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PHOTO-OXIDATION OF CYCLOHEXANE BY AIR IN ACETONITRILE, CATALYSED BY π-COMPLEXES OF IRON*†

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Complexes $[(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_6H_6)]BF_4$, $[(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_5CH_3)]BF_4$ and $\{[1,2,4,5\text{-}(CH_3)_4C_6H_2]_2Fe\}(BF_4)_2$ catalyse the oxidation of cyclohexane to cyclohexylhydroperoxide, cyclohexanol and cyclohexanone during the light irradiation of solutions in CH_3CN.

Methods developed in recent years for the oxidation of saturated and alkylaromatic hydrocarbons with air oxygen during catalysis by different transition metal compounds and light irradiation are of great theoretical and practical interest [2–4]. There are individual known examples of the photo-oxygenation of alkanes and arylalkanes in the presence of cerium nitrate [5], a dithiolene complex of platinum [6], palladium or copper trifluoroacetate [7], peroxide complexes of palladium [8], and porphyrin complexes of iron [9]. However, the oxidation of saturated and alkylaromatic hydrocarbons during photocatalysis by polynuclear oxo complexes (see recent papers by us [1, 10–14] and work by other authors [15–18]) and by certain transition metal chlorides [12, 19–24] have been studied in most detail. The mechanism of oxygenation of alkanes (to alkylhydroperoxides), photocatalysed by polyoxometallates, is relatively simple. In this case, the key stage is hydrogen atom detachment from the alkane RH by a photoexcited radical-like oxo complex particle

$$M^{VI} = O \xrightarrow{h\nu} [M^{VI} = O]^* \equiv M^{V} - O^{\cdot}$$

$$M^{V} - O^{\cdot} + RH \rightarrow M^{V} - OH + R^{\cdot}$$

Alkyl radicals react readily with molecular oxygen, and the reduced oxo complex derivative produced can be reoxidized by oxygen or a peroxide radical. As a result, an alkylhydroperoxide molecule and a catalytically active oxo complex particle are formed:

$$R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$$

$$M^{V} - OH + ROO^{\cdot} \rightarrow M^{VI} = O + ROOH$$

$$M^{V} - OH + O_2 \rightarrow M^{VI} = O + H_2O.$$

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The mechanism of the chloride complex-catalysed oxygenation of alkanes is less clear. In the case of photocatalysis by an $FeCl_3$ compound, the following states of the process can be assumed in a fairly simplified way: photohomolysis of the Fe–Cl bond, detachment of the hydrogen atom from the alkane RH by a chlorine atom, reaction of the alkyl radical with O_2, and, finally, reoxidation of Fe(II) to Fe(III).

$$FeCl_3 \xrightarrow{h\nu} FeCl_2 + Cl^\bullet$$

$$Cl^\bullet + RH \rightarrow Cl^- + H^+ + R^\bullet$$

$$R^\bullet + O_2 \rightarrow ROO^\bullet$$

$$FeCl_2 + ROO^\bullet + Cl^- + H^+ \rightarrow FeCl_3 + ROOH$$

$$FeCl_2 + Cl^- + H^+ + O_2 \rightarrow FeCl_3 + H_2O.$$

Detachment of the hydrogen atom from the alkane seems to proceed by a much more complex mechanism (see [25, 26]). However, since, according to [27], during the oxidation of cyclohexane the absorption spectrum of the reaction solution does not change at least in the first hours of the reaction, and the accumulation of oxygenation products occurs without an induction period and linearly [12], it can be assumed that, in the case of this photocatalyst, it is the trivalent iron derivative that is the catalytically active particle. Furthermore, this derivative must contain a chloride ligand, since $FeBr_3$, for example, is not capable of photocatalysing the oxygenation of cyclohexane [20] (note that the sudden acceleration of oxidation when hydroquinone is added, described earlier in [20], seems to be due not to the reduction of iron to its bivalent form, but to the formation of a "quinone–transition metal complex" system effectively photohydroperoxidising the alkanes [28]). In contrast to $FeCl_3$-catalysed oxygenation, with photocatalysis by the complexes $CuCl_2$, $AuCl_4^-$ and $PtCl_6^{2-}$, as early as in the first minutes of the reaction there are sharp changes in the absorption spectra, which possibly reflect transition of the metal ion to a lower degree of oxidation [27]. Here the oxidation rate can even increase. It is therefore possible for oxygenation to be catalysed by metal complexes in a low degree of oxidation.

In view of the above it was of interest to attempt to find a hydrocarbon oxygenation photocatalyst in the form of a transition metal complex with a low degree of oxidation and not containing chloride ligands. In the present work an investigation was made of the photocatalytic activity in oxidation of certain π-complexes of iron(II) with cyclopentadienyl and/or arene ligands. Preliminary results were published earlier in a brief report [29].

EXPERIMENTAL

Photo-oxidation was carried out in air in cylindrical glass vessels with sleeves cooled by running water (~15°C) during intense stirring using a magnetic stirrer. Irradiation was carried out with the full light of a luminescent lamp (125 W) or a high-pressure mercury lamp (1000 W). The concentration of the oxidation products formed was determined by means of GLC, and here, to assess the quantity of alkylhydroperoxide, each specimen was analysed twice — before and after reduction of the reaction solution by excess triphenylphosphine (see [12]). Use was made of an LKhM-80-6 chromatograph (sorbent INERTON AW-HMDS 0·2–0·315 mm, impregnated with 5% Carbowax 1500, column 2 m × 4 mm, carrier gas argon).

