ISSN 0023-1584, Kinetics and Catalysis, 2018, Vol. 59, No. 6, pp. 735–743. © Pleiades Publishing, Ltd., 2018.
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Effect of Transition Metal Compounds on the Cyclohexene Oxidation Catalyzed by *N*-Hydroxyphthalimide

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Received March 23, 2018

Abstract—*N*-Hydroxyphthalimide (NHPI) is an efficient organic catalyst in the oxidation reactions of organic compounds occurring via a radical mechanism, often used together with redox-active ions or transition metal complexes. In this work the catalytic action of NHPI is studied together with Cu(II), Fe(III), and Mo(VI) compounds in the reaction of aerobic oxidation of cyclohexene in an acetonitrile solution at 60°C. It was found that iron(III) benzoate accelerates the reaction by rapidly generating the active form of the phthalimide-*N*-oxyl radical (PINO) catalyst, but does not cause decomposition of the hydroperoxide. The oxidation product is 2-cyclohexenyl hydroperoxide formed with a selectivity of 85% at a cyclohexene conversion of 50%. Copper(II) acetate initiates oxidation and is capable of catalyzing the radical decomposition of the hydroperoxide and secondary oxidation of allyl oxygenates. When reaching a cyclohexene conversion close to 80%, the overall selectivity to the main products, 2-cyclohexenyl hydroperoxide and 2-cyclohexen-1-on, was 70%. The addition of iron(III) and molybdenum(VI) compounds led to the intensive generation of hydroperoxide and its activation as an electrophilic reactant capable of cyclohexene epoxidation. As a result of the use of the multifunctional three-component NHPI–Mo(VI)–Fe(III) catalyst, cyclohexene oxidation by molecular oxygen occurred with the formation of epoxycyclohexane. The selectivity to the products of cyclohexene epoxidation was close to 50%, which is a value expected from theory.

Keywords: cyclohexene, autoxidation, *N*-hydroxyphthalimide, transition metal compounds
DOI: 10.1134/S0023158418060083

INTRODUCTION

Of many oxidants used in liquid-phase oxidation, molecular oxygen, hydrogen peroxide, and hydroperoxides are preferred. They have the properties of environmentally friendly reagents and are capable of converting hydrocarbons to various oxygenates. Oxygen-containing products of selective oxidation of cyclic olefins are valuable reagents used in organic synthesis [1]. Allyl oxygenates, cyclohexenone and cyclohexenol, and epoxycyclohexane may be used as initial reagents in the syntheses of compounds used in agriculture, perfumery, and pharmaceutics [2–4].

The formation of allyl oxygenates and epoxide from cyclohexene occurs at moderate temperatures as a result of liquid-phase oxidative substitution at the allyl position and addition to a double bond. These reactions are typical of olefins [1, 5, 6]. At 60°C, in the absence of any catalyst and activating agents, the reaction of cyclohexene oxidation with molecular oxygen occurs via the autoxidation mechanism. 2-Cyclohexenyl hydroperoxide is the main product, and the concentrations of 2-cyclohexen-1-ol, 2-cyclohexene-1-on and epoxycyclohexane constitute only several percent of reacted cyclohexene [7]. A high temperature and the presence of catalysts accelerate the reaction and cause hydroperoxide decomposition to form cyclohexenol and cyclohexenone. Currently, it is known that aerobic liquid-phase cyclohexene oxidation to 2-cyclohexen-1-ol and 2-cyclohexen-1-on mostly occurs with the participation of soluble complexes or solid catalysts containing redox-active ions of Cr, Cu, Co, Fe, and Au [8–17]. Nonmetallic solid catalysts, such as nitrogen-doped carbon nanotubes, has also been described [18, 19]. In aerobic cyclohexene oxidation, the formation of an epoxide occurs only in small amounts, whereas common oxidants used for the synthesis of epoxides are organic peroxides. Reactions of cyclohexene epoxidation are known in which electrophilic oxygen species are generated from tert-butyl hydroperoxide or cyclohexyl hydroperoxide under the action of homogeneous or supported Mo(VI), V(V), Ti(IV), Cu(II), and Ni(II) catalysts [20–24].

Currently liquid-phase oxidation reactions catalyzed by organic catalysts, especially by *N*-hydroxyphthalimide (NHPI), are actively studied. In the works by Ishii and coauthors [25, 26], efficient catalytic systems for the oxidation of alkanes and alkylaromatic compounds by molecular oxygen have been proposed. Further studies have developed toward expanding the range of oxidized substrates and a search for suitable solvents and radical initiators [27–35]. It was found that NHPI in the absence of metal compounds catalyzes the selective conversion of cumene, ethylbenzene, and cyclohexylbenzene to the corresponding hydroperoxides [36]. The formation of carbonyl compounds and alcohols occurs when alkylaromatic compounds are oxidized in the presence of NHPI and transition metal compounds [32, 34, 37] or nonmetallic activators [29–31, 35, 38], mostly at an elevated temperature. Olefin oxidation by oxygen under the action of the NHPI catalyst were less studied. Interestingly, in a recent work [39], the electrochemically generated radical form of the NHPI catalyst or its analog was involved in the selective oxidation of natural olefins to α-β-unsaturated ketones. In the presence of redox-active compounds of transition metals, NHPI accelerated cyclohexene autoxidation to form the products of allylic oxidation [40–42]. Unfortunately, hydroperoxide was not analyzed in [41, 42] and the balance of C_6 was not checked. Therefore, the selectivity data are unreliable. In [25, 35, 38, 43, 44], the reactivity of cyclohexene in the presence of NHPI without transition metal compounds were considered in comparison with other olefins. Cyclohexene showed a higher activity than another cyclic olefin α-isophorone [43]. Other authors reported a selectivity of 82% to 2-cyclohexen-1-on in cyclohexene oxidation at 130°C when g-C_3N_4 was added [38, 39]. In the oxidation of cyclic olefins in the presence of an iron-containing organic polymer, the portion of products of cyclohexene allyl oxidation was 97%, whereas cyclooctene was selectively oxidized to epoxide [45]. According to the available literature data, it is seen that the composition of products of cyclohexene oxidation by oxygen catalyzed by NHPI can be determined by the nature of substrate, promoting additives of transition metal compounds, and reaction conditions.

