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Immobilized Osmium Clusters in the Processes of Liquid-Phase Oxidation of Cycloxehene

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Abstract—The reaction of catalytic hydroxylation of olefins by organic hydroperoxides in the presence of osmium carbonyl clusters supported on polymer matrices is studied. The process occurs with the predominant formation of unsaturated alcohols. The oxidative coupling of olefins with the formation of nonconjugated dienes and in which the double bonds remain intact occurs in parallel. In the course of the reaction, changes in the chemical structures of the initial osmium clusters are not observed.

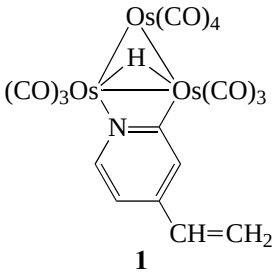
INTRODUCTION

Osmium and ruthenium tetroxides are used in fine organic synthesis for carrying out reactions of *cis*-hydroxylation of olefins, oxidation of alkynes, steroid quinones, in the synthesis of diepoxides, as well as in the selective oxidation of alcohols, ethers, alkylaromatic hydrocarbons, chlorophenols, and cycloalkanes [1]. Numerous reactions of electrophilic addition to aromatic molecules that form complexes with Os(II) [2] and C–H bond activation reactions by osmium compounds [3, 4] have been studied.

In order to create catalytic systems for the selective hydroxylation of a C–H bond in hydrocarbons, we studied the catalytic properties and specific features of the action of osmium clusters immobilized on polymer matrices, which are obtained by the copolymerization of Os_3-cluster monomers with styrene or acrylonitrile [5], in the reactions of olefin oxidation by molecular oxygen and olefin hydroxylation by organic hydroperoxides.

EXPERIMENTAL

The method for obtaining Os_3-containing monomers with 4-vinylpriridine (**1**) and allylamine (**2**) ligands



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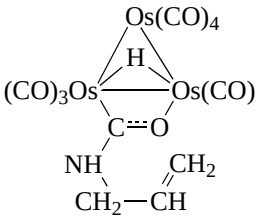

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was described in [6], their copolymerization with styrene and acrylonitrile and the properties of the respective copolymers were described in [7, 8]. Cyclohexenyl hydroperoxide (CHHP) was obtained using a method described in [9]. *tert*-Butyl hydroperoxide (TBHP) was used after the removal of water, acetone, and methanol admixtures in vacuum. The purity of the resulting TBHP was 98%. The solvents (benzene) and cyclohexene (CH) were purified using standard procedures. The products of CH oxidation were analyzed by GLC. The products of coupling of CH and its derivatives were analyzed by chromatography coupled with mass spectrometry (GC–MS) using an YEOL YMS D 3000 instrument.

The radical acceptor was 1,2-bis(4,4'-dimethylaminophenyl)-1,2-diphthaloylethane (Φ-Φ). The radical $\Phi^{\bullet}$ is the true acceptor of radicals, and it is in equilibrium with the initial dimer. The current concentration of $\Phi^{\bullet}$ was determined from the intensity of the ESR signal (a singlet with g = 2.00313 with poorly resolved hyperfine structure in argon and a singlet with the same parameters in oxygen) and from the electron spectrum of $\Phi^{\bullet}$ (λ_1 = 435 nm, λ_2 = 660 nm, and λ_3 = 732 nm; $\log\varepsilon_1$ = 4.22; $\log\varepsilon_2$ = 4.04; and $\log\varepsilon_3$ = 4.15). Measurements were carried out using a Bruker ER 200D ESR spectrometer and a Beckman DU-8 spectrophotometer in the regime of automatic recording of current values of optical density.

