

Hydrogen Peroxide Oxidation of Saturated Hydrocarbons Catalyzed by Osmium Compounds

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Abstract—Osmium derivatives, in particular OsCl_3 , catalyze the effective oxidation of saturated hydrocarbons in acetonitrile. The products formed are a ketone (aldehyde) and an alcohol. The addition of nitrogen heterocycles, such as pyridine, accelerated the reaction and increased the product yields. The ketone (aldehyde)/alcohol ratio dramatically changed in this case. In the presence of pyridine, the reaction occurred stereoselectively. The suggested reaction mechanism includes hydrogen atom abstraction from an alkane by an osmium oxo compound, resulting in the formation of the alkyl radical, which yields the alkylperoxyl radical after addition of an oxygen molecule. The latter radical degrades in the presence of the osmium complex under reaction conditions to give a ketone (aldehyde) and an alcohol.

INTRODUCTION

Inert saturated hydrocarbons can be oxidized with hydrogen peroxide under mild conditions in the presence of some transition metal complexes as catalysts [1–4]. Up to now, osmium complexes have been used in the oxidation of only unsaturated (mostly olefinic) hydrocarbons (see the latest works [5–12]). In this paper, we report the oxygenation of alkanes with hydrogen peroxide catalyzed by some simple osmium complexes (also see the preliminary communication [13]).

EXPERIMENTAL

The oxidation of higher alkanes was carried out in a cylindrical glass vessel with a jacket through which water from a thermostat was circulated. The solution volume was 10 ml. Reactions with lower alkanes were conducted in a steel autoclave (of 100 ml capacity with a reaction solution volume of 5 ml). The reaction mixture sampled (in 0.5 ml portions) at certain time intervals was analyzed by gas–liquid chromatography both before and after the 10–20-min treatment of a sample with an excess of solid triphenylphosphine. The GLC analyses were performed on an LKhM-80-6 chromatograph with 2-m columns packed with 5% Carbowax 1500-coated Inerton AW-HMDS (0.25–0.315 mm) and argon as a carrier gas and a DANI-86.10 chromatograph on a 0.25 m \times 0.32 mm \times 0.25 μm PLOT column with the CP-WAX52CB packing, an SP-4400 integrator, and helium as a carrier gas. Chromatograms were preliminarily calibrated with authentic compounds, the alkane oxidation products. The concentration of formaldehyde was measured after its conversion into 2,6-dimethyl-3,5-diacetyl-1,4-dihydropyridine [19]. Ace-

tonitrile used as a solvent was distilled over phosphorus pentoxide prior to the experiment.

RESULTS AND DISCUSSION

We found that osmium(III) chloride effectively catalyzed the transformation of saturated hydrocarbons into corresponding ketones (aldehydes) and alcohols at 80°C in acetonitrile as a solvent. GLC analysis before and after the reduction of the reaction mixture with triphenylphosphine (this method developed previously [14–18], which consists in comparing the chromatograms of samples before and after reducing the reaction solution, allows the actual concentrations of ketones, aldehydes, alcohols, and alkyl hydroperoxides present in the reaction medium to be determined) showed that alkyl hydroperoxides occurred only in insignificant concentrations under the given conditions. For example, the oxidation of cycloheptane (0.4 mol l^{-1}) with hydrogen peroxide (1.0 mol l^{-1}) in the presence of OsCl_3 (1.0 $\times 10^{-3}$ mol l^{-1}) leads to the formation of a mixture of cycloheptanol and cycloheptanone with a total turnover number (TON) of 63 attained 3 h after the beginning of the reaction. The product buildup kinetics are shown in Table 1. It is interesting that the addition of a small amount (0.125 mol l^{-1}) of pyridine noticeably increases the product yield (TON = 112) and leads to the predominant formation of ketones (see Table 1). Other nitrogen heterocycles also make the oxidation more effective. For example, the oxygenation of *n*-heptane in the presence of 3-methylpyrazole (Table 2) leads to the preferred formation of ketones and isomeric alcohols. The dependence of the reaction rate on the concentration of added pyridine displays a pro-

Table 4. Oxidation of cycloheptane in MeCN catalyzed by osmium complexes in the presence of different nitrogen bases (shown are the product concentration, *c*, mol l⁻¹, and the alcohol/ketone ratio)