In this work, we used redox-active organic soluble salts (copper(II) acetate and iron(III) benzoate) as well as soluble and supported Mo(VI) catalysts in combination with an NHPI catalyst in cyclohexene oxidation by molecular oxygen. To determine the mechanism of the influence of these compounds on the NHPI-catalyzed cyclohexene oxidation, we performed a cyclohexene oxidation by oxygen with the formation of 2-cyclohexenyl hydroperoxide and studied the transformation of 2-cyclohexenyl hydroperoxide together with cyclohexene under the action of compounds of these metals in an atmosphere of inert gas and in the presence molecular oxygen. The choice of a metal cocatalyst allowed us to control the catalytic properties of the NHPI-based systems and to find effective ways for obtaining the products of cyclohexene selective oxidation by molecular oxygen, including epoxide.

EXPERIMENTAL

Materials

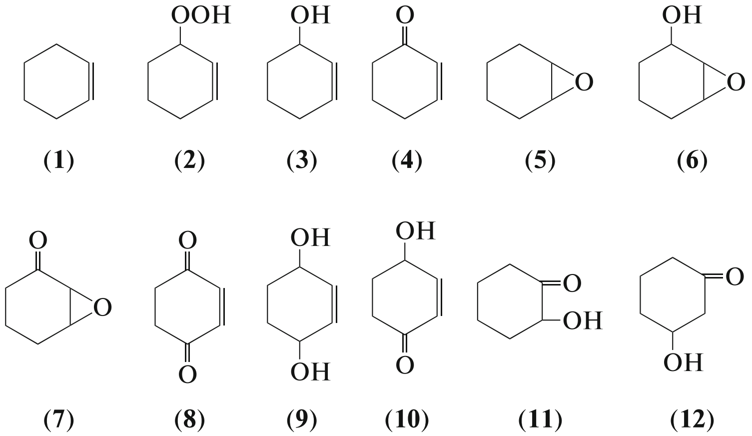
N-Hydroxyphthalimide, acetonitrile, copper(II) acetate monohydrate, molybdenyl acetylacetonate (Sigma-Aldrich) and iron(III) benzoate (Reakhim) were used without additional purification. Cyclohexene (Aldrich) was distilled and then kept in a cold storage in a tightly closed bottle.

The 3.8%V_2O_5/SiO_2 catalyst (**I-V**) was prepared by the impregnation of KSK silica gel powder (S_{sp} = 260 m^2 g^{-1}, V_{pore} = 0.84 cm^3 g^{-1}) with a solution of ammonium vanadate at 80°C. The sample was dried and calcined at 650°C in vacuum. The 15% MoO_3/SiO_2 catalyst (II-Mo) was prepared by adding the same silica gel to a solution of ammonium paramolybdate at 80°C. The mixture was slowly evaporated while stirring. Then, the sample was dried at 100°C and calcined at 500°C in air. The 7.5% MoO_3/SiO_2 catalyst (III-Mo) was prepared by the impregnation of Aerosil A-175 powder (S_{sp} = 175 m^2 g^{-1}) by a solution of ammonium paramolybdate with further treatment as in the case of the II-Mo catalyst.

Procedure of Catalytic Measurements

Cyclohexene oxidation was carried out in a glass reactor with an internal volume of 28 mL and with heating by water. The reactor was equipped with two Teflon valves for gas purging and connection with a gas burette. The contact of the solution with the gas phase was maintained by intense stirring with a magnetic stirrer. The reactor was charged with a weighed sample of a salt that was dissolved in 2.0 mL CH_3CN. Then, NHPI and 0.5 mL of cyclohexene were added. The reactor was closed, purged with O_2 at atmospheric pressure and room temperature. The burette was filled with oxygen, and heating and stirring were switched on. Within 1 min, the pressure in the system was brought to atmospheric by means of a burette and a stopping flask with water, and the beginning of reaction was recorded. The reaction was monitored by changes in the volume of the gas phase when the pressure in the system was brought to atmospheric. After the reaction, the reactor was rapidly cooled to ~15°C and the solution was diluted with 7.5 mL CH_3CN. The loss of volatile cyclohexene in these manipulations, evaluated in a blank experiment at zero reaction time, was not higher than 5% and was taken into account when calculating the balance with respect to cyclohexene.

