Brief Communications

Effect of substituents in the ligand on oxidation of alkanes catalyzed by binuclear oxo-bridged iron complexes

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Oxidation of alkanes (methane, ethane, hexane, and cyclohexane) by hydrogen peroxide and *tert*-butyl hydroperoxide in acetonitrile catalyzed by binuclear μ-oxo-bridged iron complexes $[Fe_2OL_4(H_2O)_2](ClO_4)_4$ and $[Fe_2OL_2(PhCOO)_2(H_2O)_2](ClO_4)_2$, where L = bpy, 4,4′-Me$_2$bpy, 4,4′-(ClCH$_2$)$_2$bpy, phen, and 5-NO$_2$phen, was studied. It was shown that the nature of the substituent in the ligand affects both the rate of the catalyzed peroxide decomposition and catalytic activity of the complexes studied in the alkane oxidation.

Key words: methane monooxygenase, alkane oxidation, iron complexes.

It has recently been found that binuclear μ-oxo-bridged iron complexes, analogs of the active center of methane monooxygenase (MMO), can catalyze selective oxidation of alkanes at 20 °C, but with low efficiency.[1–4] It was shown[5] in the case of chemical analogs of heme monooxygenase (cytochrome P-450) that electronegative substituents in porphyrin increase the rate of hydroxylation of alkanes by active oxygen donors catalyzed by iron and manganese complexes, owing to increase in the electrophilicity of the particle that attacks alkane. However, in the case of epoxidation of olefins with participation of manganese complexes with nonporphyrin ligands, no enhancement of the activity was observed with electron-acceptor halogenated ligands, contrary to what has been expected.[6]

The purpose of this work was to examine the effect of the nature of substituents on hydroxylation of alkanes, first of all methane, by hydrogen peroxide and *tert*-butyl hydroperoxide in the presence of binuclear iron complexes of the $[Fe_2OL_4(H_2O)_2](ClO_4)_4$ (**1**) and $[Fe_2OL_2(PhCOO)_2(H_2O)_2](ClO_4)_4$ (**2**) types with labile coordination sites (H_2O). Ligand L is the nitrogen base of the bipyridyl (bpy) or phenanthroline (phen) series: L = bpy (**a**), 4,4′-Me$_2$bpy (**b**), 4,4′-(ClCH$_2$)$_2$bpy (**c**), phen (**d**), and 5-NO$_2$phen (**e**).

All complexes were characterized by elemental analysis and visible, UV, and IR spectra (Table 1).

Table 1. Spectral parameters of complexes **1a**—**e**

Complex	λ_{max}/nm	ν_{as}(Fe—O—Fe)/cm^{-1}
1a	482 sh, 522 sh, 610 sh	825
1b	475 sh, 500 sh, 615 sh	830
1c	490 sh, 540 sh, 620 sh	820
1d	360 sh, 595 sh	820
1e	370 sh, 513 sh	820

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We have found that electron-acceptor substituents in bpy and phen increase considerably the time of peroxide decomposition (τ). This effect is similar to the influence of substituents in iron porphyrin complexes[7] and is related to the retardation of the limiting step of chain-radical decomposition of peroxide, *viz.*, reaction (1)

$$\mathrm{Fe^{II}} + \mathrm{ROOH} \longrightarrow \mathrm{Fe^{III}} + \mathrm{HO^{\cdot}} \qquad (1)$$

or reaction (2) (see below). The logarithm of the $1/\tau$, which has the dimensionality of pseudo-first-order reaction rate constant, correlates well with the Hammett parameter σ_p, and the points for bpy and phen fall almost on the same line (Fig. 1).

The effect of substituents on the activity of the catalysts studied in oxidation of methane, ethane, and cyclohexane was more complex (Table 2).

When Bu^tOOH was used instead of H_2O_2, the maximum turnover number with respect to products was 3 times as high, and the effect of the substituent in the ligand remained the same. The maximum turnover number was proportional to the pressure in the range of pressures of gaseous hydrocarbons studied. The value of catalytic activity of complex **1d** in the oxidation of hexane by hydrogen peroxide (3.6), as expected, occupied an intermediate position between the values for ethane and cyclohexane, while the regioselectivity of the attack at the corresponding C—H bonds, C(1) : C(2) : C(3) = 1 : 9.5±0.5 : 7.5±0.5, differed noticeably from that for the $HO^{\cdot}$ radical (1 : 5 : 5).

As follows from Table 2, in the case of methane the catalytic activity increases as the electronegativity of the substituent in the ligand increases, the reverse dependence is observed for cyclohexane, and ethane occupies an intermediate position, although this would rather characterize methane. It is also seen from Table 2 that for the most accepting nitro group the maximum turnover number for cyclohexane is only twice as high as that for methane, this number increases by more than 20-fold for the most donating methyl group. This result is most probably related to the fact that the reaction of catalyzed oxidation of alkanes occurs *via* several, at least two routes with different sensitivities to the nature of the metal complex.

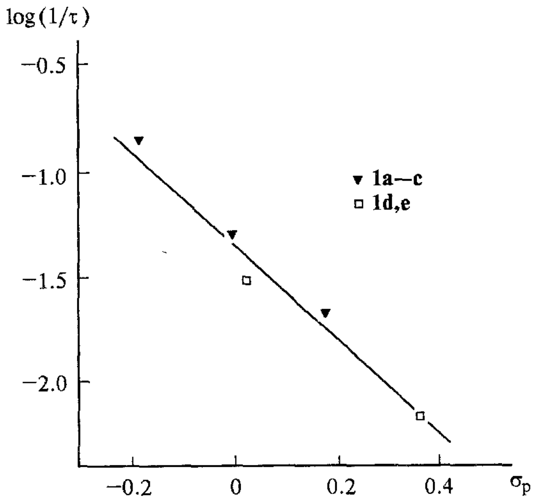

Fig. 1. Correlation between the time (τ) of decomposition of *tert*-butyl hydroperoxide catalyzed by complexes **1a—e** and Hammett constants (σ_p) of substituents in *para*-positions of bpy (**a—c**) or phen (**d,e**) ligands.

