

MOLYBDENUM HEXACARBONYL CATALYZED PHOTOOXYGENATION OF  
CYCLOHEXANE BY AIR DIOXYGEN IN ACETONITRILE SOLUTION

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Under irradiation, cyclohexane is oxidized by air oxygen in acetonitrile in the presence of catalytic amount of  $\text{Mo}(\text{CO})_6$ . After the induction period cyclohexanol and cyclohexanone are formed in approximately equal quantities. The catalytically active species is likely to be peroxy (or oxo) complexes of molybdenum.

При облучении светом циклогексан окисляется кислородом воздуха в растворе в ацетонитриле в присутствии каталитических количеств  $\text{Mo}(\text{CO})_6$ . После индукционного периода образуются циклогексанол и циклогексанон примерно в равной пропорции. Каталитически активной частицей, возможно, является пероксидный (или оксо) комплекс молибдена.

Recently we have shown that alkanes and arylalkanes can be oxygenated to form alcohols and ketones if the solutions of these substrates in acetonitrile, methylene chloride or acetic acid are irradiated in air in the presence of catalytic amounts of metal oxo-compounds ( $\text{CrO}_3$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{Cr}_4\text{O}_{13}^{2-}$ ,  $\text{PW}_{12}\text{O}_{40}^{3-}$ ,  $\text{PMo}_6\text{V}_5\text{O}_{39}^{12-}$ ,  $\text{VO}_3^-$ ,  $\text{UO}_2^{2+}$ , etc.) [1-6] or chloride complexes ( $\text{FeCl}_3$ ,  $\text{AuCl}_4^-$ ,  $\text{CuCl}_2$ ,  $\text{PtCl}_6^{2-}$ ,  $\text{RhCl}_3$ , etc.) [6-11]. It should be noted that recently the polyoxometalates catalyzed photooxygenation of alkanes or arylalkanes by dioxygen has also

been described by three other groups of authors [12-14].

In the case of photooxygenation catalyzed by high-valent metal complexes, the reaction mechanism is likely to include the detachment of hydrogen atom by the photoexcited complex (with participation of O or Cl ligands) and the subsequent reaction of  $R^{\cdot}$  with  $O_2$  to produce  $ROO^{\cdot}$  radicals. The latter can oxidize the reduced metal complex to yield  $ROO^-$  and the initial form of the photocatalyst. However, during the photooxygenation reaction catalyzed by  $CuCl_2$ ,  $AuCl_4^-$  or  $PtCl_6^{2-}$ , one can observe changes in the absorption spectra of the reaction solution and a decrease in the accumulation rate of products [10]. In the presence of  $FeBr_3$ , cyclohexane is not photooxygenated and for the reaction in the presence of  $CuBr_2$  the kinetic curve has a long induction period. When adding a reducing agent (hydroquinone) to the reaction mixture, photooxygenation takes place in both cases. These data suggest that during the initial period the metal complex is reduced by hydrocarbon and then a low-valent metal compound is responsible for the oxygenation process (it is possible that both low- and high-valent complexes act simultaneously as photocatalysts). Indeed, it is a well-known fact that copper(I) complexes coordinate dioxygen [15]. Thus it appeared that in our photoreaction peroxy- or oxo-species can be active.

Here we present preliminary results of our experiments with oxygenation of alkanes catalyzed by low-valent metal complexes under irradiation. Molybdenum hexacarbonyl  $Mo(CO)_6$  was used as a photocatalyst. It should be noted that this complex was used previously to induce thermal hydroxylation of benzene by dioxygen to produce phenol [16]. Photooxygenation of cyclohexane was performed in acetonitrile solution in air. Reactions were carried out in a glass cylindrical reaction vessel with a water-cooled ( $T \sim 15^{\circ}C$ ) jacket under stirring. Light from a DRSh-1000 (1000 W) high-pressure mercury arc lamp was used for irradiation. Products were identified using gas-liquid chromatography on a LKhM-80-6 chromatograph.

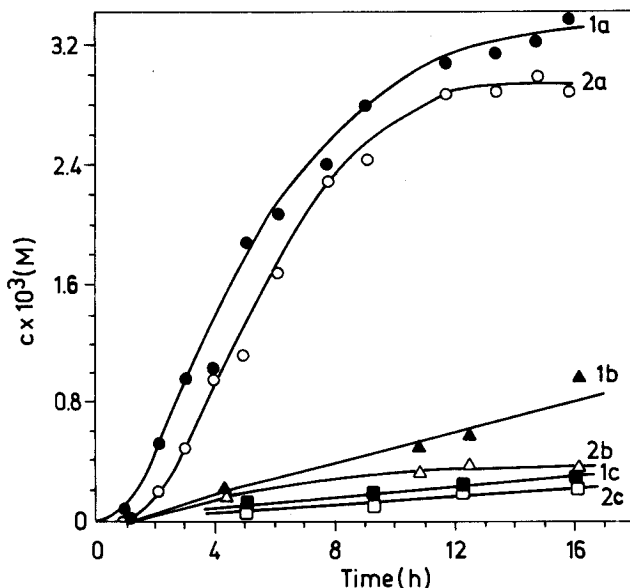


Fig. 1. Kinetic curves of cyclohexanol (1) and cyclohexanone (2) formation in photoreaction of cyclohexane (0.46 M) with dioxygen of air in  $\text{CH}_3\text{CN}$  in the presence of  $\text{Mo}(\text{CO})_6$  (a -  $5 \times 10^{-4}$  M; b -  $1 \times 10^{-4}$  M; c - without photocatalysts)

Kinetic curves for accumulation of cyclohexane oxidation products are illustrated in Fig. 1. Cyclohexanol and cyclohexanone are formed in approximately equal amounts. Kinetic curves have an induction period. It should be noted that after about 1 h irradiation the reaction solution turns blue and the absorption spectrum exhibits a new band at 700 nm. The catalytically active species are rather unstable and after about 12 h irradiation the photooxidation process stops. During this period approximately 12 mol oxidation products per mol  $\text{Mo}(\text{CO})_6$  are formed.

One can suggest that the first stage of the oxidation reaction is the loss of one or two carbon monoxide ligand under the effect of light quanta on the molybdenum carbonyl molecule.

Then coordinatively unsaturated species can add a dioxygen molecule to produce a peroxy-complex, e.g.  $(OC)_x MoO_2$ . Under irradiation the latter will oxygenate alkane. If the coordinatively unsaturated species  $Mo(CO)_x$  ( $x < 6$ ) is regenerated after oxygenation, the process will be catalytic. Allylic thermal oxygenation of cyclohexene by peroxy-compounds obtained from the low-valent phosphine complexes of Pt(0) was described in [17]. Peroxy-complex can also be transformed into an oxo-derivative and in this case the mechanism will be similar to that for the photoreactions catalyzed by oxometalates [1-6, 12-14]. In this case the blue color of reaction solution can be due to a reduced form of an oxometalate. The mechanism of the above reaction needs further investigation. Studies of photooxygenation of alkanes and other compounds in the presence of various metal carbonyls is in progress in this laboratory.

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