Test reactions with the portions of solution (2.5 mL) of 2-cyclohexenyl hydroperoxide prepared according to the procedure described below, were carried out in a similar way, but with oxygen replaced by argon.



(1) (2) (3) (4) (5) (6)

(7) (8) (9) (10) (11) (12)

Fig. 1. Products of cyclohexene oxidation by oxygen in the presence of the NHPI catalyst as determined by gas chromatography.

Analysis of Oxidation Products

The amount of peroxide oxygen O_2^{2-} in the solution after reaction was determined by iodometric titration. Glacial acetic acid (5 mL) mixed with 0.5 g KJ was added to a 1.0-mL solution and allowed to stay for 30 min in an argon atmosphere at 60°C. Then, 50 mL of water was added and the mixture was titrated by a 0.04 N solution of sodium thiosulfate.

The products of cyclohexene oxidation (Fig. 1) were identified by gas chromatography—mass spectrometry (GCMS) using an Agilent 7000 triple quadrupole GC/MS system (Agilent, USA) with a WAX20M 10 m × 0.25 mm × 0.25 μm column. The quantitative GC analysis was carried out using an Agilent 7890B chromatograph (Agilent, USA) with a SOLGEL-WAX 30 m × 0.25 mm × 1 μm column. The amount of products was calculated using calibration curves taking the solvent as an internal standard. The reaction solution was analyzed twice: immediately after the reaction and after the addition of Ph_3P, which reduced peroxide compounds to alcohols [46]. The amount of cyclohexene was calculated from chromatogram of the solution reduced by Ph_3P. The content of cyclohexanol was determined as a difference between its amount after the reduction of solution and the amount of peroxide found by iodometric titration. The amount of epoxycyclohexene did not change as a result of solution treatment with Ph_3P.

Preparation of the Solution of 2-Cyclohexenyl Hydroperoxide

To prepare solutions of 2-cyclohexenyl hydroperoxide, cyclohexene was oxidized by oxygen in a titanium autoclave (Parr Instrument Company, USA) with a volume of 300 mL. The reactor was charged with 40 mL CH_3CN, 10 mL C_6H_{10}, and 0.6 g NHPI. The reactor was fed with air to a pressure of 2 atm and heated to 60 or 70°C, and the solution was stirred at this temperature for 7 h. The reaction was carried out at an oxygen partial pressure of 0.5—0.6 atm adding it to the reactor as it was consumed. After that, the reactor was cooled to room temperature and depressurized, the solution was discharged from the reactor, and was then used in subsequent experiments. The contents of peroxides and other oxidation products were determined according to the above procedure.

RESULTS AND DISCUSSION

Cyclohexene Oxidation by Oxygen in the Presence of NHPI and Soluble Compounds of Transition Metals

Cyclohexene (**1**) oxidation in the solution of the NHPI catalyst was carried out without adding any initiators for several hours. The reaction had a pronounced induction period (1 h). The main product was 2-cyclohexenyl hydroperoxide (**2**) (the selectivity was $S_2 = 89\%$ at an olefin conversion of 22%) (Table 1, no. 1). 2-Cyclohexen-1-ol (**3**) was apparently absent or formed in trace amounts, because the concentration of **3** determined by chromatography after treatment with Ph_3P coincided with the concentration of peroxide determined by iodometric titration. In addition to **2**, 2-cyclohexen-1-on (**4**) was also formed in small amounts. Thus, 2-cyclohexenyl hydroperoxide was stable under the conditions of NHPI-catalyzed oxidation, which is typical of other alkyl hydroperoxides as well [36, 37]. Reactions (I)—(IV) describe NHPI-catalyzed formation of **2**:

$$\mathrm{NHPI} \rightarrow \mathrm{PINO}, \qquad \mathrm{(I)}$$

$$\mathrm{PINO} + C_6H_{10} \rightarrow \mathrm{NHPI} + C_6H_9, \qquad \mathrm{(II)}$$

$$C_6H_9^{\bullet} + O_2 \rightarrow C_6H_9OO^{\bullet}, \qquad \mathrm{(III)}$$

$$C_6H_9OO^{\bullet} + \mathrm{NHPI} \rightarrow C_6H_9OOH + \mathrm{PINO}. \qquad \mathrm{(IV)}$$

In the absence of initiators, the generation of the phthalimide-N-oxyl radical (PINO) (I) in the initial reaction period was due to organic peroxides [36],

Table 1. Composition of the main products of cyclohexene oxidation in the presence of NHPI and metal salts[a]