Analysis of changes in the catalyst structure due to the reaction was carried out using FTIR spectroscopy. The catalyst (based on copolymers with styrene), which was soluble in the reaction mixture, was isolated by recrystallization in methanol. The spectra were registered using a Bruker IFS 45 with the working range 4700–400 cm^{-1} in KBr pellets in an atmosphere of dry

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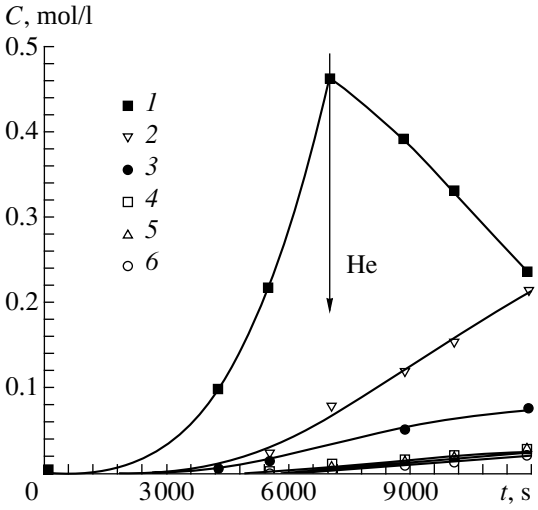


Fig. 1. Kinetic curves of accumulation and transformation of products (*1*) CHHP, (*2*) CHOL, (*3*) CHON, (*4*) bi-2-cyclohexene-4-hydroxy-1-yl, and (*5*) 2-hydroxycyclohexanon in the process of CH oxidation (11.0 mol/l) by molecular oxygen in the presence of catalyst **I** (1.31×10^{-5} g-atom/l, 50°C). The arrow points to the moment of replacement of O_2 by the inert gas.

nitrogen. The integral intensities of absorption bands were determined by multicomponent analysis using the FIT Bruker program.

RESULTS AND DISCUSSION

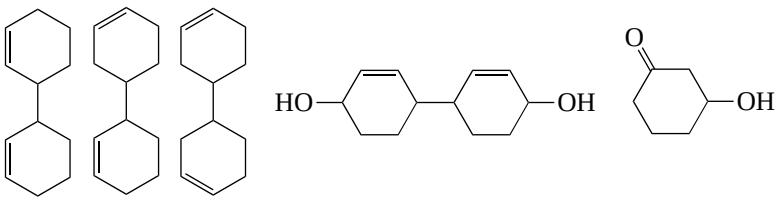
The catalytic activity of osmium clusters immobilized on polymer matrices was studied in a model reaction of cyclohexene oxidation by molecular oxygen. Because the catalysts with a polyacrylonitrile (PA) matrix are insoluble in cyclohexene, reactions were carried out in the heterogeneous regime. The reaction mixtures containing the catalysts with a polystyrene (PS) matrix were soluble.

For all catalysts studied, kinetic curves of O_2 consumption in CH oxidation had an autocatalytic nature: the time of achieving the maximal rate of the process was 30–80 min and was determined by the type of a ligand, the type of a polymer matrix, and by the concentration of metal in a polymer catalyst. Note that CH autooxidation studied under analogous conditions (O_2, 50°C) is characterized by a considerable (~3 h) induction period and by a low initial rate of the process. Thus, the conversion of CH was ~0.2% for 13 h of oxidation.

Data on the composition of products in CH oxidation in the presence of the catalysts studied are shown in the table. The main products of CH oxidation are: cyclohexanol (CHOL), cyclohexanone (CHON), epoxycyclohexane (EPCH), and cyclohexenyl hydroperoxide (CHHP)

CHHP is the main primary product of CH oxidation under conditions of an autocatalytic process. It was shown that when it is added to the initial mixture in a concentration of 0.15 mol/l, the initial rate of O_2 consumption increases. Thus, the autocatalytic nature of the process is stipulated by hydroperoxide formation.

In order to study the processes of CHHP transformation in the course of the reaction and accumulation of secondary products, we carried out experiments on CH oxidation with interrupted oxygen supply. Figure 1 shows the kinetic curves of product accumulation when oxygen is present in the system and after purging the reactor with helium. It is important to note that cyclohexenyl dihydroperoxide was not found in the oxidation products, although according to [9] it is the main product of radical chain oxidation of CHHP. In the catalytic system studied in the absence of oxygen, secondary processes are observed with the participation of virtually all components of the reaction mixture. The concentration of hydroperoxide decreases in this case, and the rate of CHOL formation increases, whereas the concentration of CHON becomes stationary. Products **3**–**5** are accumulated, which were characterized by GC–MS.