Catalyst	Additive	Cycloheptanol, mol l ⁻¹	Cycloheptanone, mol l ⁻¹	Cycloheptanol/Cycloheptanone
Na ₂ OsCl ₆	3,5-Dimethylpyrazole	0.022	0.026	0.85
Na ₂ OsCl ₆	3-Methylpyrazole	0.035	0.077	0.45
OsCl ₃	—	0.049	0.010	4.9
OsCl ₃	Pyridine	0.020	0.092	0.2
OsCl ₃	3-Methylpyrazole	0.035	0.077	0.45
OsCl ₃	3,5-Dimethylpyrazole	0.022	0.026	0.85
OsCl ₃	2,2'-Bipyridyl	0.059	0.026	2.3
OsCl ₃	2,5-Dichloropyridine	0.076	0.014	5.4
OsCl ₃	Pyrazine-2-carboxylic acid	0.022	0.007	3.1

Reaction conditions: [cycloheptane]₀ = 0.4 mol l⁻¹, [H₂O₂]₀ = 1.0 mol l⁻¹, [catalyst] = 1.0 × 10⁻³ mol l⁻¹, 80°C. The concentrations were measured after reduction with triphenylphosphine.

Table 5. OsCl₃-catalyzed oxidation of lower alkanes in MeCN in the presence of different nitrogen heterocycles (given in parentheses after the products are their concentrations, *c*, mol l⁻¹)

Alkane	Pressure, bar	Additive	Products
Methane	40	2,5-Dichloropyridine	CH ₃ OH (0.0075)
		Pyridine	CH ₃ OH (0.017); HCHO (0.00003)
Ethane	20	2,5-Dichloropyridine	CH ₃ CHO (0.042); CH ₃ CH ₂ OH (0.06)
		Pyridine	CH ₃ CHO (0.08); CH ₃ CH ₂ OH (0.022)
Propane	6	2,5-Dichloropyridine	CH ₃ CH ₂ CHO (0.014); CH ₃ COCH ₃ (0.053); CH ₃ CH(OH)CH ₃ (0.054); CH ₃ CH ₂ CH ₂ OH (0.032)
		Pyridine	CH ₃ CH ₂ CHO (0.034); CH ₃ COCH ₃ (0.054); CH ₃ CH(OH)CH ₃ (0.018); CH ₃ CH ₂ CH ₂ OH (0.044)
<i>n</i> -Butane	2	2,5-Dichloropyridine	CH ₃ CH ₂ CH ₂ CHO (0.029); CH ₃ COCH ₂ CH ₃ (0.025); CH ₃ CH(OH)CH ₂ CH ₃ (0.0013); CH ₃ CH ₂ CH ₂ CH ₂ OH (0.0016)
		Pyridine	CH ₃ CH ₂ CH ₂ CHO (0.011); CH ₃ COCH ₂ CH ₃ (0.026); CH ₃ CH(OH)CH ₂ CH ₃ (0.011); CH ₃ CH ₂ CH ₂ CH ₂ OH (0.002)

Reaction conditions: [H₂O₂]₀ = 1.0 mol l⁻¹, [OsCl₃] = 1.0 × 10⁻³ mol l⁻¹, 80°C, 1.5 h. The concentrations were measured after reduction with triphenylphosphine.

2,5-dichloropyridine, methanol is formed in an amount of only 0.0075 mol l⁻¹. Ethane, propane, and *n*-butane are oxidized with a much higher efficiency. As follows from the data presented in Table 5, the use of 2,5-dichloropyridine instead of pyridine as an additive to the reaction mixture noticeably decreases the relative amount of ketone (aldehyde) in the product mixture of ketones and alcohols. The reaction occurs very effectively in the case of inert ethane; TON approaches 102 in the presence of pyridine. In the oxidation of propane, this quantity is even greater (153 in the presence of 2,5-dichloropyridine).

We determined the selectivity parameters for this reaction and, for the sake of comparison, measured corresponding parameters for some other, similar oxidation processes. It turned out that these parameters had greater values than in the case of oxidation with sys-

tems that suggest the formation of hydroxyl free radicals as reactive species (H₂O₂-FeSO₄, H₂O₂-*hν*, and H₂O₂-VO₃⁻-pyrazine-3-carboxylic acid (PCA)). The data obtained are summarized in Table 6. It is interesting that the selectivity parameters significantly increase in all cases when pyridine is added to the reaction mixture. The osmium chloride-catalyzed oxidation of *cis*-decalin with hydrogen peroxide occurs without conservation of the configuration at the tertiary carbon atom; the *trans/cis* ratio (i.e., the concentration ratio of *cis*- to *trans*-isomers of the tertiary alcohols formed) is even somewhat greater than unity. However, the reaction becomes more selective in the presence of pyridine; the *trans/cis* factor is 0.56 at its concentration of 6.25 mol l⁻¹. The reaction proceeds even more selectively in an acetic acid medium in the absence of pyridine: the *trans/cis* ratio is 0.26.

