

Oxygenation of alkanes with hydrogen peroxide catalysed by osmium complexes

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Efficient oxidation of alkanes, including methane and ethane, with H₂O₂ in the presence of catalytic amount of an Os complex in MeCN (addition of nitrogen-containing heterocycles significantly enhances the yield of the products) or in MeCO₂H gives the corresponding ketones and alcohols.

Unlike aromatic and olefinic hydrocarbons, alkanes are known to exhibit only negligible reactivity in reactions with a variety of normal reagents and the yields of the products are usually low, especially in the case of light saturated hydrocarbons (methane, ethane and propane).¹ Osmium compounds, particularly OsO₄, oxidize unsaturated hydrocarbons and some other organic compounds stoichiometrically and catalyse their oxygenations with various reagents.^{2,3}

Here, we report that soluble osmium derivatives, especially OsCl₃, catalyse efficiently the oxygenation of saturated hydrocarbons with hydrogen peroxide. All reactions⁴ were carried out at 80 °C. The oxidation of cycloheptane (0.4 mol dm⁻³) in MeCN with H₂O₂ (1.0 mol dm⁻³) in the presence of OsCl₃ (1.0 × 10⁻³ mol dm⁻³) gave after 3 h cycloheptanol (0.05 mol dm⁻³) and cycloheptanone (0.013 mol dm⁻³), the total turnover number (TON) being 63. Addition of a small amount of pyridine (0.125 mol dm⁻³) gave rise to a noticeable increase in the yield and to the predominant formation of the ketone (after 90 min: cycloheptanol, 0.020 mol dm⁻³; cycloheptanone, 0.092 mol dm⁻³; TON, 112). Other nitrogen-containing heterocycles also promote the oxidation: for example, the reaction with *n*-heptane in the presence of 3-methylpyrazole (Fig. 1) affords predominantly isomeric ketones (after 60 min total concentration 0.028 mol dm⁻³) as well as isomeric alcohols (total 0.04 mol dm⁻³). Heptanal has been detected only in negligible concentration. The reaction is accompanied by non-productive H₂O₂ decomposition to give molecular oxygen, and the oxidation decreases when hydrogen peroxide concentration becomes low (after approximately 1 h, as shown in Fig. 1). By varying the additive, it is possible to control the ketone/alcohol ratio (Table 1). Lower alkanes can be easily oxidized in MeCN, if pyridine is added to the reaction solution (Table 2). In contrast to methane which is the least reactive hydrocarbon in this reaction and affords methanol as the main product, ethane and propane give mainly carbonyl compounds and only smaller amounts of alcohols with TON values of 102 and 150, respectively.

The selectivities of the alkane oxidations catalysed by OsCl₃ are higher than those determined for analogous hydroxylations by the systems 'H₂O₂-hν' and 'H₂O₂-FeSO₄' as well as 'H₂O₂-VO₃⁻-pyrazinocarboxylic acid (PCA)'⁷ which are believed to produce free hydroxyl radicals (Table 3). It is noteworthy that selectivities significantly increase when pyridine is added to the reaction solution. Moreover, while the oxidation of *cis*-decalin with H₂O₂-OsCl₃ in MeCN occurs without retention of the configuration (the *trans/cis* ratio of the products formed being more than unity), in the presence of