No.	M^{n+}, µmol	NHPI, mmol	Conversion of **1**, %[b]	Main products, mmol					S_{2-7}, %[c]	C_6 balance, %[f]
				2	**3**	**4**	**5**	**6 + 7**		
1	0	0.23	22	0.91	0	0.04	0	0	93	98
				$Fe(benz)_3$						
2	6	0	<1	0.07	0	<0.01	0	0	Not determined	Not determined
3	3	0.09	33	1.14	0	0.09	0.02	0	80	94
4	6	0.09	27	1.02	0	0.08	0.01	0	88	97
5	6	0.18	48	1.90	0	0.01	0.03	0	85	94
				$Cu(OAc)_2 \cdot H_2O$						
6	8.5	0	30	0.71	0.19	0.35	0.05	0.03	89	98
7	8.5	0.09	66	1.08	0	0.92	0.05	0.06	71	79
8	3	0.09	66	1.2(1.4)[d]	0	0.96	Not determined		Not determined	Not determined
9	Traces	0.09	38	1.5(1.6)[d]	0	0.14	0.01	<0.01	94	98
10	3	0.23	79	1.16(1.4)[d]	0	1.16	0.08	0.02	66	73
11[e]	3	0.23	80	1.33(1.7)[d]	0	1.18	0.01	<0.01	68	74
				$MoO_2(acac)_2$						
12		0.23	8	0.04	0.12	0.02	0.08	0.03	78	98

[a] Conditions: 2.5 mL of 4.65 mmol solution of **1** in CH_3CN, 60°C, the reaction duration was 4 h, except no. 1 (3 h).

[b] Conversion of **1** = 100% × ($\mathbf{1}_{initial} - \mathbf{1}_{final}$)/$\mathbf{1}_{initial}$ (mol/mol).

[c] Selectivity S_{2-7} = 100% × (**1** + **2** + **3** + **4** + **5** + **6** + **7**)/($\mathbf{1}_{initial} - \mathbf{1}_{final}$) (mol/mol).

[d] The amount of peroxide according to iodometric titration.

[e] 2 mmol of H_2O added to the solution.

[f] Relative to the initial solution.

which are usually present in small amounts in hydrocarbons.

We studied the effect of soluble Fe(III) and Cu(II) salts on the catalytic action of the organic catalyst NHPI in cyclohexene oxidation. As can be seen from Table 1 (no. 3), the presence of small amounts of Fe(III) benzoate resulted in the increase of conversion of **1**. Note that iron benzoate did not show activity in cyclohexene oxidation in the absence of NHPI (Table 1, no. 2). It is important to emphasize that the product of oxidation of **1** was still 2-cyclohexenyl hydroperoxide. The conversion of **1** and the amount of **2** formed increased in the presence of Fe(III) benzoate because of the faster oxidation and degeneration of the induction period. Interestingly, the amount of products remained almost the same when the concentration of Fe(III) benzoate increased (Table 1, no. 4), but increased with an increase in the concentration of the NHPI catalyst (Table 1, no. 5). The selectivity to **2** was 85% with cyclohexene conversion of 48%, and the C_6 balance remained at the same level as in the absence of iron ions. These results show that iron ions do not catalyze side transformations of **1**. It is likely that the promoting effect of iron is in the acceleration of the formation of PINO through NHPI oxidation by the Fe(III) ion [47, 48] with its regeneration by reactions (V) and (VI):

$$\text{NHPI} + \text{Fe(benz)}_3 \rightarrow \text{PINO} + \text{Fe(benz)}_3^- + \text{H}^+, \quad \text{(V)}$$

$$2\text{Fe(benz)}_3^- + 1/2\,\text{O}_2 + 2\text{H}^+ \rightarrow \rightarrow 2\text{Fe(benz)}_3 + \text{H}_2\text{O}. \quad \text{(VI)}$$

Copper(II) acetate catalyzed autoxidation with a prolonged induction period and the formation of the three main products **2**, **3**, and **4** (Table 1, no. 6). The addition of NHPI resulted in a noticeable acceleration of the oxidation process; the induction period shortened to several minutes, the conversion of cyclohexene increased. The main products were **2** and **4**, and alcohol **3** was absent (Table 1, no. 7). In catalysis by the Cu(II) salt and Cu(II) in combination with NHPI, epoxycyclohexane (**5**) was formed in small amounts. Its formation was also observed in the preceding series of experiments with NHPI and Fe(III) benzoate. A low selectivity to epoxide compared with allylic products is characteristic of cyclohexene autoxidation. An increased selectivity to the epoxide was observed in [16, 17] on gold-containing catalysts, which was attributed by the authors to the properties of gold. It is also known that a high selectivity to the epoxide in the aerobic oxidation of olefins is possible as a result of the intramolecular interaction of the double bond with hydroperoxide oxygen, which can be seen in the oxidation of cyclooctene in the presence of the CrMCM-41 catalyst [8]. However, a similar conversion is not typical of cyclohexenyl hydroperoxide intermediate. The conversion of **1** and the amount of products did not decrease with decreasing $Cu(OAc)_2 \cdot H_2O$ content (Table 1, no. 8) up to the trace amount (Table 1, no. 9), and the main product was **2**. With an increase in the amount of NHPI, the conversion of **1** increased to ~80%, but the amount of the main products only slightly changed. As a result, the selectivity to the main products and the C_6 balance became worse (Table 1, no. 10). At the conversion of **1** in the range 66–80%, the overall selectivity to the main products calculated on the basis to the substrate consumed was ~70%. The addition of water, which usually accumulates in the course of oxygenate formation, had little effect on the catalytic action (Table 1, no. 11), except for a decrease in the amount of **5**.