Table 1. OsCl₃-catalyzed oxidation of cycloheptane in MeCN (shown is the product concentration, *c*, mol l⁻¹)

Reaction time, min	Additive-free		In the presence of pyridine		In the presence of 2,5-dichloropyridine	
	cycloheptanone	cycloheptanol	cycloheptanone	cycloheptanol	cycloheptanone	cycloheptanol
10	0.002	0.005	0.030	0.010	0.001	0.004
20	0.003	0.008	0.050	0.012	0.002	0.010
40	0.005	0.015	0.071	0.016	0.002	0.030
60	0.006	0.022	0.075	0.017	0.006	0.050
90	0.008	0.032	0.085	0.018	0.010	0.065
120	0.010	0.044	0.092	0.020	0.014	0.076
180	0.013	0.048	0.085	0.020		
240	0.018	0.044				

Conditions: [cycloheptane]₀ = 0.3 mol l⁻¹, [H₂O₂]₀ = 1.0 mol l⁻¹, [additive] = 0.125 mol l⁻¹, [OsCl₃] = 1.0 × 10⁻³ mol l⁻¹, 80°C.

Table 2. OsCl₃-catalyzed oxidation of *n*-heptane in MeCN in the presence of 3-methylpyrazole (shown is the product concentration, mol l⁻¹; ONE is ketone and OL is alcohol; and the number specifies the position of the functional group in the alkane chain) and the reaction selectivity (i.e., the ratio of substitution products in the 1-, 2-, 3-, and 4-positions of the hydrocarbon chain with reference to the number of hydrogen atoms in these positions)

Reaction time, min	Carbonyl compounds, mol l ⁻¹			Alcohols, mol l ⁻¹				Selectivity C(1) : C(2) : C(3) : C(4)
	ONE-4	ONE-3	ONE-2	OL-4	OL-3	OL-2	OL-1	
10	0.0006	0.0013	0.0016	0.0004	0.0004	0.0010	0.0002	1.0 : 7.9 : 7.8 : 6.0
20	0.0024	0.0043	0.0062	0.0013	0.0035	0.0048	0.0009	1.0 : 9.3 : 6.8 : 5.2
40	0.0040	0.0081	0.0098	0.0021	0.0049	0.0067	0.0015	1.0 : 8.2 : 5.9 : 5.2
60	0.0056	0.0110	0.0118	0.0020	0.0043	0.0061	0.0015	1.0 : 6.2 : 4.3 : 4.1
90	0.0042	0.0080	0.0096	0.0013	0.0035	0.0040	0.0008	1.0 : 9.4 : 8.2 : 6.2
60 ^a	0	0	0	0.0014	0.0011	0.0013	0.0002	1.0 : 11.8 : 9.8 : 3.5

Reaction conditions: [*n*-heptane]₀ = 0.4 mol l⁻¹, [H₂O₂]₀ = 1.0 mol l⁻¹, [3-methylpyrazole] = 0.12 mol l⁻¹, [OsCl₃] = 1.0 × 10⁻³ mol l⁻¹, 80°C. The concentrations were measured after reduction with triphenylphosphine.

^a In the absence of 3-methylpyrazole, other conditions being the same.

Table 3. Cycloheptanone and cycloheptanol concentrations in the oxidation of cycloheptane in MeCN depending on the concentration of pyridine added (shown is the product concentration, mol l⁻¹)

[Pyridine], mol l ⁻¹	Cycloheptanone, mol l ⁻¹	Cycloheptanol, mol l ⁻¹
0	0.048	0.013
0.125	0.092	0.025
0.5	0.092	0.023
1.0	0.080	0.019
3.0	0.062	0.020
5.8	0.057	0.013

Conditions: [cycloheptane]₀ = 0.4 mol l⁻¹, [H₂O₂]₀ = 1.0 mol l⁻¹, 80°C, 3 h. The concentrations were measured after reduction with triphenylphosphine.

nounced maximum at as low a pyridine concentration as 0.125 mol l⁻¹ (Table 3). As the amount of pyridine admixture further increases, the 3-h yield of both ketone and alcohol decreases.