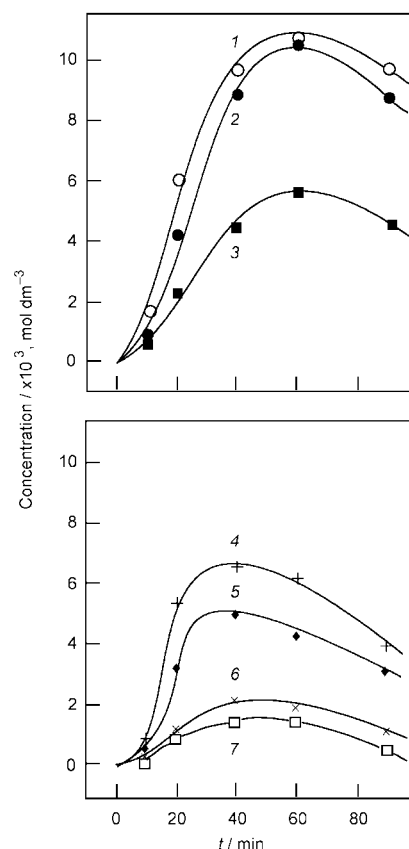


Fig. 1 Accumulation of heptan-2-one (1), heptan-3-one (2), heptan-4-one (3), heptan-2-ol (4), heptan-3-ol (5), heptan-4-ol (6) and heptan-1-ol (7) in the *n*-heptane (0.4 mol dm⁻³) oxidation with H₂O₂ (1.0 mol dm⁻³) catalysed by OsCl₃ (10⁻³ mol dm⁻³) in MeCN in the presence of 3-methylpyrazole (0.12 mol dm⁻³) at 80 °C.

Table 1 Oxidation of cycloheptane (0.4 mol dm⁻³) with H₂O₂ (1.0 mol dm⁻³) in MeCN (80 °C, 2 h)⁴

Catalyst	Additive	Products/mol dm ⁻³		
		Cycloheptanol (OL)	Cycloheptanone (ONE)	Ratio OL/ONE
OsCl ₃	2,5-Dichloropyridine	0.076	0.014	5.4
OsCl ₃	None	0.049	0.010	4.9
OsCl ₃	2,2'-Bipyridine	0.059	0.026	2.3
Na ₂ OsCl ₆	3,5-Dimethylpyrazole	0.022	0.026	0.85
Na ₂ OsCl ₆	3-Methylpyrazole	0.030	0.070	0.45
OsCl ₃	3-Methylpyrazole	0.035	0.077	0.45
OsCl ₃	Pyridine	0.020	0.092	0.2

Table 2 Oxygenation of lower alkanes ($\text{H}_2\text{O}_2 = 1 \text{ mol dm}^{-3}$, $\text{OsCl}_3 = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $\text{py} = 0.125 \text{ mol dm}^{-3}$; MeCN 80 °C, 1.5 h)⁴

Alkane (pressure/bar)	Products/mol dm ⁻³
Methane (40)	CH_3OH (0.017); HCHO (3.0×10^{-5})
Ethane (20)	CH_3CHO (0.08); $\text{CH}_3\text{CH}_2\text{OH}$ (0.022)
Propane (6)	$\text{CH}_3\text{CH}_2\text{CHO}$ (0.034); CH_3COCH_3 (0.054); $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ (0.018); $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (0.044)
<i>n</i> -Butane (2)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ (0.011); $\text{CH}_3\text{COCH}_2\text{CH}_3$ (0.026); $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$ (0.011); $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ (0.002)

Table 3 Selectivities of alkane oxidations by various systems

Substrate	System	Selectivity ^a
<i>n</i> -Heptane	H_2O_2 - <i>hν</i> in MeCN	C(1):C(2):C(3):C(4)
	H_2O_2 - FeSO_4 in MeCN- H_2O	1.0:7.3:6.3:8.1
	H_2O_2 - OsCl_3 in MeCN	1.0:5.0:4.8:4.6
2,2,4-Trimethyl- pentane	H_2O_2 - <i>hν</i> in MeCN	1°:2°:3°
	H_2O_2 - FeSO_4 in MeCN- H_2O	1.0:1.75:6.2
	H_2O_2 - Bu_4NVO_3 -PCA in MeCN	1.0:2.75:6.0
	H_2O_2 - OsCl_3 in MeCN	1.0:3.0:4.8
	H_2O_2 - OsCl_3 in MeCN-py	1.0:2.2:8.7
	H_2O_2 - OsCl_3 in MeCN-py (0.125 mol dm ⁻³)	1.0:2.1:18.3
<i>cis</i> -Decalin		<i>trans/cis</i>
	H_2O_2 - <i>hν</i> in MeCN	1.3
	H_2O_2 - <i>hν</i> in py	1.9
	H_2O_2 - FeSO_4 in MeCN- H_2O	3.4
	H_2O_2 - Bu_4NVO_3 -PCA in MeCN	2.1
	H_2O_2 - OsCl_3 in MeCN-py (0.125 mol dm ⁻³)	1.2
	H_2O_2 - OsCl_3 in MeCN-py (6.25 mol dm ⁻³)	0.56
H_2O_2 - OsCl_3 in MeCO ₂ H	0.26	