3 **4** **5**

Bicyclohexenyl (BCH) **3** was found in the form of two isomers with resolved chromatographic peaks of the same intensity and with identical mass spectra, *m/z*: 81 (100%), 80(61), 79(17), 41(16), 53(12), 39(11), 77(8), 65(4), 91(4), 162(0.45). Note that the possibility of the presence of all the three isomers of product **3** cannot be excluded. Bi-2-cyclohexene-4-hydroxy-1-yl is present as a single isomer (**4**), *m/z*: 81(100%), 41(48), 80(36), 39(27), 79(18), 27(12), 53(12), 29(9), 68(9), 194(0.42); 2-hydroxycyclohexanon (**5**) is characterized

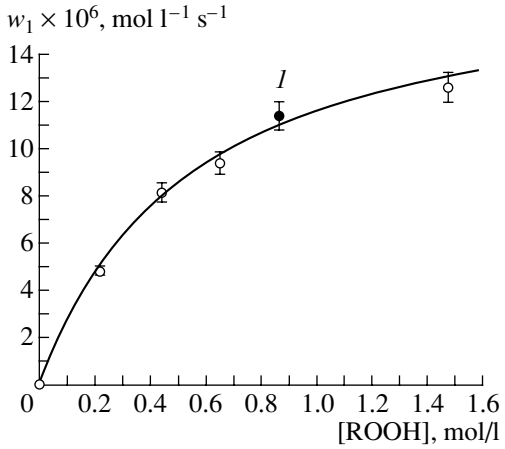


Fig. 2. Dependence of the rate of free radical generation (w_i) on the concentration of CHHP in the presence of catalyst **II** ($[Os]_0 = 8.20 \times 10^{-5}$ g-atom/l) and Φ-Φ ($[Φ\text{-}Φ]_0 = 6.15 \times 10^{-3}$ mol/l). 50°C, Ar, and benzene. Point *1* was obtained in the presence of CH (4.1 mol/l).

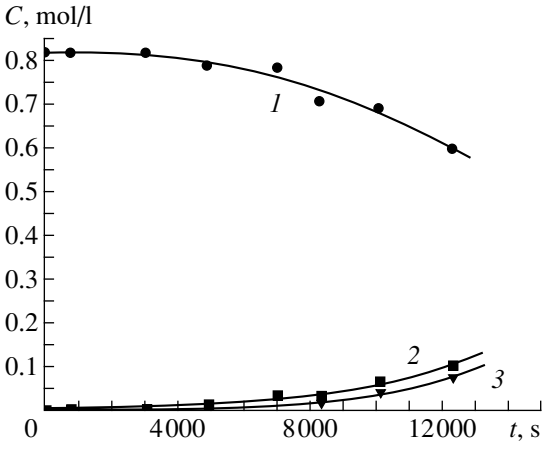


Fig. 3. Kinetic curves of (*1*) CHHP consumption and the accumulation of CHHP decomposition products (*2*) CHOL and (*3*) CHON in the presence of catalyst **II** ($[Os]_0 = 8.20 \times 10^{-5}$ g-atom/l, benzene, Ar, 50°C).

by the following spectrum, *m/z*: 57(100%), 70(70), 44(41), 29(30), 41(26), 27(26), 39(22), 42(22), 43(22), 114(11).

