

**PHOTOCATALYTIC OXIDATION OF CHLORINATED PHENYLALKANES
WITH DIOXYGEN**

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The photocatalytic oxidation of some chlorinated derivatives of the following mono- and biphenyl-substituted alkanes - 1-chloro-4-ethylbenzene (CEB); 4,4'-ichlorodiphenylmethane (DDM); 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (DDT) – with dioxygen in the presence of the photocatalyst – heterogenized dioxo-Mo organometallic complex (dioxo-molybdenum(VI)-dichloro[4,4'-dicarboxylato-2,2'-bipyridine]) anchored on the photosensitive TiO₂ support under UV-irradiation ($\lambda = 253.7 \text{ nm}$) has been investigated. The catalytic role of the anchored on Mo-metal-organic complex in the selective activation of the benzylic C-H bonds of these compounds with the formation of the corresponding oxygenated products in mild conditions has been shown.

The catalytic cycle consists of two successive stages, involving the oxidation of substrate by the oxo-atom transfer from dioxo-Mo(VI)-complex under UV-irradiation and regeneration of the reduced Mo(IV)-center by the oxidation with dioxygen in the dark. Experimentally, these two stages are separated in time. It has been shown that under these conditions even such a persistent pollutant as DDT can be selectively oxidized to dicofol, which is currently not available by other ways. The possible mechanism suggested for this group of reactions is discussed. It has been suggested that the formation of oxo-peroxo-Mo(VI) moieties, apparently, enhances the oxo-atom transfer from the Mo-complex to the substrate.

Figs. 3, table 1, references 11.

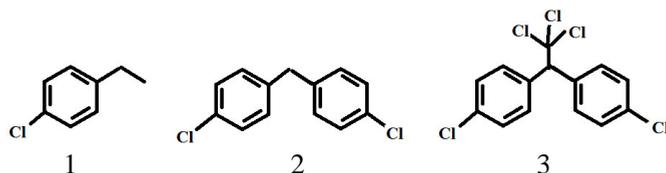
Introduction

Chlorinated derivatives of mono- and biphenyl-substituted alkanes are used as pesticides, dyestuffs; they are also used in various chemical syntheses [1]. The wide use of them causes different environmental problems [2,3]. One of the ways to neutralize these compounds is photocatalytic oxidation or oxidative destruction by air or oxygen. The existing methods for the transformation of these compounds to corresponding oxygenates in industrial scale are usually multistage complex

processes. For example, the transformation of DDT to dicofol (2,2,2-trichloro-1,1-bis-(4-chlorophenyl)ethanol) occurs as a four stages complex process [4].

Selective activation and functionalization of the benzylic C-H bonds of these compounds [5] permits directly to synthesize a great number of different halogenated derivatives of aromatic alcohols, ketones, carboxylic acids, etc.

In this work the oxidation of 1-chloro-4-ethylbenzene(chloroethylbenzene (CEB)- 1), 4,4'-dichlorodiphenylmethane(dichlorodiphenylethane (DDM)-2) and 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (dichlorodiphenyltrichloroethane (DDT)- 3)



1- CEB; 2-DDM; 3-DDT.

with dioxygen was tested in the presence of the photocatalyst: dioxo-Mo(VI)-dichloro[4,4'-dicarboxylato-2,2'-bipyridine] complex, anchored on TiO_2 (Fig. 1) under UV-irradiation ($\lambda = 253.7 \text{ nm}$). The catalytic activity of dioxo-molybdenum(VI) complexes in the presence of dioxygen was well known in oxidation reactions of the organic compounds, such as alkylarenes, olefins, alcohols, phosphines, etc., in homogeneous conditions (in different solvents) [6,7]. The applied catalyst is a heterogenized modification of a dioxo-Mo(VI) organometallic complex on the photosensitive material like TiO_2 [8].

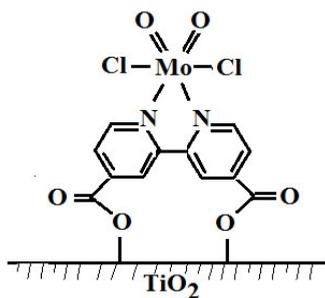


Fig. 1. Complex 1. Dioxo-Mo(VI)-dichloro[4,4'-dicarboxylato-2,2'-bipyridine] complex, anchored on TiO_2 surface.

