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Liquid-Phase Catalytic Oxidation of C₆–C₇ Cycloolefins into Carboxylic Acids in a Pseudohomogeneous System

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Abstract—Liquid-phase oxidation of cyclohexene, methylcyclohexene isomers, and norbornene with a 30% solution of hydrogen peroxide in a pseudohomogeneous system involving highly dispersed compounds of Group-VIb and -VIIIb metals supported by nanosize carbon particles was studied.

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Dicarboxylic acids are important monomers in manufacture of synthetic fibers and plastics and also are of interest as intermediates in syntheses of biologically active compounds and pharmacological preparations [1]. These compounds are produced by oxidation of unsaturated hydrocarbons and their functional derivatives with various oxidizing agents, such as ozone [2], potassium permanganate, manganese dioxide, ruthenium dioxide (in combination with NaHgO₄, where Hlg = Cl, Br), potassium persulfate, organic hydroperoxides, peroxy acids [3–6], and nitric acid [7].

At present, dicarboxylic acids and, in particular, adipic acid are industrially manufactured by the two-stage scheme: oxidation of cyclohexane with atmospheric oxygen into cyclohexanol and cyclohexanone, followed by treatment of the resulting mixture with nitric acid [8]. This process yields, together with the main product, also mono- and dicarboxylic acids (acetic, oxalic, glutaric, and succinic) [9]. In addition, use of nitric acid as oxidizing agent results in that toxic gases, nitrogen oxides, are evolved, which is ecologically and economically unfavorable.

There has been report in the literature that dicarboxylic acids were produced by oxidation of cycloalkanes with molecular oxygen in the presence of isoamyl nitrite [10, 11]. The main reaction product at temperatures $T \leq 120^\circ\text{C}$ is a mixture of the corresponding cycloalkanol,

cycloalkanone, and dicarboxylic acid.

Oxidation of cyclohexene with hydrogen peroxide, with compounds of bisquaternary ammonium and sodium tungstate involved, gives, depending on reaction conditions, cyclohexanone in 82% yield or adipic acid (75%) [12].

It has been found that cyclohexene is oxidized by hydrogen peroxide into adipic acid in the presence of Ti-substituted aluminophosphate molecular sieves (TAPO-5) without any organic solvent via stages in which 1,2-cyclohexanediol is formed and the process selectivity is determined by the specific structural feature of the intermediate [13].

It has also been suggested to oxidize cyclohexene and cyclooctene into hexane-1,6- and octane-1,8-dioic acids with peroxopolyoxo tungsten phosphate complexes combined with quaternary ammonium cations [14]. A higher yield of adipic acid (89%) is reached in oxidation of cyclohexene with 30% H₂O₂ in the presence of an oxidiperoxo tungsten complex and a nitrogen-containing heterocycle [15]. Cyclopentene and cyclohexene can also be oxidized into, respectively, glutaric and adipic acids in the presence of 50% H₂O₂, with peroxy complexes of tungsten [16, 17], H₂WO₄ [18, 19], or Na₂WO₄ [20] involved and oxalic, orthophosphoric, and boric acids used as a complexing agent.

Thus, analysis in one system with the use of aqueous or dioxane solutions of hydrogen peroxide and highly dispersed Mo-Co- and W-Co-containing nanocarbon catalysts.

EXPERIMENTAL

Cycloolefins were oxidized at 60–90°C in a thermostated glass reactor equipped with a mechanical stirrer, thermometer, and reflux.