We traced the consumption of substrate **1** and accumulation of the products **2**, **3**, and **4** in time. 2-Cyclohexene-1-ol (**3**) was observed during the initial period of the reaction, and then its amount decreased to zero, probably because of alcohol oxidation to ketone **4** catalyzed by NHPI [28]. The resulting data shown in Fig. 2 suggest that the selectivity to the main products decreased from 99 to 66% with time and with an increase in the conversion of **1** from 15 to 80%. A decrease in the selectivity and the C_6 balance points to the formation of byproducts, which are likely formed due to secondary oxidation processes. In addition to the main products, several dioxygenates (**6–12**), which are the products of cyclohexene oxidation both at the allyl position and at the double bond, were identified by GCMS (Fig. 1). GC analysis of the reaction solution before and after the reductive treatment by Ph_3P showed a qualitatively identical composition of oxygenates, but their quantitative distribution changed after reduction toward alcohols. The detection of dioxygenates **8–12** pointed to the fact that, along with **2**, dihydroperoxides and substituted hydroperoxides were formed. The latter was confirmed by the fact that for a rather high conversion of **1**, the amount of hydroperoxide found by titration (given in parentheses in Table 1, nos. 8–11) was higher than the amount of **2** determined by GC. At a high conversion of **1,** dioxygenates shown in Fig. 1 could account for more than 20% of the overall amount of products. However, we did not find any other compounds from the long list of products of cyclohexene autoxidation in the presence of metal-containing catalysts found by Finke et al. [49].

Unlike redox-active metal compounds, molybdenum(VI) acetylacetonate had an inhibitory effect on the rate of cyclohexene oxidation catalyzed by NHPI. Correspondingly, the conversion of cyclohexene in the presence of NHPI and dissolved $MoO_2(acac)_2$ (Table 1, no. 12) was three times lower than in the presence of NHPI only. At the same time, the composition of oxidation products has changed towards the preferential formation of **3** and **5**. In addition to epoxycyclohexane **5**, epoxy derivatives **6** and **7** appeared in noticeable amounts. The autoxidation reactions of isobutane or alkylbenzenes are known as a method for the synthesis of hydroperoxides, which can further be used to epoxidize olefins [50]. It can be assumed that the 2-cyclohexenyl hydroperoxide formed in cyclohexene oxidation is consumed for the formation of epoxides with the participation of $MoO_2(acac)_2$, which is known as an efficient catalyst for epoxidation [20]. The disadvantage of the NHPI–Mo(VI) system was the low reaction rate, which was likely caused by the presence of the Mo(VI) compound.

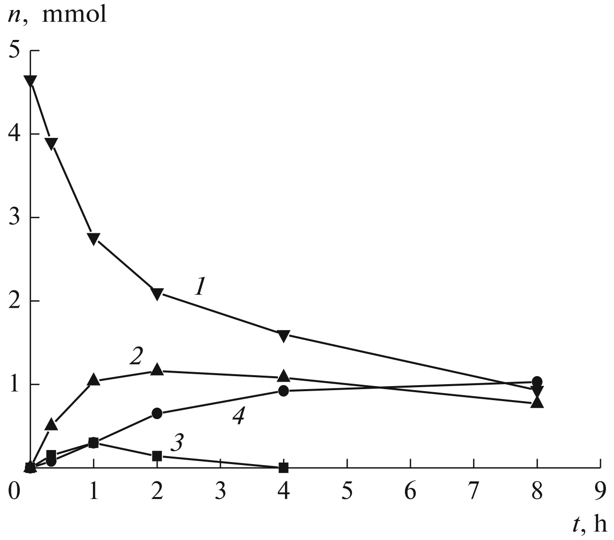


Fig. 2. Kinetics of cyclohexene (**1**) consumption and accumulation of the products of oxidation of 2-cyclohexenyl hydroperoxide (**2**), 2-cyclohexen-1-ol (**3**) and 2-cyclohexen-1-on (**4**). Reaction conditions: 1.7 mg (8.5 μmol) $Cu(OAc)_2 \cdot H_2O$, 15 mg (0.092 mmol) NHPI, 4.65 mmol (**I**), 2 mL CH_3CN, 60°C.

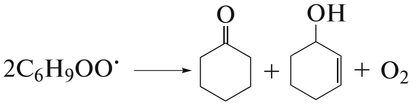
Reactions of Cyclohexene and 2-Cyclohexenyl Hydroperoxide in an Atmosphere of Inert Gas

In this part of the work, we determined the mechanism of participation of the chosen transition metal compounds in reactions leading to cyclohexene oxidation. With this goal, the transformations of the primary product of 2-cyclohexenyl hydroperoxide reaction under the influence of metal catalysts were studied. Test reactions in the argon atmosphere were carried out with the portions of the solution prepared by cyclohexene oxidation according to the procedure described in the experimental section of this work. In addition to **2**, this solution contained unreacted **1**, NHPI, and the products of decomposition of **2** in small amounts. Experimental conditions for the use of transition metal compounds, the conversions of **1** and **2**, and the composition of the main C_6 products, are given in Table 2.

