Oxidation of Saturated Hydrocarbons with Peroxides Catalyzed by Iridium and Palladium Complexes

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Received March 17, 2005; in final form, May 25, 2005

Abstract—A comparative study of the reactions of alkane oxidation with peroxides in acetonitrile showed different behavior of the complexes cyclopentadienylbenzeneiridium(III) tetrafluoroborate $[\pi\text{-}C_5H_5)Ir(\pi\text{-}C_6H_6)](BF_4)_2$ (complex **1**) and tetrakis(methyldiphenylphosphine)palladium(0) $[(CH_3)(C_6H_5)_2P]_4Pd$ (complex **2**) as catalysts. Complex **1** was completely inactive in oxidation with hydrogen peroxide and *tert*-butyl hydroperoxide but exhibited a moderate activity in oxidation with *m*-chloroperoxybenzoic acid (MCPBA) at room temperature. On the basis of the regio- and stereoselectivity parameters found for the latter reaction, it was assumed that the role of iridium(III) ion consists in the formation of Lewis adducts with MCPBA, which enhances the activity of the acid. Unlike the iridium derivative, palladium complex **2** showed a moderate activity in oxidation with hydrogen peroxide. The relatively high values of the regioselectivity parameters suggest the formation of oxo or peroxo complexes of palladium. Steps involving these complexes include hydrogen-atom abstraction from an alkane yielding the alkyl radical. Adding to an oxygen molecule, this radical forms the alkylperoxy radical and, ultimately, alkyl hydroperoxide. Complex **2** showed activity in the oxidation of alkanes with MCPBA, wherein the reaction with *cis*-2,2-dimethylcyclohexane was not stereoselective. It was supposed that iridium and palladium catalyze the reactions of alkanes with MCPBA via different mechanisms.

INTRODUCTION

Soluble derivatives of platinum metals can act as catalysts for some oxidative conversions of saturated hydrocarbons effected by molecular oxygen or organic and inorganic peroxides [1–6]. In this work, we examined the catalytic action of iridium(III) and palladium(0) complexes in the oxidation of alkanes with various peroxides.

EXPERIMENTAL

Oxidation of higher alkanes was carried out in a cylindrical glass reactor with a jacket through which water from a thermostat was circulated. The volume of the test solution was 2 ml. The solution was sampled (by 0.5 ml) at certain intervals for further GLC analysis both before and after treatment (for 10–20 min) with an excess of solid triphenylphosphine. Gas-chromatographic analyses were carried out on a LKhM-80-6 chromatograph with a 2-m column packed with 5% Carbowax 1500 on Inerton AW-HMDS (0.25–0.315 mm) and argon as a carrier gas; a DANI-86.10 chromatograph equipped with a SP-4400 integrator, a 25 m × 0.32 mm × 0.25 μm capillary column coated with CP-WAX52CB and helium as a carrier gas; and a

3700 chromatograph with a 30 m × 0.2 mm × 0.3 μm capillary column coated with FFAP/OV-101 20/80 w/w and helium as a carrier gas. Chromatograms were preliminarily calibrated with authentic compounds—the alkane oxidation products. Acetonitrile was preliminarily distilled over phosphorus pentoxide.

The catalysts tested were cyclopentadienylbenzeneiridium(III) tetrafluoroborate, $[\pi\text{-}C_5H_5)Ir(\pi\text{-}C_6H_6)](BF_4)_2$ (**1**) prepared according to a procedure described in [7], tetrakis(methyldiphenylphosphine)palladium(0) $[(CH_3)(C_6H_5)_2P]_4Pd$ (**2**) (Aldrich), and bis(triphenylphosphine)palladium(II) chloride $[(C_6H_5)_3P]_2PdCl_2$ (**3**) (Aldrich). The oxidants were hydrogen peroxide (35% aqueous solution) (Fluka), *tert*-butyl hydroperoxide (70% aqueous solution) (Fluka), and 3-chloroperoxybenzoic acid (Fluka).