Being a photosensitive material, TiO_2 promotes oxo-atom transfer reactions via enhanced electronic flux from support onto the molybdenum coordination sphere under UV or visible light irradiation [6-8].

The catalytic action of the anchored complex is based on the redox capacity of the Mo-active centers, performing catalytic cycle ($\text{Mo}^{\text{VI}} \rightleftharpoons \text{Mo}^{\text{IV}}$) in the presence of dioxygen.

In the above context, the aim of this work is examination of the possibility of catalytic oxidation, or oxidative destruction of the mentioned chlorinated mono- and biphenyl-substituted alkanes, directly with the cheapest oxidant, like dioxygen, in

mild conditions, under UV-irradiation or visible light, using heterogenized transition metal complexes on the photosensitive support.

Experimental Section

The experimental studies of the photocatalytic oxidation and oxidative destruction of 1-chloro-4-ethylbenzene (CEB); 4,4'-dichlorodiphenylmethane (DDM); 1,1,1-trichloro-2,2-bis (p-chlorophenyl)ethane (DDT) with dioxygen were performed in a reaction vessel (quartz, 30 mL) with a magnetic stirrer. The source of UV-irradiation was high pressure Hg-lamp DRT- 230. $\lambda = 253.7 \text{ nm}$ irradiation was applied. The experimental setup was described in previous works [9].

The dioxo-molybdenum(VI)-dichloro-[4,4'-dicarboxylato-2,2'-bipyridine] complex, anchored on the TiO_2 was synthesized by the transesterification of trimethylsilylated titania with the carboxylic ligand, giving trimethylsilanol (eliminated as hexamethyldisiloxane and water), then, the complexation was done by treating the anchored complex with a tetrahydrofuran solution, containing the calculated amount of MoO_2Cl_2 [10]. The method for the synthesis, as well as characterization of the obtained samples by a number of spectroscopic methods (^{13}C CAP NMR, FTIR and others) was also described in our previous works. The chemical and thermogravimetric analyses were performed for determination of the quantities of this complex on the surface of TiO_2 .

The typical experiment was carried out by the following sequence of stages. The reaction mixture was exposed to UV-irradiation under stirring conditions and in the absence of dioxygen for 6-7 h. It was a suspension of the mentioned chlorinated alkanes (about $\text{N} \times 10^{-5} \text{ mol}$) in acetonitrile, containing 10 mg of Complex 1. This was the first stage (period) of the experimental cycle. The second stage (period) was regeneration of the used catalyst in the presence of oxygen (2-2.5 h) in the dark. Before the beginning of every new experimental cycle, dioxygen was removed from the reaction medium and replaced by argon or helium. Identification and qualitative analyses of the reaction products were mostly carried out by gas-liquid chromatography and mass-spectrometry.

Results and Discussion

All observation tests of the consumption of substrates and formation of products in interactions of the chosen compounds with dioxygen, in the absence of the anchored complex, were negative in comparable experimental conditions. In the presence of "pure" TiO_2 (without anchored complex), as well as under UV-irradiation, the conversion of the initial substrates and detected products was quantitatively about two or three orders lower than in experiments with the anchored complex, with the exception of DDT. In the latter case, the conversion of DDT was no more than 5-7% in the time intervals comparable with the experiments with anchored complex.

In experiments with 1-chloro-4-ethylbenzene (CEB), in the first period of the first experimental cycle, the chromatographic and chemical analyses showed formation of $\text{Cl-C}_6\text{H}_5$, accompanied with small quantities of $\text{Cl-C}_6\text{H}_4\text{-CH(-OH)-CH}_3$ and $\text{Cl-C}_6\text{H}_4\text{-C(=O)-CH}_3$, traces of $\text{Cl-C}_6\text{H}_4\text{-CH(O-OH)-CH}_3$ and other chlorinated derivatives of the oxygen containing aromatic organic compounds, as well as CO_2 , H_2O . No Cl^- ions were found in the reaction zone. The time evolution profiles of some products in the first and consequent experimental cycles are presented in Fig. 2. The horizontal sections on the curve of the main reaction product, chlorobenzene, corresponding to the second time-periods (“dark” reaction) of the experimental cycles, the aim of which was re-oxidation of Mo(IV) , formed in the first periods, into Mo(VI) with dioxygen, indicate practically the absence of the accumulation of the product. Contrarily, in the first periods of the second and consequent experimental cycles the amounts of the product permanently increase under UV irradiation in argon atmosphere.