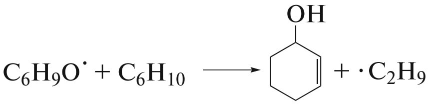
The mechanism of decomposition of **2** under the action of transition metal ions to form unsaturated alcohol and ketone is described by reactions (VII)–(XI). Since in our experiments the hydroperoxide solution also contained olefin **1**, the hydroperoxide could be consumed not only for decomposition, but also for the formation of epoxide and alcohol by reaction (XII).

$$C_6H_9OOH + M^{n+} \longrightarrow C_6H_9O^{\bullet} + M^{(n+1)+} + OH^- \quad (VII)$$

$$C_6H_9OOH + M^{(n+1)} \longrightarrow C_6H_9OO^{\bullet} + M^{n+} + H^+ \quad (VIII)$$

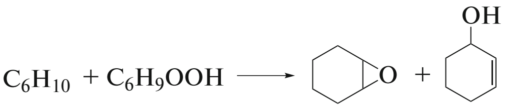


(IX)



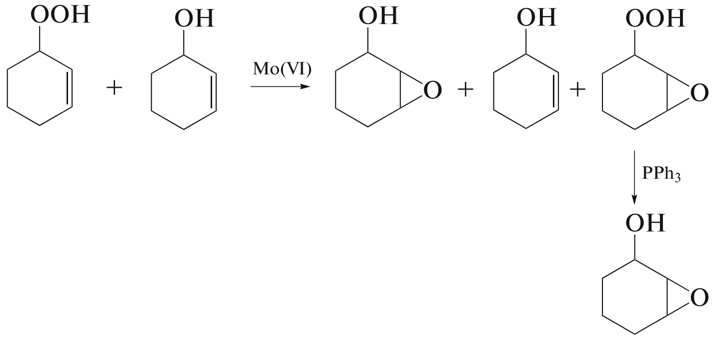
(X)

$$C_6H_9OO^{\bullet} + C_6H_{10} \longrightarrow C_6H_9OOH + {}^{\bullet}C_6H_9 \quad (XI)$$



(XII)

Iron(III) benzoate was inactive in the conversion of **2** (Table 2, no. 1). In contrast, copper(II) acetate caused the rapid decomposition of **2** to alcohol **3** and ketone **4**; **5** and other epoxy derivatives are found only as admixtures (Table 2, no. 2). In reaction of **2** with V(V)- and Mo(VI) catalysts, we observed the epoxidation of a double bond [20–22], In addition to epoxycyclohexane (**5**), 1,2-epoxycyclohexanol-3 (**6**) and a small amount of 1,2-epoxycyclohexanone-3 (**7**) were determined (Table 2, nos. 3–6). Apparently, epoxy alcohol **6** appeared as a result of epoxidation of hydroperoxide **2** or unsaturated alcohol **3** by reactions (XIII). After the reductive treatment of the analyzed solution by Ph_3P, both epoxidized alcohol and hydroperoxide were detected by gas chromatography as **6**. Since ketone **4** is weakly susceptible to epoxidation and was present in the solution in small amounts, the contribution of **7** to the sum of epoxy compounds was small.



(XIII)

As can be seen from Table 2, the overall selectivity of the consumption of **2** for epoxidation was 63% for the **I-V** catalyst supported on SiO_2 and was higher for Mo(VI) catalysts: both homogeneous $MoO_2(acac)_2$ and SiO_2-supported **II-Mo** and **III-Mo**. In the latter case, the selectivity was higher than 100%, which is explained by the participation in the epoxidation of **2** and other organic peroxides determined by iodometric titration. As a result of reduction of **2** by reaction (XII), alcohol **3** was formed. Under the action of heterogeneous Mo(VI) oxide catalysts, **2** was almost completely consumed for epoxidation, and radical

Table 2. Conversion of cyclohexene (**1**) and 2-cyclohexenyl hydroperoxide (**2**) in the presence of metallic catalysts[a]

No.	Catalyst (M^{n+}, μmol)	Time, h	$\mathbf{1}_{initial}$	$\mathbf{2}_{final}$	Main products, mmol				S_{ep}, %[b]	C_6 balance, %[c]
					3	**4**	**5**	**6** + **7**		
1	$Fe(benz)_3$ (18)	4.8	3.49	1.0	~0	0.05	0.01	0.01	0	99
2	$Cu(OAc)_2 \cdot H_2O$ (15)	2.0	2.72	0.10	0.45	0.52	0.02	0.02	0	83
3	20 mg **I-V** (8)	4.3	2.75	0.22	0.12	0.14	0.20	0.28	63	80
4	$MoO_2(acac)_2$ (17)	2.8	2.57	0.03	0.53	0.08	0.49	0.2 + 0.01	74	84
5	30 mg **II-Mo** (30)	4.0	2.14	0.14	0.43	0.08	0.54	0.21	91	77
6	20 mg **III-Mo** (10)	4.3	2.49	0.30	0.38	0.09	0.53	0.20	110	86

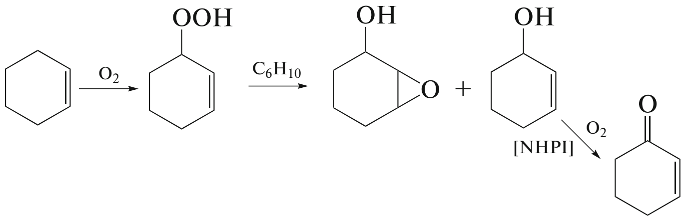
[a] Conditions: 2.5 mL of the initial solution containing 3.61 mmol (**1**), 0.14 mmol NHPI, 0.92 mmol (**2**) (1.0 mmol according to iodometric titration), 0.05 mmol (**4**), 0.04 mmol (**5** + **6** + **7**), Ar, 60°C.
[b] Selectivity $S_{ep} = 100\% \times \Sigma(\mathbf{5} + \mathbf{6} + \mathbf{7})/(\mathbf{2}_{initial} - \mathbf{2}_{final})$ (mol/mol).
[c] Relative to the initial solution.