To elucidate the role of hydroperoxide ROOH in the process of CH oxidation in the presence of polymer osmium cluster catalysts, we carried out a number of kinetic experiments on CHHP decomposition in the presence and absence of CH. To determine the rate of generation of radical species in this process, we used the inhibitor method using the dimeric acceptor of free radicals Φ-Φ. The applicability of Φ-Φ for the quantitative determination of the rate of generation of radicals in the catalytic systems, including those containing hydroperoxides, was discussed in [10, 11]. Figure 2 shows the dependence of the rate of formation of radicals on the concentration of CHHP in the presence of CH, which is described by the mechanistic scheme involving a step of complex formation of the hydroperoxide and osmium-containing center with further homolytic decomposition of hydroperoxide.

$$Os_3 + n\text{ROOH} \overset{K}{\rightleftharpoons} [Os_3 \cdots n\text{ROOH}] \xrightarrow{k_i} Os_3 + \text{RO}^\bullet + \text{HO}^\bullet + (n-1)\text{ROOH}.$$

This scheme corresponds to the kinetic equation for the rate of radical generation:

$$w_i = \frac{k_i K[\text{ROOH}]^n[\text{Os}]}{1 + K[\text{ROOH}]^n}.$$

The resulting dependence was approximated by the function $y = abx^n/(1 + bx^n)$ with the following parameters: $n = 1$, $a = 1.78 \times 10^{-5}$, $b = 1.86$, which corresponds to the values of the rate constants $K = 1.86$ l/mol and $k_i = 0.24$ s^{-1}.

Note that these parameters are comparable with the analogous parameters of other processes. Thus, for

Product composition in the catalytic oxidation of cyclohexene by molecular oxygen in the presence of osmium clusters on polymer matrices

Catalyst	$[Os]_0 \times 10^5$, g-atom/l	Time, min	Selectivity, %			
			CHOL	CHON	EPCH	CHHP
Os**1**-PS (**I**)	1.31	65	2.2	2.2	0.03	95.5
Os**1**-PS (**II**)	8.20	44	7.5	2.3	0.03	89.4
Os**1**-PA (**III**)	6.52	192	5.0	52.4	0.05	41.8
Os**1**-PA (**IV**)	7.84	204	4.5	51.2	0.05	43.3
Os**2**-PS (**V**)	0.63	57	7.2	16.3	0.2	71.7
Os**2**-PS (**VI**)	0.73	42	12.2	7.3	2.2	77.8
Os**2**-PA (**VII**)	6.13	108	22.1	23.8	1.0	52.2

Note: $[CH]_0 = 11$ mol/l, $\Delta[O_2] = 0.112$ mol/l, 50°C.

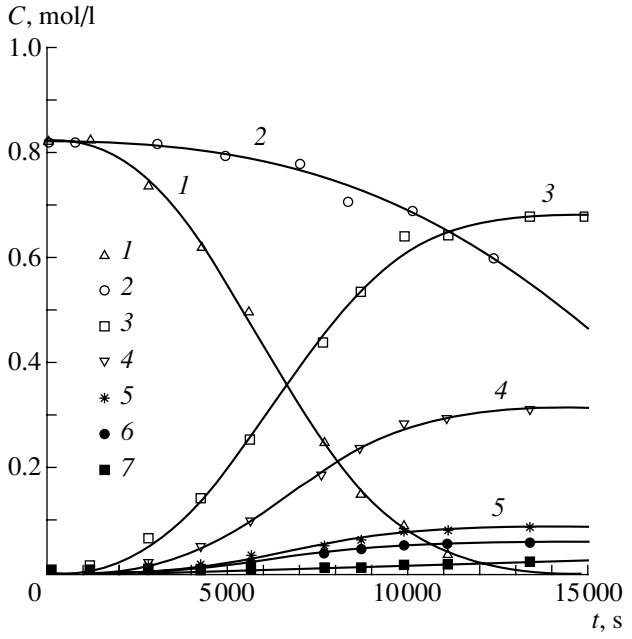


Fig. 4. Kinetic curves of CHHP consumption (*1*) in the presence and (*2*) in the absence of CH and accumulation of products in the presence of CH: (*3*) CHOL, (*4*) CHON, (*5*) bi-2-cyclohexene-4-hydroxy-1-yl, (*6*) 2-hydroxycyclohexanone, and (*7*) BCH in CHHP decomposition (catalyst **II**, $[Os]_0 = 8.20 \times 10^{-5}$ g-atom/l, $[CH]_0 = 4.1$ mol/l; benzene, Ar, 50°C).