The analyses showed that about 0.5 mol of CEB was transformed into products per 1 mol of the Mo-complex at the first period (about 7 h of experiment) of the first experimental cycle.

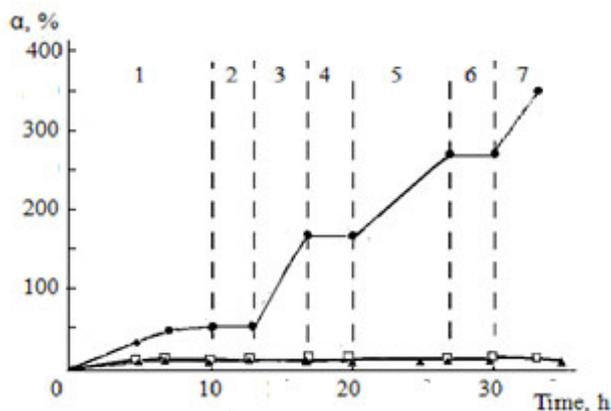
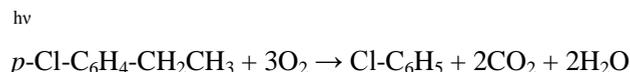


Fig. 2. Time evolution profiles of products: $\text{Cl-C}_6\text{H}_5$ (●), $\text{Cl-C}_6\text{H}_4\text{-C(O)-CH}_3$ (□), $\text{Cl-C}_6\text{H}_4\text{-CH(OH)-CH}_3$ (▲) on oxidative decomposition of 1-chloro-4-ethylbenzene. 1; 3; 5; 7: periods under UV irradiation and argon; 2; 4; 6: periods of O_2 flow, in the dark. $\alpha = ([\text{final product}] \text{ mmol} / [\text{dioxo-Mo-complex}] \text{ mmol}) \times 100$ (%).

The qualitative and quantitative analyses indicate the existence of the stoichiometric relations between the products in the following reaction:

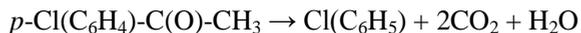


Thus, one of the main products of this reaction is chlorobenzene. Usually the main products of the oxidation of the aromatic hydrocarbons in the presence of Complex I correspond to alcohols or ketones [5-7,11].

Apparently, the formation of chlorobenzene is a result of the oxidative destruction of other intermediates, such as 4'-chloroacetophenone and 1-(4-

chlorophenyl)ethanol. This hypothesis has been verified by studying the photocatalytic decomposition of the 1-(4-chlorophenyl)ethanol in the same experimental conditions, under argon atmosphere, in the presence of Complex I. The following reaction may be written on the basis of the obtained data:

$h\nu, 4[O]$



where [O] is oxo-atom in Complex 1. On the other hand, in analogous conditions, under visible light, ethylbenzene produces acetophenone, as a main product of the reaction [10, 11].

The multiple increase of the turnover number (ratio of [substrate] mmol/[anchored complex] mmol) in the second and consequent experimental cycles indicates that Complex 1 plays the role of a catalyst in the presence of dioxygen in oxidative destruction of CEB. Apparently, it occurs by the oxygen atom transfer to benzylic carbon by the formation of the chlorinated phenyl alcohol and ketone, which in their turn form all observed varieties of the decomposition products.

The oxidation of 4,4'-dichlorodiphenylmethane (DDM), in the same experimental conditions, showed analogous behavior, nearly repeating the form of the above presented time profile, obtained for CEB: the consumption of initial substrate and formation of reaction products in the first periods of the experimental cycles, and practically absence of the conversion of a substrate in the second periods. Composition of the products was relatively more complex for this compound than for CEB. The main reaction products were 4,4'-dichlorodiphenylmethanol, 4,4'-dichlorobenzophenon, chlorobenzene, as well as the products of complete oxidation, CO₂ and H₂O. Taking into account the results of all other experiments without anchored complex, on "pure" TiO₂, under UV-irradiation or in its absence, it may be concluded that the anchored complex plays the catalytic role in oxidative decomposition of DDM.