RESULTS AND DISCUSSION

We found that iridium derivative **1** was completely inactive as a catalyst for the oxidation of alkanes with hydrogen peroxide or *tert*-butyl hydroperoxide in acetonitrile. However, the H_2O_2–**1** system showed a moderate activity in the oxidation of secondary alcohols. For example, cyclohexanol was oxidized at room tem-

Table 1. Cyclohexane oxidation with MCPBA in acetonitrile in the absence and presence of complex **1** (product concentration c in mmol l^{-1} is given)

Reaction time, h	In absence of 1		In presence of 1	
	cyclohexanone	cyclohexanol	cyclohexanone	cyclohexanol
5	0.0005	0.05	0.05	0.24
24	0.003	0.28	0.16	0.80
52	0.007	0.6	0.26	2.5
72	0.07	0.8	0.26	2.5
120	0.12	1.3	0.27	2.5

Conditions: $[\text{cyclohexane}]_0 = 0.46$ mol l^{-1}, $[\text{MCPBA}]_0 = 0.3$ mol l^{-1}, $[\mathbf{1}] = 1.0 \times 10^{-3}$ mol l^{-1}, and 22°C. The product concentrations were measured after the addition of triphenylphosphine.

Table 2. Cyclooctane oxidation with hydrogen peroxide in acetonitrile catalyzed by complex **2**

Time, h	Total product concentration, mmol l^{-1}
0.5	2.0
1	2.5
3	3.0
5	6.5
7	6.3
9	6.0

Reaction conditions: $[\text{cyclooctane}]_0 = 0.42$ mol l_{-1}, $[\text{H}_2\text{O}_2]_0 = 1.2$ mol l^{-1}), $[\mathbf{2}] = 2.0 \times 10^{-4}$ mol l^{-1}, and 60°C. The product concentrations were measured after the reduction of the reaction mixture with triphenylphosphine.

perature to cyclohexanone (30% yield for 6 h) when a fourfold excess (in terms of **1**) of pyrazine-2-carboxylic acid as a cocatalyst was added to the reaction solution.

Unexpectedly, complex **1** turned out to increase the efficiency of alkane oxidation with *m*-chloroperoxybenzoic acid (MCPBA). From the data presented in Table 1, it follows that the admixture of catalyst **1** leads to acceleration of cyclohexane oxidation approximately by a factor of three as with the blank run. In the presence of **1**, the reaction goes to completion within about 50 h to give a product yield about twice that of the uncatalyzed reaction after 120 h. We found that as the concentration of catalyst **1** increased, the rate of formation of cyclohexane oxidation products ($[\text{cyclohexane}]_0 = 0.46$ mol l^{-1} and $[\text{MCPBA}]_0 = 0.3$ mol l^{-1}) increased from 4×10^{-9} mol l^{-1} s^{-1} at $[\mathbf{1}] = 0$ (i.e., in the absence of the catalyst) to 5×10^{-9} and 10×10^{-9} mol l^{-1} s^{-1} at $[\mathbf{1}] = 5 \times 10^{-4}$ and 1.0×10^{-3} mol l^{-1}, respectively.

The oxidation of *n*-heptane ($[\text{heptane}]_0 = 0.4$ mol l^{-1}, $[\text{MCPBA}]_0 = 0.75$ mol l^{-1}) and $[(\mathbf{1})] = 1.0 \times 10^{-3}$ mol l^{-1}, 24°C) yielded the following products (given in the parentheses are the concentrations, in mmol l^{-1}, mea-