The catalysts were prepared by reacting individual metal powders, or binary mixtures of metallic powders of chromium, molybdenum, tungsten, and cobalt, or molybdenum or tungsten blue (mixture of oxohalides of composition MoO_nBr_m or WO_nBr_m, where $n = 1, 2$; $m = 2-4$) and chromium(VI) oxochlorides produced by the method described in [21, 22] with carbon tetrachloride or bromoform at 75–76°C. Metallic aluminum served as activator of CCl₄ (CHBr₃) [23]. After filtration, the resulting metal-containing carbon nanoparticles were dried at 20–30°C and thermally treated at 170–180°C until AlCl₃ ceased to be released. The supported catalysts were identified by X-ray phase analysis on a DRON-3M diffractometer (CuK_α radiation, Ni filter). The structure and composition of the mixture of molybdenum and tungsten oxobromides was determined by IR, EPR, and UV spectroscopies [21, 22]. The surface profile of metal-containing carbon nanoparticles (MCNPs) was examined by atomic-force microscopy (AFM) on an NC-AFM scanning atomic-force microscope. AFM images of the surface of the starting Mo- and W-containing catalysts are shown in Fig. 1.

We used in our experiments cyclohexene, mixture of 3- and 4-methylcyclohexene produced by dehydration of the corresponding alcohols [24], and nonbornene, a product formed in condensation of cyclopentadiene and ethylene [25]. According to GLC data, the purity of the starting compounds was 98.5–99.5%. As oxidizing agent served 30% aqueous or dioxane solution of hydrogen peroxide. Oxalic or acetic acid was used as a complexing agent. In the course of an experiment, samples of the reaction mixture were taken and analyzed for the content of H₂O₂ (by permanganometric titration [26]) and oxidation products (chromatographically, upon a pretreatment of a sample with a weak NaOH solution to reduce unreacted hydrogen peroxide). The analysis was made on an LKhM-8 MD×5 chromatograph with a heat conductivity detector, 2000 × 3 mm column packed with 5 wt % XE-60 silicone on N-AW DMCS Chromaton at

a column temperature of 130°C and carrier-gas (helium) flow rate of 40 cm³ min⁻¹. Cycloolefins and dicarboxylic acids were quantitatively determined with an internal standard (*n*-tridecane) and by TLC on Silufol UV-254 plates, with hexane–ethyl acetate as eluent (3 : 2 by volume, iodine as developer). For quantitative recovery of a dicarboxylic acid, the reaction mixture from which the catalyst was filtered off was cooled to room temperature, 25–35 ml of a 10% NaHCO₃ solution was added, the mixture was transferred into a separating funnel, 30–40 ml of CH₂Cl₂ was added, and the resulting mixture was agitated. The organic layer was separated from the aqueous layer and washed 2–3 times with a saturated NaHCO₃ solution. HCl (1 : 1) was added dropwise to the aqueous phase under agitation to pH 3 and the mixture was kept at 8–10°C for 10–12 h. The crystalline precipitate formed was filtered off, washed with a small amount of cooled water (≤5°C), and dried in air.

The direction of the reaction of oxidation of cycloolefins and the yield of its products depend on