The reaction of DDT with oxygen was investigated in more detail, proceeding from its practical importance. The results obtained in 5 consecutive cycles are presented in Fig. 3. The curve (b) corresponds to the photochemical oxidation of DDT on the surface of "pure" TiO₂ (without anchored Complex 1), in the presence of dioxygen. Note, the amount of the "pure" TiO₂ in the reaction mixture was twice as much than that in experiments with Complex 1. The simple comparison of two curves indicates a significant increase of the consumption of DDT in the presence of the anchored complex (curve (a)), reaching 32% of the initial amount of the substrate. The post-reaction mixture, in this case, contains not only chlorinated products and Cl-ions, but also non-chlorinated organic compounds (C₁-C₁₄), CO₂, and H₂O. As the results show, the sum of a dozen dechlorinated products was about 53-57%. Correspondingly, other products (43-47%) were non-dechlorinated and partially dechlorinated compounds.

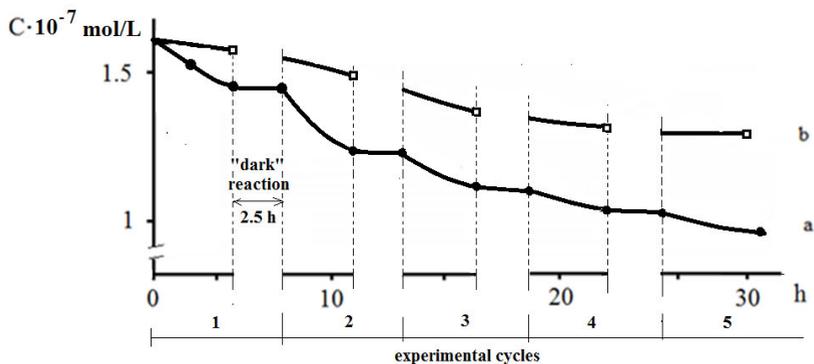
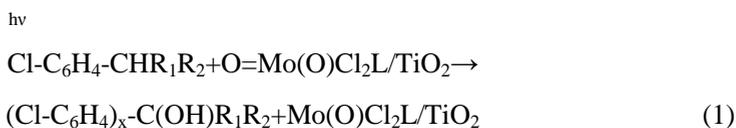


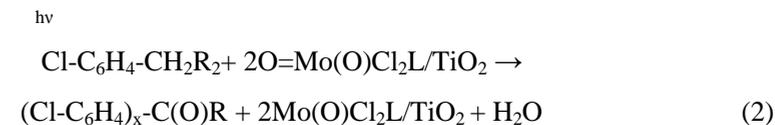
Fig. 3. Time profiles of the consumption of DDT ($C \times 10^{-7}$ mol/L), under UV-irradiation: (a) - in the presence of the anchored Complex (1); (b) - in the presence of the "pure" TiO_2 (in amounts 2 times more than Complex 1) with O_2 .

The main product of the reaction dicofol (2,2,2-trichloro-1,1-bis(4-chlorophenyl)ethanol), (21 mol %), apparently, was also playing the role of an intermediate for the formation of a number of other chlorinated and non-chlorinated products. Note, under the same conditions, but in the absence of the anchored complex (on the "pure" TiO_2), the formation of dicofol was very slow, and the reaction gave a more complex mixture of other oxidative/reductive decomposition products, including the products of the complete degradation in small amounts.