We showed that, using different heterocyclic additives in different concentrations, it was possible to alter the ketone/alcohol ratio in the product mixture; relevant examples are summarized in Table 4. From the data presented in Table 4, it follows that the use of 2,5-dichloropyridine as a base bearing two electron-withdrawing substituents leads to the preferred formation of alcohol (the cycloheptanol/cycloheptanone ratio is 5.4), whereas the reaction in the presence of unsubstituted pyridine affords products in the ratio of only 0.2.

It turned out that methane (initial pressure 40 bar) was oxidized with this system ([H₂O₂]₀ = 1.0 mol l⁻¹, [pyridine] = 0.125 mol l⁻¹, 80°C, 1.5 h) to produce only a very small amount of methanol (0.017 mol l⁻¹) and formaldehyde (3 × 10⁻⁵ mol l⁻¹). In the presence of

Table 6. Selectivity parameters in the oxidation of alkanes with different systems

Alkane	Oxidant system	Selectivity parameter
Isooctane	H ₂ O ₂ - <i>hν</i> in MeCN	1° : 2° : 3° 1.0 : 1.75 : 6.2
	H ₂ O ₂ -FeSO ₄ in MeCN-H ₂ O	1.0 : 2.75 : 6.0
	H ₂ O ₂ -Bu ₂ NVO ₃ -pyrazine-2-carboxylic acid in MeCN	1.0 : 3.0 : 4.8
	H ₂ O ₂ -OsCl ₃ in MeCN	1.0 : 2.2 : 8.7
	H ₂ O ₂ -OsCl ₃ in MeCN-py ([py] = 0.125 mol l ⁻¹)	1.0 : 2.1 : 18.3
<i>n</i> -Heptane		C(1) : C(2) : C(3) : C(4)
	H ₂ O ₂ - <i>hν</i> in MeCN	1.0 : 7.3 : 6.3 : 8.1
	H ₂ O ₂ -FeSO ₄ in MeCN-H ₂ O	1.0 : 5.0 : 4.8 : 4.6
<i>cis</i> -Decalin	H ₂ O ₂ -OsCl ₃ in MeCN	1.0 : 11.8 : 9.8 : 3.5
		<i>trans/cis</i>
	H ₂ O ₂ - <i>hν</i> in MeCN	1.3
	H ₂ O ₂ - <i>hν</i> in pyridine	1.9
	H ₂ O ₂ -FeSO ₄ in MeCN-H ₂ O	3.4
	H ₂ O ₂ -Bu ₂ NVO ₃ -pyrazine-2-carboxylic acid in MeCN	2.1
	H ₂ O ₂ -OsCl ₃ in MeCN-py ([py] = 0.125 mol l ⁻¹)	1.2
	H ₂ O ₂ -OsCl ₃ in MeCN-py ([py] = 6.25 mol l ⁻¹)	0.56
H ₂ O ₂ -OsCl ₃ in MeCOOH	0.26	

The parameter C(1) : C(2) : C(3) represents normalized (i.e., calculated with reference to the number of hydrogen atoms in each position) relative reactivities of hydrogen atoms in the 1-, 2-, and 3-positions of the carbon chain; the parameter 1° : 2° : 3° represents the normalized reactivity ratio of hydrogen atoms on the primary, secondary, and tertiary carbon atoms, respectively; and *trans/cis* = [*trans*-decalol-9]/[*cis*-decalol-9] (where [*trans*-decalol-9] and [*cis*-decalol-9] are the concentrations of the respective tertiary alcohols formed in the oxidation of decalin isomers).

The data obtained in this work suggest that the oxidation of an alkane with the H₂O₂-OsCl₃ system starts from the abstraction of a hydrogen atom by the osmium oxo complex. The reaction in this case may occur in the solvent cage. The alkyl radicals produced rapidly react with ambient molecular oxygen, resulting in alkylperoxy radicals which are converted into alkyl hydroperoxide. The hydroperoxide is quantitatively transformed into a ketone (aldehyde) and alcohol mixture at a relatively high (80°C) temperature in the presence of an osmium compound. It is likely that the nitrogen heterocycle present in the reaction mixture has an effect on the alkyl hydroperoxide degradation process, altering the concentration ratio between the carbonyl compound and alcohol.

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