decomposition was almost absent, which was also confirmed by the formation of only a small amount of ketone **4**. Material balance with respect to C_6 after the reaction was usually >80%. The balance that is different from 100% can be associated with the secondary conversion of unsaturated products that are easily oxidized at a double bond, as well as the formation of high-boiling resinous products in the decomposition of peroxides. Thus, metal compounds demonstrated different behavior with respect to 2-cyclohexenyl hydroperoxide: from the inertness of Fe(III) benzoate and the high activity of radical initiator Cu(II) acetate to the activation of hydroperoxide oxygen for nonradical oxidation on V(V) and Mo(VI) oxides. These results agree with data on the effect of metal compounds on NHPI-catalyzed oxidation of **1**. Thus, copper(II) acetate was an active catalyst for the decomposition of **2** to form final products **3** and **4**. Iron(III) benzoate participated in the generation of the active form of the PINO catalyst, but its oxidative ability appeared to be insufficient for catalyzing the decomposition of hydroperoxide **2**. Cyclohexene epoxidation by hydroperoxide obtained during cyclohexene oxidation is of interest. Supported MoO_3 catalysts proved to be quite efficient in the activation of 2-cyclohexenyl hydroperoxide, but in the experiments described above, we failed to combine the reactions of formation and consumption of **2** due to inhibition of the autoxidation process under the action of the Mo(VI) catalyst (Table 1, no. 12) In the next cycle of experiments, we performed cyclohexene epoxidation under conditions of the formation of 2-cyclohexenyl hydroperoxide in an oxygen atmosphere.

Cyclohexene Epoxidation by 2-Cyclohexenyl Hydroperoxide Formed in the Process of Autoxidation

For epoxidation, we used either a solution of cyclohexene in acetonitrile or a solution with a similar composition already containing a certain amount of hydroperoxide **2**. The latter was used in the experiments described in the previous section, and the preparation procedure for such solutions is given in the experimental section of this work. In both cases, the reaction mixture contained NHPI and supported molybdenum oxide epoxidation catalysts. The kinetics of the reaction with oxygen is illustrated by the gas absorption curves (Fig. 3). It was assumed that not only **2**, which is already present in the solution, reacted with the olefin. Further oxidation of **1** to **2** occurred under the action of the NHPI catalyst. It turned out that **2** weakly affects the intensity of cyclohexene oxidation by oxygen (Fig. 3, curve *1* for gas consumption in the absence of **2** and curves *2* and *3* in the presence of **2**), and most of epoxides were formed from **2**, which was initially present in the solution (Table 3, nos. 2 and 3).

The initial catalyst system was activated by the addition of iron(III) benzoate. With the promoting effect of iron by reactions (V), (VI), the rate of cyclohexene oxidation increased several times (Fig. 3, curve *4*), resulting in the formation of 2-cyclohexenyl hydroperoxide (Table 3, no. 4). The resulting **2** was consumed for epoxidation and converted into alcohol **3** and then to ketone **4** (reaction sequence (XIV)):



(XIV)

Both cyclohexene and the products of its transformation underwent epoxidation, so in addition to epoxycyclohexane **5**, dioxygenates **6** and impurity **7** were formed (Table 3, no. 4). Similar reactions were also observed in the presence of a homogeneous $MoO_2(acac)_2$ catalyst (Table 3, no. 5). According to the mechanism of epoxide formation (reactions (XII) and (XIII), (XIV)), the overall amount of epoxides should be equal to half of the reacted cyclohexene minus the remaining **2**. The other half of the reacted cyclohexene should transform into allylic oxygenates. In our experiments, the sum of amounts of ketone **4** and alcohol **3** taking into account the secondary transformation of part of **3** into epoxides **6** and **7** was lower than the amount of epoxides. This discrepancy is due to the high reactivity of unsaturated oxygenates, which easily undergo various secondary reactions with oxygen. As a consequence, C_6 balance was ~90% taking into account oxidation products (Table 3). Thus, using NHPI and small amounts of Fe(III) benzoate combined with Mo(VI) catalysts, we carried out in situ epoxidation of cyclohexene by 2-cyclohexenyl hydroperoxide formed in the process of autoxidation. Reactions with alkyl hydroperoxides are typical of var-

