	1:9:37	0.75
6	$Ni(ClO_4)_2$/L[d,e]	1:6:7:6	1:7:15	
7	$Al(NO_3)_3$[f]	1:6:6:5	1:6:23	0.8
8	$NaAuCl_4$[g]	1:35:25:23	1:116:255	
9	$[Mn_2L_2(O)_3]^{2+}$/ $MeCO_2H$[d,h]	1:30:25:24	1:26:200	0.34

[a] Parameter C(1):C(2):C(3):C(4) reflects the relative normalized (calculated taking into account the number of hydrogen atoms at each carbon) reactivities of hydrogen atoms at carbons 1−4 of the chain of *n*-octane or *n*-heptane (in entries 1 and 2, this parameter was calculated using the data given in Table S1 in the SI). Parameter 1°:2°:3° reflects the relative normalized reactivities of hydrogen atoms at the primary, secondary, and tertiary carbons of methylcyclohexane. Parameter trans/cis is the ratio of isomers of *tert*-alcohols with mutual trans and cis orientation of the methyl groups formed in the oxidation of *cis*-1,2-dimethylcyclohexane. All parameters were measured after reduction of the reaction mixtures with triphenylphosphine before GC analysis and calculated based on the ratios of isomeric alcohols. [b] See ref 6a. [c] For this system, see refs 6b−6e. [d] L is 1,4,7-trimethyl-1,4,7-triazacyclononane. [e] For this system, see ref 6f. [f] For this system, see ref 6g. [g] For this system, see ref 6h. [h] For these systems, see refs 6i−6l.

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 that can compete with cyclooctane are pyridine, hydrogen peroxide, and solvent acetonitrile. This concurrence can be described by the following kinetic scheme:

$$H_2O_2 + \text{catalyst} \rightarrow X \quad W_i \tag{i}$$

$$X + RH \rightarrow \text{products} \quad k_1 \tag{1}$$

$$X + py \rightarrow \text{products} \quad k_2 \tag{2}$$

$$X + H_2O_2 \rightarrow \text{products} \quad k_3 \tag{3}$$

$$X + MeCN \rightarrow \text{products} \quad k_4 \tag{4}$$

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 eq 5.

$$W_0 = \frac{d[ROOH]}{dt} = \frac{W_i}{1 + \frac{k_2[py] + k_3[H_2O_2] + k_4[MeCN]}{k_1[RH]}} \tag{5}$$

In accordance with eq 5, we can see the linear dependence of the experimentally measured reciprocal parameter $1/W_0$ on the reciprocal concentration $1/[RH]_0$ (Figure 3d). The tangent of this straight-line slope angle corresponds to the value $(k_2[py] + k_3[H_2O_2] + k_4[MeCN])/k_1W_i$. The segment that is cut off by the line on the Y axis is equal to $1/W_i$. Using these data, we can calculate the following value:

$$\frac{k_2[py] + k_3[H_2O_2] + k_4[MeCN]}{k_1} = 0.14 \tag{6}$$

Because the selectivity parameters summarized in Table 1 indicate that the oxidizing species X is a hydroxyl radical, it is reasonable to use rate constants of the interaction between $HO^\bullet$ and pyridine, hydrogen peroxide, and acetonitrile that are known from the literature. The comparison of the term values in the numerator of the fraction given in eq 6 can evaluate the dominating reaction that competes with alkane oxidation.

The constant values for reactions (2)−(4) ($X = HO^\bullet$) are known ($M^{-1}\,s^{-1}$): $k_2 = 2.3 \times 10^9$ or 4.5×10^9; $k_3 = (4.5 \pm 1.4) \times 10^7$; $k_4 = 3.6 \times 10^6$ or 2.2×10^7 (see ref [6a]). Taking into account that under conditions of the experiments presented in Figure 3c (concentrations [py] = 0.1 M, $[H_2O_2]$ = 2 M, and [MeCN] ≈ 18 M), we can calculate the following parameters (s^{-1}): $k_2[py] = 2.3 \times 10^8$ or 4.5×10^8; $k_3[H_2O_2] = (9 \pm 2.8) \times 10^7$, and $k_4[MeCN] = 6.4 \times 10^7$ or 3.9×10^8. This estimation shows that the most probable competitors of cyclooctane for hydroxyl radicals are pyridine and acetonitrile. Rate constants ($M^{-1}\,s^{-1}$) for reaction (1) can be calculated: $k_1 = 1.6 \times 10^9$ or 3.2×10^9 in the case of pyridine; $k_1 = 4.5 \times 10^8$ or 2.8×10^9 in the case of acetonitrile. These values are typical for the reactions of hydroxyl radicals with alkanes (see ref [6a]): $k_1 = 1.2 \times 10^9$ for cyclopentane, $k_1 = 1.3 \times 10^9$ for cyclohexane, and $k_1 = 1.6 \times 10^9$ 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 a hydroxyl radical. Radical $HO^\bullet$ attacks the hydrocarbon RH to generate alkyl radical $R^\bullet$, which very rapidly reacts with molecular oxygen. Produced peroxy radical $ROO^\bullet$ 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 (for details, see Appendix 5 in the S I).

In conclusion, we have discovered a new extremely powerful oxidizing system. This is one of the most efficient alkane-oxidizing reagents, exhibiting very high TON and TOF values.

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Supporting Information Available: Experimental details, calculations of maximum possible yields, and tables, schemes, and figures with formulas of the products and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.