RESULTS AND DISCUSSION

In the present work, in the photo-oxygenation of alkanes and alkylaromatic compounds with air oxygen, the photocatalysts employed were iron(II) complexes not containing chloride ligands: cyclopentadienylbenzeneiron in the form of tetrafluoroborate salt: $[(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_6H_6)]BF_4$(I) produced as described in [30], cyclopentadienyltolueneiron $[(\pi\text{-}(C_5H_5)Fe(\pi\text{-}C_6H_5CH_3)]BF_4$(II) [30] and bisdureneiron $\{[\pi\text{-}(CH_3)_4C_6H_2]_2\}Fe(BF_4)_2$(III) [31]. In all cases, a catalyst concentration of 5×10^{-4} mole/l was used.

The kinetics of accumulation of cyclohexane oxygenation products with photocatalysis by complex I and luminescent lamp irradiation is shown in Fig. 1*a*. It is clear that, in the first hours of the reaction, only cyclohexylhydroperoxide accumulates, and this then begins to decompose, yielding cyclohexanol and cyclohexanone that are stable under these conditions. Within 14 hr irradiation, $2{\cdot}9 \times 10^{-3}$ mole/l of cyclohexane oxidation products is formed in total. It is interesting that, during irradiation with the full light of a high-pressure mercury lamp of higher power in a glass vessel ($\lambda > 310$ nm), the reaction is not more rapid ($2{\cdot}5 \times 10^{-3}$ mole/l of products within 14 hr of irradiation). Oxidation in the presence of catalyst II proceeds at virtually the same speed. Ethylbenzene is oxygenated slightly more rapidly under these conditions (a total of 4·2 mole/l of ketone, alcohol and hydroperoxide — substitution by the α-methylene group).

It is significant that the form of the curves of cyclohexane oxidation (light irradiation with a luminescent lamp) in the presence of complex III differs considerably from the curves for the

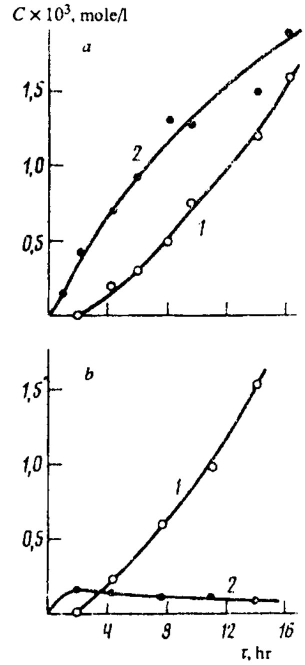

FIG. 1. Kinetics of accumulation of cyclohexanol and cyclohexanone (in total, curves *1*) and cyclohexylhydroperoxide (curves *2*) during the photo-oxidation (full light of luminescent lamp) of a solution of cyclohexane (0·46 mole/l) in CH_3CN in the presence of cyclopentadienylbenzeneirontetrafluoroborate (*a*) and bisdureneirontetrafluoroborate (*b*). Catalyst concentration 5×10^{-4} mole/l.

case of catalyst I (cf. Fig. 1*a* and *b*). Catalysis by complex III is less efficient, and the cyclohexylhydroperoxide accumulating at the start of the process quickly begins to break down.

The results obtained in the present work may indicate that the mechanism of oxygenation catalysed by iron(II) π-complexes differs fundamentally from the mechanism of catalysis by iron(III) chloride. In fact, in the first case, oxidation proceeds much more slowly. It can be assumed that, in the case of complexes I and II, during irradiation of the solution in acetonitrile, at the first stage the replacement of an arene ligand by CH_3CN occurs. It is therefore not surprising that the two complexes exhibit the same catalytic activity. Note that photochemical conversions of cyclopentadienylarene complexes of iron have been studied in fair detail (see, for example, [32] and references in this paper). Here a coordination-unsaturated particle, for example $[(\pi\text{-}C_5H_5)(CH_3CN)_2Fe]^+$, can arise. If this particle adds an oxygen molecule, a metal-containing radical with an Fe–OO* fragment arises. In the case of complex III, both labile arene ligands can split off, and a coordination-unsaturated particle can arise. For complexes I–III in general it is possible to write the formation of a peroxide derivative as

$$L_nFe^{II} + O_2 \rightarrow L_nFe^{III} - OO^{\cdot}.$$

This radical is able to detach the hydrogen atom from the alkane molecule in the solution:

$$L_nFe^{III} - OO^{\cdot} + RH \rightarrow L_nFe^{III} - OOH + R^{\cdot}$$

Note that a similar process was assumed for oxygenation by a vanadium peroxide complex [33]. Then it seems to be possible to visualize the stage of detachment of the OOH fragment from a metal ion by an alkyl radical:

$$L_nFe^{III} - OOH + R^{\cdot} \rightarrow L_nFe^{II} + ROOH$$

and the reaction of this radical with an oxygen molecule with subsequent conversions (DH is the donor hydrogen atom (see, for example, [34])):

$$R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$$

$$2ROO^{\cdot} \rightarrow R'R''CHOH + R'R''CO + O_2$$

$$ROO^{\cdot} + DH \rightarrow ROON + D.$$

All these processes lead to the formation of both alkylhydroperoxide and stable alcohol and ketone. The iron complex is capable of breaking down the alkylhydroperoxide formed, its activity in this process evidently depending strongly on the ligand surroundings of the iron ion. This difference is reflected in the kinetic curves of product accumulation with catalysis by complexes I and II.

In conclusion, note that, as we found, a similar ruthenium(II) complex $[(\pi\text{-}C_5H_5)Ru(\pi\text{-}C_6H_6)]PF_6$ [35] of known photoactivity (see [36]) exhibits no catalytic activity in the photooxygenation of alkanes.

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