sured after the addition of triphenylphosphine): heptanone-2 (4.0), heptanone-3 (3.5), heptanone-4 (1.4), heptanol-2 (1.8), heptanol-3 (1.9), heptanol-4 (1.0), heptanol-1 (0.0092), and heptanoic acid (0.0040). Heptanal was not found. The total amount of products corresponds to a turnover number of 14. From these data, we calculated the normalized (i.e., with reference to the number of hydrogen atoms attached to carbon atoms of each type in the heptane linear chain) regioselectivity parameters. If all the products of heptane oxygenation are taken into account in the calculations, the regioselectivity (i.e., the ratio between the products substituted in the 1-, 2-, 3-, and 4-positions of the hydrocarbon chain) of heptane oxidation is $C(1) : C(2) : C(3) : C(4) = 1 : 66 : 61 : 55$. If we calculated based on the concentrations of isomeric alcohols alone (as we did in the previous studies on the oxidation of alkanes), this parameter turns out to be somewhat lower, $C(1) : C(2) : C(3) : C(4) = 1 : 29 : 31 : 32$. However, it should be noted that the reaction selectivity in any of these variants is markedly higher than in the case of reactions that follow the free-radical mechanism involving hydroxyl radicals. For example, the values of these parameters are $1 : 7 : 6 : 7$ and $1 : 9 : 7 : 7$ for *n*-heptane oxidation with the hν–H_2O_2 and *n*-Bu_4NVO_3–pyrazine-2-carboxylic acid–H_2O_2 systems, respectively [8, 9]. *n*-Hexane oxidation with the MCPBA–**1** system also gives high values of regioselectivity, $C(1) : C(2) : C(3) = 1 : 43 : 36$. When methylcyclohexane is used as the substrate, the high value of bond selectivity $1° : 2° : 3° = 1 : 28 : 560$ also indicates that free radicals do not participate in the reaction. Indeed, this parameter is $1 : 6 : 18$ for the *n*-Bu_4NVO_3–pyrazine-2-carboxylic acid–H_2O_2 system versus $1 : 20 : 520$ for the oxidation with the MCPBA alone. The mechanisms of alkane oxidation with free MCPBA and MCPBA in the presence of catalyst **1** are similar to each other as the reactions are stereoselective in both cases. In *cis*-decalin oxidation, for example, the value of the *trans/cis* parameter (defined as the [*trans*-decalol-9]/[*cis*-decalol-9] ratio, where [*trans*-decalol-9] and [*cis*-decalol-9] are the concentrations of corresponding tertiary alcohols) was 0.24. In the similar case of oxidation of *cis*-1,2-dimethylcyclohexane with MCPBA, the values of the *trans/cis* parameter for the uncatalyzed reaction and that catalyzed by complex **1** were 0.32 and 0.42, respectively.

Unlike iridium complex **1**, the zerovalent-palladium derivative $[(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P}]_4\text{Pd}$ (complex **2**) was active in the oxidation of alkanes with hydrogen peroxide at a temperature of 60°C. Total concentrations of cyclooctane oxygenation products measured at various reaction times are given in Table 2. The reaction mainly yields cyclooctyl hydroperoxide, as follows from the finding that the cyclooctanone concentration measured in the reaction mixture prior to its reduction with triphenylphosphine practically decreases to zero after the reduction of the reaction solution with triphenylphosphine. Only cyclooctanol is detected in the reduced solutions in this case. As is seen, the buildup of prod-

ucts (i.e., basically cyclooctyl hydroperoxide) lasts for 5 h; then the reaction ceases; and the amount of products even somewhat decreases, presumably owing to their subsequent transformations. The maximum turnover number attains 20. The oxidation of cyclooctane under the same conditions catalyzed by the divalent-palladium complex $[(C_6H_5)_3P]_2PdCl_2$ (**3**) led to the formation of cyclooctanol (3.0 mmol l^{-1}) and cyclooctanone (0.15 mmol l^{-1}) within 13 h. Since the ketone was found a small amount after reduction with triphenylphosphine, it may be concluded that the reaction mainly yields alkyl hydroperoxide and that only after it has run for 13 h does the peroxide slightly decompose to give cyclooctanone. The reaction with *n*-hexane and 3-methylcyclohexane predominantly gives the products of oxidation of methylene groups and tertiary C–H bonds in the first and the second substrate, respectively. Thus, the high regioselectivity and bond selectivity of this reaction suggests that the process does not involve free hydroxyl radicals. Oxidizing species can be the peroxo derivatives of palladium [10].

Complex **2** also shows the activity in the oxidation of alkanes with MCPBA. The reaction with cyclohexane at room temperature mainly gives cyclohexanol after reduction with triphenylphosphine (the turnover number reaches 15). It is interesting that (unlike the catalysis by iridium complex **1**) the reaction with *cis*-1,2-dimethylcyclohexane is not stereoselective (*trans*/*cis* ratio is 0.83). This finding leads to the conclusion that iridium and palladium catalyze the reactions of alkanes with MCPBA via different mechanisms. It is likely that the palladium-catalyzed oxidation involves the transfer of oxygen atoms from MCPBA to the palladium ion.

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