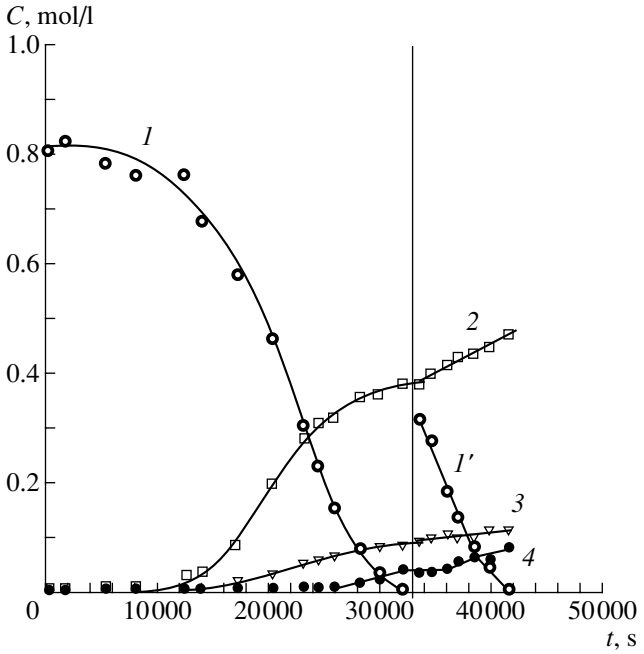


Fig. 5. Kinetic curves of (*1*, *1'*) TBHP consumption and the accumulation of (*2*) CHOL, (*3*) 2-hydroxycyclohexanone, and (*4*) BCH in the process of CH hydroxylation (4.1 mol/l) by *tert*-butylhydroperoxide in the presence of catalyst **II** ($[Os]_0 = 8.20 \times 10^{-5}$ g-atom/l, benzene, Ar, 50°C).

$Co(acac)_2$ at 55°C $n = 1$, $K = 5$–10 l/mol, $k_i = 0.2$–0.7 s^{-1} [12]; for copper(II) bis(2-phenyliminomethylene)benzo(β)thiophenate, $n = 1$, $K = 140$ l/mol (20°C), $k_i = 1.15 \times 10^{-2}$ s^{-1} (55°C) [13]. Thus, the high rate of CH oxidation in the developed process is stipulated by the efficient generation of radicals.

The rate of free radical formation measured using Φ-Φ coincides with the rate of CHHP consumption in an inert atmosphere (according to GLC); CHOL and CHON are primarily formed in equimolecular amounts (Fig. 3) at the initial stage the of radical CHHP decomposition in the presence of osmium-containing catalysts. In the presence of CH the rate of initiation does not change (point **1** in Fig. 2), and the rate of CHHP consumption becomes substantially higher, which is clear from curves *1* and *2* in Fig. 4. Therefore, there is a nonradical pathway of hydroperoxide transformation with the participation of the olefin. This is also clear from the product composition (mol % of all identified products according to data presented in Fig. 4: CHOL, 58; CHOL, 27; **4**, 7.7; **5**, 5.1; BCH, 2.1), specifically from the high (compared to the radical decomposition of CHHP, Fig. 3) fraction of the alcohol. According to ^{1}NMR data, ~2% of carboxyl-containing products were identified in the reaction mixture. Thus, the product composition points to the monooxygenating action of the catalysts based on osmium clusters in the reaction of olefin oxidation in the presence of organic hydroperoxides. This was supported by experiments on CH hydroxylation in the presence of catalyst **II** using *tert*-butyl hydroperoxide. Hydroxylation was carried out in an argon atmosphere. Figure 5 shows kinetic data on the consumption of TBHP and the accumulation of reaction products. The kinetics in these experiments is similar to that observed in oxygenation of CH in the presence of CHHP (Fig. 4). In both cases, the kinetic curves of hydroperoxide consumption and product accumulation are S-shaped. The main product is CHOL (74.5%). Other products are 2-hydroxycyclohexanone (17.6%) and bicyclohexenyl (7.8%). After the complete consumption of TBHP a new portion of hydroperoxide (0.32 mol/l) was added. The kinetics of hydroperoxide consumption after adding the second portion is exponential (Fig. 5, curve *1'*) and the initial segment of the curve is close to linear. This is different from the kinetics of hydroperoxide consumption in the initial portion. The products are accumulated according to practically linear law and their proportions remain constant (CHOL, 62.5%; 2-hydroxycyclohexanon, 12.5%; BCH, 25%). Both the first and second portions of TBHP in the course of the experiment were completely consumed. In both cases, the overall concentration of products of CH conversion was approximately half the initial concentration of hydroperoxide $[ROOH]_0$.