The above results of the oxidation and oxidative destruction of CEB, DDM and DDT permit to conclude that the primary reaction in the interaction of Complex 1 with substrate is the formation of the corresponding oxygenated products, such as alcohols and often ketones, via photo-stimulated O-atom transfer from the anchored complex to substrate (reactions 1).



where, $\text{R}_1 = \text{H}$, $\text{R}_2 = \text{CH}_3$ for CEB; $\text{R}_1 = \text{H}$, $\text{R}_2 = \text{ClC}_6\text{H}_4$ for DDM; $\text{R}_1 = \text{CCl}_3$, $\text{R}_2 = \text{ClC}_6\text{H}_4$ for DDT; L is 4,4'-dicarboxylato-2,2'-bipyridine ligand of Complex 1. For compounds $\text{R}_1 = \text{H}$, the formation of ketenes may take place (reaction 2)



Correlation between the yield of dicofol and turnover number ($\Delta[\text{DDT}]/[\text{anchored complex}]$) in experimental cycles, is presented in Table 1. The turnover number in the second cycle increases more than two times after the re-oxidation in the second period of the first cycle, becoming 2.13 from 0.63 (Table 1), while it could be no more than 2, or no more than 1 for only one cycle, taken

separately, in consideration that the reaction (1) is a predominant way of the consumption of DDT. In other words, the consumption of DDT quantitatively exceeds the initial stoichiometric quantities of the reaction (1), which proceeds under UV-irradiation, after the “dark” reaction, in the absence of dioxygen.

Table 1

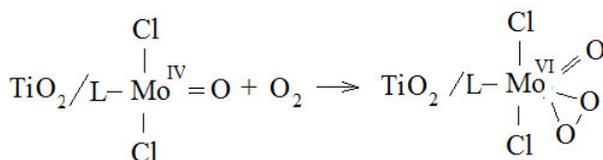
Experimental data of the dependence of the turnover number ($\Delta[\text{DDT}]/[\text{anchored complex}]$) and the yield of dicofol on the number of experimental cycles (the reaction time (h) is given in parentheses)

Number of the experimental cycles	1	2	3	4	5
Turnover number	0.63 (5)	2.13(11)	2.58(17)	3.38(23)	3.68(32)
Yield of dicofol (<i>mole %</i>)	9.5	13.5	15.4	18.2	21.0

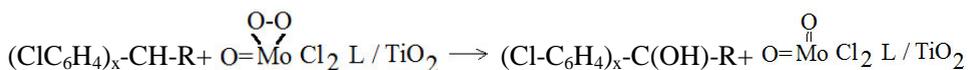
It is noteworthy that the yield of dicofol also increases (about 1.42 times) with the increase of the consumed amount of DDT in the nearly the same reaction time interval in the first period of the second cycle. In further experimental cycles, apparently, the different reaction channels of oxidation and decomposition become more significant than the selective formation of dicofol by the reactions (1)-(3).

Nearly analogous situation can be observed in experiments of the oxidative destruction of CEB (Fig. 1). The accumulated amounts of the main product 4'-chlorobenzene in the first period of the second experimental cycle were more than possible stoichiometric amounts of the reactions (1)-(2).

These facts permitted to assume that in the second periods of the experimental cycles, the re-oxidation with dioxygen of the reduced Mo(IV) into Mo(VI) occurred by the formation of the oxo-peroxo-Mo(VI) moiety in coordination sphere of the anchored complex.



As a result, the capacity of Complex 1 in oxygen atom transfer reactions may be either doubled or, at least, noticeably increased. In this regard, the primary reaction in the first periods of the second and consecutive experimental cycles may be represented as:



Although the main peculiarities of the photocatalytic oxidation or/and oxidative destruction by the applied catalyst for the mentioned three compounds, in general, are similar, the oxidation of DDT exhibits some important differences. For example, the post-reaction mixture also contains products of the reductive decomposition, such as DDE (1,1-dichloro-2,2-bis(p-chloro-phenyl)ethylene about 9%), DDD (1,1-

dichloro-2,2-bis-(p-chlorophenyl)ethane), DDM (2,2-bis-(p-chlorophenyl)methane, diphenylmethane), and others, summarily about 13-14%.

Conclusions

As it was shown on the given examples, in photocatalytic oxidation of the mentioned compounds, the main primary reaction occurs by the selective activation and functionalization with the anchored Complex 1 of the benzylic (or bibenzylic) C-H bond, producing alcohols or ketones via oxo-atom from transition-metal to substrates. Note that, in this case, the chlorophenyl fragments of the mentioned compounds may rest untouched in the formation of the main products of primary reaction.