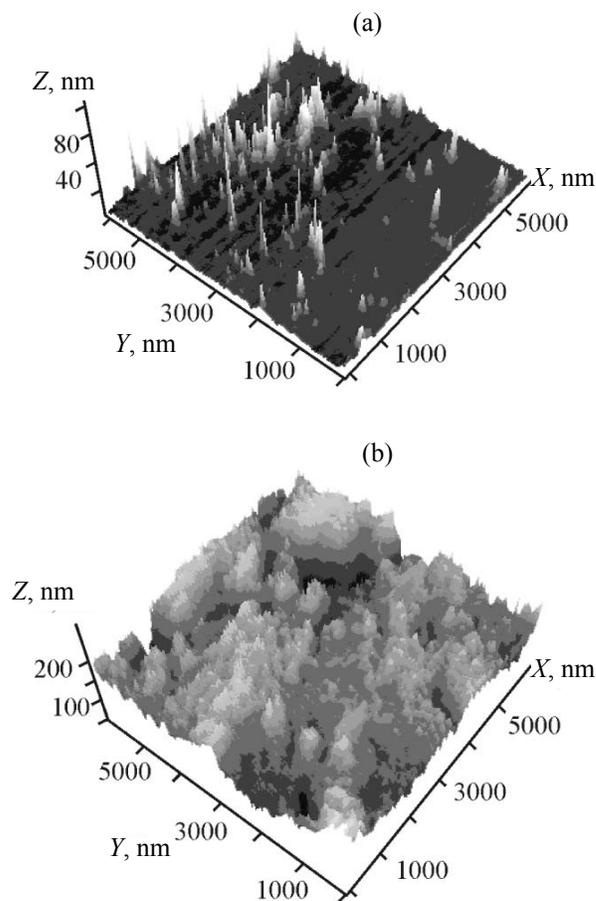


Fig. 1. AFM image of the surface of (a) Mo- and (b) W-containing carbon nanoparticles.

Table 1. Oxidation of cyclohexene in the presence of soluble transition metal compounds and those and supported by carbon nanoparticles (CNPs). $\tau = 24$ h, molar ratio $C_6H_{10} : H_2O_2 : CH_3COOH = 1 : 2 : 0.1$, catalyst content 0.03 wt %

Catalyst	$T, ^\circ C$	Cyclohexene conversion, %	Composition of liquid catalyzate, wt %				
			epoxide	diol and its monoacetate	oxy ketone	adipic acid	unknown substances
MoCl ₅	70	82.4	13.6	68.8	6.1	4.8	6.7
Molybdenum blue	70	91.8	5.7	80.2	3.8	3.7	6.6
CrO ₂ Cl ₂	70	73.0	–	49.6	24.2	13.9	12.1
WCl ₆	70	75.7	27.3	59.0	5.3	–	8.4
Tungsten blue	70	90.4	31.8	58.2	2.0	2.1	5.9
Molybdenum blue/CNPs	40	21.7	41.5	56.3	–	–	2.2
	60	60.4	12.7	70.0	14.2	–	3.1
	70	80.2	11.2	71.7	7.3	4.5	5.3
	80	87.9	8.0	66.4	9.6	8.1	7.9
CrO ₂ Cl ₂ /HY/CNPs	40	18.2	2.4	37.8	41.2	2.2	16.4
	60	44.7	5.1	42.3	38.8	5.9	7.9
	70	69.3	–	44.5	36.4	8.1	11.0
	80	79.0	–	39.2	26.1	12.2	22.5
Tungsten blue + CoBr ₂ /CNPs	40	24.1	51.8	41.3	2.1	–	4.8
	60	59.2	22.4	64.6	5.4	4.0	3.6
	70	86.0	17.0	49.1	16.8	14.7	2.4
	80	88.3	11.5	47.4	18.4	15.2	7.5
Molybdenum blue + CoBr ₂ /CNPs	40	27.3	40.6	51.0	4.1	–	4.3
	60	54.6	17.2	67.6	4.8	5.9	4.5
	70	81.0	12.3	62.2	8.2	12.1	5.2
	80	86.4	4.0	67.5	8.3	14.2	6.0

the nature of the catalysts used, temperature, H_2O_2 : cycloolefin molar ratio (Tables 1 and 2), and intensity of agitation of the reaction mass. To compare the results obtained, Table 1 also lists the results obtained in oxidation of cyclohexene in the presence of solutions of some salts of the above metals in ethanol.

The cycloolefins studied are substances poorly soluble in water, and, therefore, their oxidation occurs (in the case when a 30% aqueous solution of H_2O_2 is used) in the heterophase system at the phase boundary. To perform the process in the presence of homogeneous catalysts, phase transfer agents are commonly used, such as salts of quaternary ammonium cations that transport anions of the oxidizing agent to substrate molecules [14, 27, 28]. However, utilization of these compounds requires solution of a number of ecological and technological problems. Application of pseudohomogeneous catalytic systems with MCNPs makes it possible to perform the process, without using compounds of this kind, by vigorous agitation of the reaction mass (500–600 rpm). In this case, the reaction

mixture should not occupy more than 1/3 of the total volume of the reactor.