^a Parameter C(1):C(2):C(3) is normalized (*i.e.* calculated taking into account the number of hydrogen atoms at each position) relative reactivities of hydrogens at carbon atoms 1, 2 and 3 of the alkane chain, respectively; parameter 1°:2°:3° is normalized relative reactivities of hydrogen atoms at primary, secondary and tertiary carbons, respectively; parameter *trans/cis* = [*trans*-decal-9-ol]/[*cis*-decal-9-ol], where [*trans*- and *cis*-decal-9-ol] are concentrations of *trans*- and *cis*-decal-9-ol formed in the oxidation, respectively.

pyridine the reaction becomes more selective, the *trans/cis* ratio decreasing with increasing pyridine concentration. It is important to note that in MeCO₂H the reaction exhibits a high value of the *trans/cis* parameter (0.26) and the parameter $\text{RC}_{cis} = 100(c_{cis} - c_{trans})/(c_{cis} + c_{trans}) = 58\%$. The value of the *trans/cis* parameter for the system ' H_2O_2 - OsCl_3 ' in MeCO₂H is only slightly higher than that (*trans/cis* = 0.12) for the hydroxylation in MeCN by the system ' H_2O_2 -LMn^{IV}(O)₃-Mn^{IV}L⁺-MeCO₂H (L = 1,4,7-trimethyl-1,4,7-triazacyclononane)' described recently.⁸

On the basis of the results obtained and especially taking into account the selectivity parameters, one may assume that oxidation by the system H_2O_2 - OsCl_3 starts with hydrogen atom abstraction from the alkane by an oxo osmium complex, and the reaction occurs in a solvent cage. The alkyl radicals formed react then with dioxygen to generate the corresponding alkyl hydroperoxide which decomposes to afford the corresponding ketone and alcohol. The system described here can be considered as a model for the oxidations of C-H compounds catalysed by iron-containing enzymes, osmium being an iron homologue in the Periodic System. Indeed, oxidations with participation of cytochrome P-450, methane monooxygenase and chloroperoxidase are believed to begin with hydrogen atom abstraction by a high-valent iron oxo species.^{1,9} Coordination of a nitrogen-containing heterocycle (and/or acetate) to osmium

may produce a catalytically active oxo species surrounded with voluminous ligands, and the relatively high bond- and stereo-selectivities of the alkane oxidation may be due in this case to the bulkiness of the ligands at the reaction centre.

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- The oxidations of higher hydrocarbons were carried out in air in thermostated Pyrex cylindrical vessels with vigorous stirring. The total volume of the reaction solution was 5 or 10 mL. In a typical experiment, initially, a portion of 35% aqueous solution of hydrogen peroxide (Fluka) was added to the solution of the catalyst, substrate and heterocycle in acetonitrile (Fluka). The oxidations of lower alkanes were carried out in a stainless steel autoclave with intensive stirring (volume of the reaction solution was 5 mL and total volume of autoclave was 100 mL). Before the oxidation the autoclave was charged with the alkane under appropriate pressures. The reactions were stopped by cooling with ice and the reaction solution was analysed by GC (DANI-86.10; fused silica capillary column 25 m × 0.32 mm × 0.25 mm, CP-WAX52CB; integrator SP-4400). Comparison of the chromatograms of the reaction samples before and after their treatment with PPH₃ (for this method, see refs. 1(a),(b),5-8) demonstrated that concentrations of alkyl hydroperoxides were very low. The concentration of formaldehyde was measured spectrophotometrically after its transformation into 2,6-dimethyl-3,5-diacetyl-1,4-dihydropyridine as described previously.⁶
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