Table 2. Relative catalytic activity* of complexes **1a—e** in oxidation of alkanes by hydrogen peroxide ([Fe] 0.7 mmol L^{-1}, CH_4 52 atm,** C_2H_6 40 atm,** [*cyclo*-C_6H_{12}] 0.8 mol L^{-1}, [H_2O_2] 100 mmol L^{-1})

Complex	Substituent in the ligand	CH_4	C_2H_6	*cyclo*-C_6H_{12}
1e	NO_2	2.1±0.2	—	4.5±0.5
1c	CH_2Cl	1.7±0.2	2.3±0.5	8.5±1.0
1d	H	1.5±0.2	2.4±0.5	9.3±1.0
1a	H	1.4±0.2	2.0±0.5	11.0±1.0
1b	Me	0.6±0.1	2.0±0.5	14.2±1.0

* Calculated by dividing the total number of moles of products (alcohols and ketones) by the complex concentration during complete decomposition of peroxide (the maximum turnover number of the catalyst, average values of two to five experiments).

** Pressure at which the concentration of gaseous hydrocarbons approximately corresponds to that of cyclohexane (0.8 mol L^{-1}).

We suppose that two processes are imposed: (1) the transfer of an O atom from peroxide to the C—H bond of alkane with participation of the metal complex as a mediator and (2) the oxidation of alkane with participation of oxygen radicals that are formed in the catalyzed decomposition of peroxide. It should be mentioned for comparison that the 10—15-fold increase in the rate of the liquid-phase reaction with the Í Î· radical was expected on going from methane to hexane, and this increase should be even higher for less reactive radicals. Taking into account our data on the effect of the nature of the metal complex on the decomposition of *tert*-butyl hydroperoxide (see Fig. 1) and the fact that the radical-induced detachment of the H atom from the C—H bond should be more difficult for the strongest C—H bonds in methane, one can expect that the contribution of the oxygen transfer should increase on going from Me to nitro substituents and from *cyclo*-C_6H_{12} to CH_4 (see Table 2). In fact, this is the case. Moreover, it is seen that the oxidation rate is almost independent of the nature of the alkane in the case of the most accepting ligands, which was never observed for radical oxidation of alkanes but is typical of their biological oxidation.

A weak dependence of the oxidation rate on the nature of alkanes in the case of MMO has recently been rationalized on the basis of a new concept of the catalytic cycle of MMO. It is suggested that the active oxidant of MMO is not the ferryl complex, as in the case of cytochrome P-450, but binuclear bis-μ-oxo iron complex.[8,9] It is evident that further studies are necessary to elucidate, whether the complexes studied in this work mimic the mechanism of MMO. It is likely that the use of more accepting ligands should sufficiently enhance the catalytic activity of similar complexes. However, our attempts to synthesize the corresponding complexes were either unsuccessful or the complexes obtained were insoluble in acetonitrile, which was the medium for oxidation reactions. A relatively low turnover number for the oxidation of alkanes is associated with the competitive decomposition of peroxide catalyzed by the same complexes probably *via* the common intermediate:

$$\mathrm{Fe_2^{III}O + R'OOH \longrightarrow Fe_2^{IV}O(O) + R'OH}\ , \tag{2}$$

$$\mathrm{Fe_2^{IV}O(O) + RH \longrightarrow Fe_2^{III}O + ROH}\ , \tag{3}$$

$$\mathrm{Fe_2^{IV}O(O) + R'OOH \longrightarrow Fe_2^{III}O + R'OH + O_2}\ . \tag{4}$$

$$\mathrm{R' = H,\ Bu^t}$$

The best results obtained in the case of $\mathrm{Bu^tOOH}$ are explained by the low rate of its decomposition.

We also found that the catalytic activity of the complexes studied decreases approximately fivefold, when bridged carboxylates are introduced (type **2** complexes). This is likely explained by a decrease in the electrophilicity of the reactive intermediate.

Thus, the electrophilicity of the reactive intermediate plays an important role in the activation of C—H bonds of alkanes by nonheme systems, as is the case for iron porphyrin systems. The sensitivity of the catalytic activity toward the nature of a complex and the data on the regioselectivity of oxidation of hexane prove that certain iron complex containing active oxygen is involved in reactions with alkanes as an intermediate.

Experimental

Ligands **c** and **e** were prepared and purified by known procedures. The other ligands were commercially available (Aldrich), and they were used without additional purification. Complexes **1b,c,e** were synthesized by a procedure analogous to that used for preparing **1a** and **1d** (see Ref. 3), the only difference being that methanol was replaced by water as the reaction medium in the case of complex **1b**. Other complexes were obtained by the known procedures.[1—3] Liquid alkanes were oxidized in 5-mL closed glass vessels with magnetic stirring; gaseous alkanes were oxidized in metallic autoclaves with glass inserts. Products were analyzed on a Hewlett-Packard 5880A chromatograph with a flame-ionization detector and a capillary column (30 m×32 mm, Carbowax 20M as the stationary phase, high purity argon as carrier gas). The yields of products were determined as the sum of the amount of alcohol and ketone obtained in the oxidation of cyclohexane or as the amount of alcohols obtained following reduction of the products with sodium borohydride in the case of other hydrocarbons after completion of the reaction.

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