According to [29], the intensity of agitation of two-phase solutions increases only to a certain rotation speed of the stirrer. Above this value, the agitation intensity and, consequently, the phase boundary area remain unchanged despite the increasing rotation speed. Use of a dioxane solution of hydrogen peroxide as the oxidizing agent promotes interaction between cycloolefins and the forming catalytic complex throughout the volume of the reaction mass, because these hydrocarbons are well soluble in 1,4-dioxane. In this case, the intensity of agitation of the reaction mixture has no significant effect on the yield of the reaction product. For example, even at an agitation speed of 150–200 rpm, the yield of dicarboxylic acids in 8 h reaches values obtained in the presence of an aqueous solution of H_2O_2 at a rotation speed of the stirrer of 500–600 rpm.

Thus, even though performing the reaction in an organic solvent homogenizing the liquid phase eliminates the influence of hydrodynamic mixing

Table 2. Yield of dicarboxylic acids at various molar ratios between hydrogen peroxide and cycloolefin

Starting cycloolefin	Sub : H ₂ O ₂ molar ratio	T, °C	Dicarboxylic acid	Yield, %
Catalyst: molybdenum blue + CoBr ₂ /CNPs				
Cyclohexene	1:3	75	Hexane-1,6-dioic	20.0
	1:4	75		27.5
	1:5	75		66.4
	1:6	75		78.0
	1:8	75		80.0
				80
Methylcyclohexene ^a	1:5	85	2(3)-Methylhexane-1,6-dioic	62.3
	1:6	85		80.5
	1:8	85		83.1
				90
Bicyclo[2,2,1]hept-2-ene	1:5	85	1,3-Cyclopentanedicarboxylic	71.3
	1:6	85		81.0
	1:8	85		84.3
				90
Catalyst: tungsten blue + CoBr ₂ /CNPs				
Cyclohexene	1:5	75	Hexane-1,6-dioic	6.7
	1:6	75		79.4
	1:8	75		81.3
Methylcyclohexene ^a	1:5	90	2(3)-Methylhexane-1,6-dioic	65.0
	1:6	90		82.0
	1:8	90		84.5
Bicyclo[2,2,1]hept-2-ene	1:5	85	1,3-Cyclopentanedicarboxylic	59.0
	1:6	85		75.0
	1:8	85		83.0

^a Mixture of 3- and 4-methylcyclohexene

parameters, it hardly changes the yield of dicarboxylic acids. The same yield of dicarboxylic acids is achieved by using a 1 : 1 dioxane–water binary mixture, with the reaction mass agitated at a rate of 300–350 rpm, although the reaction selectivity decreases by 10–12%. Probably, dioxane used as the solvent strongly affects the course of elementary stages. This effect is due to the solvation of the intermediate state formed in interaction between the catalyst, oxidizing agent, and cycloolefin, which changes the direction of the substrate conversion and the accumulation rate of intermediate and final reaction products [30].

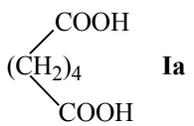
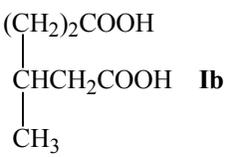
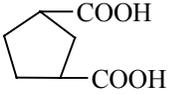
The oxidation of cycloolefins to dicarboxylic acids occurs by a more complex scheme, via stages of oxygen transport from the peroxo complex being formed to the substrate [26, 31]. In this case, the primary product is epoxide, further transformed in an acid medium to the corresponding diatomic alcohol.

Use of oxohalides and halides of the above-mentioned transition metals, strongly dispersed on carbon nanoparticles, in the presence of an aqueous solution of hydrogen peroxide promotes their hydrolytic conversion and in situ formation of carbon-containing peroxo molybdenum–cobalt or peroxo tungsten–cobalt systems of composition [MeO(O₂)_pHlg_mCoBr₂]_n/NC (where $p = 1$ and 2 , $m = 1$ and 2 , $n = 1-4$) [32, 33].