The transformation of osmium carbonyl clusters on polymer supports in the processes of CH oxygenation was studied by FTIR. The IR spectra of immobilized and free osmium carbonyl clusters were reported in [5–7].

The insertion of the Os_3 monomer into a cluster chain (immobilization) practically does not result in the distortion of carbonyl clusters. We studied the spectra of catalyst samples **II** after the experiments on CH oxidation by molecular oxygen, CHHP and TBHP. In all cases, IR data pointed to the stability of the structure of immobilized clusters inside the polymeric matrix in oxygenation processes. Therefore, immobilized osmium clusters can be used many times as catalysts because their isolation from the reaction medium is simple. This is an advantage of these compounds over homogenous metal-complex catalysts.

We found that in the first use of the catalyst **II**, there is a decrease in the integral intensity of the bands of stretching vibrations of carbonyl groups: $\nu = 2103$ cm^{-1} and a doublet $\nu = 2062$, 2051 cm^{-1} by 7%. The overall absorbance in the region of stretching vibrations of C–H groups of the polymer matrices ($\nu = 3137$–2985 cm^{-1} for aromatic groups and $\nu = 2975$–2824 cm^{-1} for aliphatic groups) was used as an internal standard. In further catalytic cycles, there was no decrease in the intensity of the bands.

The structural stability of the catalytic center in oxygenation processes was confirmed by ^{1}H NMR data: the intensity of the characteristic absorption band of the hydride hydrogen atom (–14.83 ppm) was practically constant after the reaction.

Thus, all data presented in this paper point to a dual function of catalysts based on osmium-containing carbonyl clusters in olefin oxidation by molecular oxygen and organic hydroperoxides.

The efficiency of these catalysts in the process of liquid-phase oxidation of CH by molecular oxygen is due to their high activity in the reaction of radical decomposition of hydroperoxides. The self-acceleration of the processes is explained by an increase in the concentration of CHHP, its decomposition in the course of the reaction and the possibility of additional activation of the catalyst in its interaction with ROOH. The values of the rate constants of reversible formation of the adduct $[Os_3\cdots CHHP]$ and its transformation with the formation radicals for catalyst **II** are found to be 1.86 l/mol and 0.24 s^{-1}, respectively.

In the presence of immobilized osmium clusters, CH monooxygenation by organic hydroperoxides occurs via a molecular mechanism, possibly in the triple complex $[Os_3\cdot\cdot n\mathrm{ROOH}\cdot\cdot \mathrm{RH}]$. One may assume when, for instance, inspecting curves *1* in Figs. 4 and 5 that the formation of this complex is rather slow, so that the time needed for reaching the equilibrium concentration is comparable with the rate of substrate transformation. The formation of this triple complex is possible due to the high local concentration of reactants (hydroperoxide and cyclohexene) near the immobilized Os_3 center due to chemisorption processes. It was shown in [12] that the chemisorption processes determine the kinetic description of cyclohexene oxidation in the presence of polymer-immobilized cobalt complexes.

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