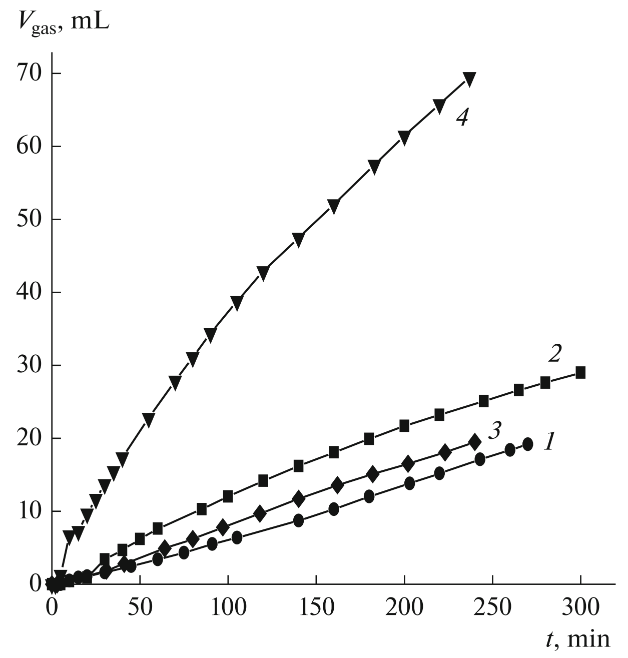


Fig. 3. Kinetics of gas consumption in cyclohexene oxidation by oxygen in the presence of SiO_2-supported MoO_3 catalysts **II-Mo** (20 mg, curves *1* and *2;* 40 mg, curve *4*) and **III-Mo** (40 mg, curve *3*) at 60°C. The compositions of initial mixtures for curves *1–4* corresponds to experiments nos. 1–4 in Table 3.

ious olefins and are used for the synthesis of the corresponding epoxides. There are also examples of the preparation of alkyl hydroperoxides by the interaction of oxygen with reactive alkanes or alkylbenzenes. However, it is rarely possible to carry out two reactions together. Until recently, we knew only the publication by Ishii et al. [51], in which the epoxidation of olefins, including cyclohexene, together with the oxidation of ethylbenzene, was described. The reaction occurred in the NHPI–$Co(OAc)_2$–$Mo(CO)_6$ system in the tenfold excess of ethylbenzene over the olefin. In contrast to this example of parallel reactions of two substrates with different reactivity, we managed to find conditions when one olefin participates in two simultaneous reactions of radical oxygenation at the allyl position and the addition of electrophilic oxygen to a double bond.

CONCLUSIONS

Thus, we studied the effects of different additives of transition metal compounds on the NHPI-catalyzed reaction of cyclohexene oxidation. The iron(III) salt accelerated the generation of the active PINO radical and thus accelerated 2-cyclohexenyl hydroperoxide formation, but did not participate in its decomposition. The copper(II) salt initiated the reaction of cyclohexene oxidation, and catalyzed the radical decomposition of 2-cyclohexenyl hydroperoxide and secondary oxidation of allyl oxygenates. In the reaction of cyclohexene with oxygen, epoxycyclohexane was detected in small amounts both in the catalysis by NHPI, and together with NHPI iron and copper salts. However, cyclohexene epoxidation occurred under the action of 2-cyclohexenyl hydroperoxide and Mo(VI) compounds. It was found that the polyfunctional three-component NHPI–Mo(VI)–Fe(III) catalyst is capable of causing cyclohexene oxidation by molecular oxygen with the formation of epoxides **5**

Table 3. Products of oxidation of **1** by oxygen in the presence of NHPI and Mo(VI) catalysts II-Mo (nos. 1, 2, 4), **III-Mo** (no. 3), and $MoO_2(acac)_2$ (no. 5)[a]

No.	Initial composition, mmol				Time, h	Composition of the solution after the reaction, mmol						C_6 balance, %[c]
	NHPI	M	**1**	**2**		**1**	**2**	**3**	**4**	**5**	**6 + 7**	
1	0.23	Mo 0.02	4.65	0	4.5	3.86	0.22	0.13	0.04	0.22	0.07	98
2[b]	0.05	Mo 0.02	3.26	1.10	5	1.68	0.60	0.16	0.29	0.9	0.30	88
3[b]	0.13	Mo 0.02	2.56	1.76	4	1.25	1.25	0.06	0.50	0.70	0.18	84
4	0.18	Mo 0.04 + Fe 0.006	4.65	0	4	1.89	1.0	0	0.43	0.70	0.20	91
5	0.23	Mo 0.02 + Fe 0.006	4.65	0	4	2.62	0.27	0.29	0.33	0.49	0.24	91

[a] Conditions: 2.5 mL of C_6H_{10} solution in CH_3CN, 60°C.

[b] Initial solution no. 2 contained also the impurity, $P = 0.07$ mmol (**4**); initial solution no. 3 contained also the admixture of products, $P = 0.27$ mmol (**4**) + 0.04 mmol (**5**) + 0.03 mmol (**6 + 7**).

[c] $100\% \times \Sigma(\mathbf{1}_{final} + \mathbf{2}_{final} + \mathbf{3} + \mathbf{4} + \mathbf{5} + \mathbf{6} + \mathbf{7})/(\mathbf{1}_{initial} + \mathbf{2}_{initial} + P)$ (mol/mol).

and **6** and 2-cyclohexen-1-on (**4**). Epoxidation occurred due to the hydroperoxide formed in cyclohexene oxidation.

ACKNOWLEDGMENTS

We thank Dr. L.V. Piryutko for providing us with the vanadium oxide catalyst and Dr. M.V. Shashkov for carrying out GCMS analyses. This work was carried out in the framework of state assignment of Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences (project AAAA-A17-117041710083-5).

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Translated by Andrey Zeigarnik