Based on the data in Tables 1 and 2, we can make a conclusion that the reaction direction widely varies in the presence of these heterogenized catalysts, depending on the nature of a metal. This is due to the variation of the electronegativity, ionic radius, complexing capacity, and other properties of the supported metals [34, 35].

For example, the main reaction products formed at 30–35°C in the presence of the molybdenum and tungsten catalysts used in the study are the

Table 3. Yield, melting points, spectra, and analysis data for dicarboxylic acids

Compound	Yield, %	mp, °C	Found, % Calculated, %		IR spectrum, cm ⁻¹	¹ H NMR spectrum, δ, ppm
			C	H		
Hexane-1,6-dioic acid  Ia	85.6	151–152 (from water) 151–153 [30]	<u>49.56</u> 49.32	<u>7.02</u> 6.85	938, 1410, 1730, 2600–3020	1.54–2.34 m (8H, 4CH ₂), 12.34 br.s (2H, carboxy groups) [31, 32]
3-Methylhexane-1,6-dioic acid  Ib	78.5	147–148 (from water)	<u>52.65</u> 52.49	<u>6.62</u> 6.37	938, 1252, 1410, 1725, 2600–3020	1.07 d (3H, CH ₃), 2.08– 2.33 d.d (4H, 2CH ₂), 1.97 t (1H, CH–CH ₃), 1.51–2.23 d.d (2H, CH ₂), 12.34 br.s (2H, carboxy groups)
Cyclopentane-1,3-dicarboxylic acid  Ic	72.6	194–196 (from water)	<u>53.45</u> 53.16	<u>6.65</u> 6.33	935, 1415, 1612–1645, 1725, 2500–3000	1.63–2.11 d (6H, 3CH ₂ and cyclopentane ring), 2.39 m (2H, 2CH), 12.35 br.s (2H, 2OH for two carboxy groups)

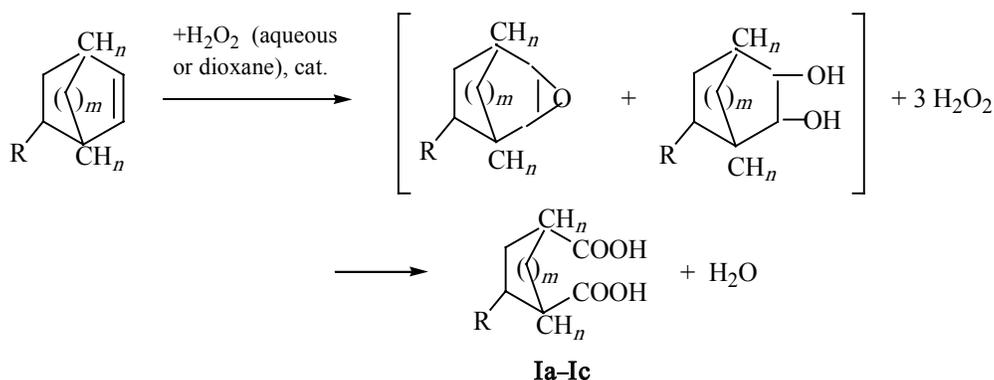
corresponding diols and epoxides, and those formed in the presence of chromium-containing catalysts are keto-alcohols and diols. The oxidation with cleavage of the double bond in the cycloolefin molecule selectively occurs in the presence of two-component Mo–Co- and W–Co-containing catalytic systems at a 500–600-rpm agitation intensity of the reaction mass, H₂O₂ : hydrocarbon molar ratio of ≥4, and temperature of 70–80°C. The highest yield of hexane-1,6-dioic acid is obtained in the presence of MoO_nBr_m·CoBr₂/NC and WO_nBr_m·CoBr/NC.