In the aspects of the reaction mechanism, the observed acceleration of the reaction in the first periods of the second and consequent experimental cycles may be assigned to the formation of oxo-peroxo-Mo(VI) moieties in coordination sphere of the complex in the second periods, which, apparently, are more active in oxo-atom transfer reactions to benzylic carbon-atom.

ՔՆՈՐԱՅՎԱԾ ԱԼԿԱՆՆԵՐԻ ՖՈՏՈԿԱՏԱԿԱԼԻԶԱՅՅԻՆ ՕՔՍԻԴԱՅՈՒՄԸ Թ-ՎԱԾՆՈՎ

Լ. Ա. ՄԱՆՈՒՉԱՐՈՎԱ, Ռ. Ա. ԲԱԽՉԱԶՋԱՆ և Լ. Ա. ԹԱՎԱԴՅԱՆ

Ուսումնասիրվել է մոնո- և դիֆենիլտեղակալված ալկանների որոշ քլորացված ածանցյալների 1-քլոր-4-էթիլբենզոլ; 4,4'-դիքլորդիֆենիլմեթան; 1,1,1-տրիքլոր-2,2-բիս (p-քլորֆենիլ)էթան ֆոտոկատալիզային օքսիդացումը թթվածնով, հետերոգենացված դիօքսո-Մո-մետաղօրգանական կոմպլեքս (դիօքսո-մոլիբդեն(VI)-դիքլոր[4, 4'-դիկարբոքսիլատո-2,2'-բիպիրիդին]) TiO_2 լուսազգայուն կրիչի վրա ֆոտոկատալիզատորի ներկայությամբ, ՈւՄ ($\lambda = 253.7$ նմ) ճառագայթման տակ: Ցույց է տրվել, որ այդ միացությունների բենզիլային C-H կապի ընտրողական ակտիվացման մեջ խարսխված Մո-մետաղօրգանական կոմպլեքսի կատալիտիկ դերը մեղմ պայմաններում համապատասխան օքսիդների առաջացմամբ: Քննարկվել են այս խմբի ռեակցիաների հնարավոր մեխանիզմները: Առաջարկվել է, որ օքսո-պերօքսո-Մո(VI) մասնիկների ձևավորումն, ըստ երևույթին, խթանում է օքսո-ատոմի փոխանցումը Մո-կոմպլեքսից դեպի սուբստրատ:

ФОТОКАТАЛИТИЧЕСКОЕ ОКИСЛЕНИЕ ХЛОРИРОВАННЫХ ФЕНИЛАЛКАНОВ КИСЛОРОДОМ

Л. А. МАНУЧАРОВА, Р. А. БАХЧАДЖЯН и Л. А. ТАВАДЯН

Исследовано фотокаталитическое окисление некоторых хлорированных производных моно- и дифенилзамещенных алканов: 1-хлор-4-этилбензола; 4,4'-дихлордифенилметана; 1,1,1-трихлор-2,2-бис(p-хлорфенил)этана, молекулярным кислородом в присутствии фотокатализатора: гетерогенизированного диоксо-Мо органометаллического комплекса (диоксо-молибден(VI)-дихлоро[4,4'-дикарбоксилато-2,2'-бипиридин]), закрепленный на фоточувствительном носителе TiO_2 , при УФ-облучении ($\lambda = 253.7$ нм). Показана каталитическая роль закрепленного на носителе Мо-металлорганического комплекса в селективной активации бензиль-

ных С-Н связей этих соединений с образованием соответствующих продуктов окисления в мягких условиях. Каталитический цикл состоит из двух последовательных стадий, включающих окисление субстрата посредством переноса оксо-атома от диоксо-Мо(IV)-комплекса при UV-облучении, и регенерации восстановленного Мо(IV)-центра окислением молекулярным кислородом в темноте. Показано, что в этих условиях даже такой устойчивый загрязнитель как ДДТ может быть селективно окислен до дикофола, что в настоящее время другими путями невозможно. Предложен возможный механизм для этой группы реакций. Очевидно, что формирование оксо-пероксо-Мо(VI) частиц способствует переходу оксо-атома от Мо-комплекса к субстрату.

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