The oxidation of bicyclo[2,2,1]hept-2-ene (norborn-

ene) occurs under the conditions specified with opening of the cyclohexene moiety of the molecule at the multiple bond to give cyclopentane-1,3-dicarboxylic acid (Table 2). The composition and structure of the dicarboxylic acids synthesized were confirmed by IR and ¹H NMR spectroscopies (Table 3).

The selectivity of the reaction is strongly affected by the molar ratio between H₂O₂ and the substrate (Sub) (Fig. 2, Table 2). A selective conversion of the intermediately formed diols into the corresponding dicarboxylic acids can be provided by choosing the optimal [H₂O₂]/[Sub] ratio (see the scheme)

Scheme.



$n = 2, m = 0, R = H$ (**Ia**); $R = CH_3$ (**Ib**); $n = m = 1, R = H$ (**Ic**).

To provide a high yield of a dicarboxylic acid, it is necessary to use an excess amount of hydrogen peroxide. At a molar ratio $[H_2O_2] : [Sub] = 6 : 1$, the yields of hexane-1,6-dioic, 2(3)-methylhexane-1,6-dioic, and cyclopentane-1,3-dicarboxylic acids reach values of 78–85%.

The dependence of the yield of hexane-1,6-dioic acid on the ratio $[H_2O_2]/[Sub]$ (Fig. 2) shows a maximum in the range 3.0–5.0 mol/mol. To obtain a high yield of the acid, it is necessary to introduce the hydrogen peroxide solution into the reaction zone in several portions during a run.

CONCLUSIONS

(1) Liquid-phase oxidation of cyclohexene, isomers of methylcyclohexene, and bicyclo[2.2.1]hept-2-ene (norbornene) with hydrogen peroxide in the presence of a pseudohomogeneous catalytic system prepared from molybdenum, tungsten, and cobalt halides and oxohalides and nanosize carbon particles was used to obtain the corresponding dicarboxylic acids.

(2) The oxidation of cycloolefins into dicarboxylic acids occurs selectively in the presence of two-component highly dispersed Mo–Co and W–Co systems on carbon nanoparticles at 75–85°C, H_2O_2 : hydrocarbon molar ratio of no less than 4, and 300–600-rpm agitation

speed of aqueous or aqueous-dioxane solutions.

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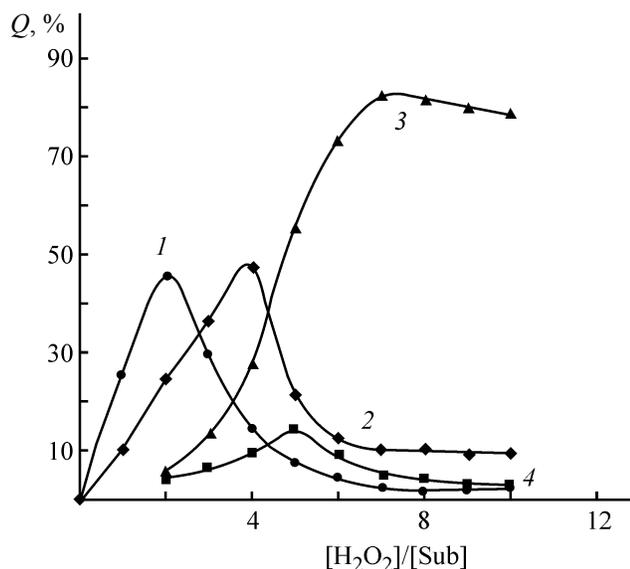


Fig. 2. Yield Q of hexane-1,6-dioic acid vs. the molar ratio $[H_2O_2]/[Sub]$ in the reaction of cyclohexene oxidation. Reaction conditions: $T = 80^\circ C$, $\tau = 10$ h, catalyst $WO_nBr_mCoBr_2/C$ (0.5 wt %). (1) Epoxide, (2) diol, (3) acid, and (4) keto-alcohol.

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