vergence of the results of works [1] and [2]. Small concentrations of NH_3 in the synthesis gas were used in [1], and in that case a change of selectivity was obtained for a small loss of activity of the Co catalyst. Éidus and Guseva [2] did not succeed in reproducing these results probably because of the higher NH_3 content in the mixture used.

By introducing NH_3 into the reaction zone, as is shown above, the formation of hydrocarbons is inhibited. In this case NH_3 is adsorbed evidently not only on the support, which has acidic sites, butalso on particles of metallic Co in the catalyst obtained, which is shown by the difference in the amount of NH_3 adsorbed on the support and on the regenerated catalyst.

CONCLUSIONS

1. At a low concentration of NH_3 (up to 1.5%) the formation of methane, CO_2 , and gaseous hydrocarbons from CO and H_2 on Co catalysts is suppressed.

2. By introducing large quantities of NH_3 (25%) into the reaction zone in the presence of Co catalysts, the synthesis of all hydrocarbons is inhibited as a result of the reversible poisoning of the catalysts.

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OXIDATION OF CYCLOHEXENE IN THE PRESENCE OF METAL MOLYBDATES

A. L. Smirnova and Yu. D. Norikov

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Depending on the nature of the heterogeneous catalyst system, oxidation of a hydrocarbon can take place by three possible mechanisms [1]: 1) heterogeneous-homogeneous, with the formation of radicals on the catalyst surface and subsequent chain reaction of these radicals in solution; 2) heterogeneous, without passage of radicals into the liquid phase; 3) a mixed mechanism in which free radicals in the liquid phase react by parallel homogeneous and heterogeneous reactions. The formation of radicals in heterogeneous systems usually proceeds by way of heterogeneous breakdown of hydroperoxide according to the mechanism

$$\begin{array}{l} \text{ROOH} + \text{S} \rightleftharpoons | \text{ROOH}...\text{S} | \rightarrow \text{RO}^{*} + | \text{OH}...\text{S} | \\ \text{ROOH} + \text{S} \rightleftharpoons | \text{ROOH}...\text{S} | \rightarrow \text{RO}_{2}^{*} + | \text{H}...\text{S} | \end{array} \tag{1}$$

Parallel with these reactions, catalytic, molecular breakdown of hydroperoxide with the formation of a ketone is possible [2]. Epoxidation of the double bond by hydroperoxides in the presence of heterogeneous contact surfaces, for example MoO_3 [3], is also a nonradical process.

Heterogeneous catalysts are known which do not influence the breakdown of hydroperoxides [1], for example Ag/Al_2O_3 . For this catalyst, a mechanism of heterogeneous, nonchain radical

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Cotolwat	Cata- lyst,	Reac- tion	Product composition, mole % of total products*				Relative rate of formation of products		
	g/ liter	time, min	CXHP	CXO	ROH	CXON	WROH/WCXON	W _{ROH} /W _{CXO}	
MoO3	40	120	Traces	48,0	48,0	4,0	12,0	1,0	
CoMoO ₄	20		* 41,5	48,0	48.0 25.0	3,9 8,0	12,3 3,1	1,0 1,0	
MnMoO ₄	40	$ \begin{array}{c} 140 \\ 30 \\ 420 \end{array} $	55,0	5,0 5,0	35,0 20,0	10,5	3,3	1,0 4,0	
Ag_2MoO_4	40	$ \begin{array}{c} 120 \\ 30 \\ 260 \end{array} $	43,0 83,0 83,5	$ \begin{array}{r} 18,0 \\ 2,6 \\ 2,5 \end{array} $	25,0 7,80 7,6	$ \begin{array}{c c} 14,0\\ 6,5\\ 6,4 \end{array} $	2,1 1,2 1,2	1,4 3,0 3,0	

TABLE 1. Oxidation of Cyclohexene in the Presence of Metal Molybdates at $60^{\circ}C$

*CXO = cyclohexene oxide, ROH = cyclohexenol, CXON = cyclohexenone.

TABLE 2. Oxidation of CX with Addition of t-BuOOH, Both without Catalyst and in the Presence of $MnMoO_4$, Ag_2MoO_4 (70°C), and MoO_3 (50°C)

	Gas phase	Concn.of t-BuooH 102:molé/	Reaction time, min	Initial rate, W·10 ⁵ mole/liter·sec		Composition of products, mole % on absorbed O_2			
Catalyst				consumption of t-BuOOH	ab- sorp. pf O ₂	ROOH	схо	ROH	CXON
No cata- 1yst	Ar O ₂	8,2 10,5	90 90	None con- sumed	- 3,1	- 96	Traces	_ Traces	– Iraces
MoO₃ MnMoO₄	Ar Ar	9,0 9,0	60 20	9,2 3,5	-	– Produ	90* act not	identif	ied
Ag2MoO4	O ₂ Ar O ₂	9,0 14,5 9,0	20 180 120	2,8 None consumed »	42,0 - 4,0	93 96	Traces Traces	Traces	5,0 Traces

*On t-BuOOH consumed.

oxidation of the hydrocarbon is proposed, involving activation of O_2 and heterogeneous recombination of radicals.

$$S + O_2 \rightleftharpoons |S \dots O_2|$$
⁽³⁾

$$|S...,O_2| + RH \rightarrow R' + |S...OOH|$$
(4)

$$|S...OOH| + R' \rightarrow ROOH + S$$
(5)

In the present paper, we have studied the oxidation of cyclohexene (CX) in the presence of MoO_3 and molybdates of Co, Mn, and Ag in order to elucidate the role of Mo-based heterogeneous catalysts in the oxidation by molecular O_2 and in hydroperoxide epoxidation.

EXPERIMENTAL

Cyclohexene (CX) was prepared by a laboratory method and purified by repeated distillation at 83°C ([RH] = 99%). Molybdates were prepared by mixing solutions of the corresponding salts, the precipitates being washed repeatedly with water and dried in air at 100°C.

The oxidation of CX by oxygen $(pO_2 + 0.1 \text{ MPa})$ was carried out in a bubbler-type, thermostatted glass cell with a reflux condenser, and in a manometric apparatus having a reactor provided with a magnetic stirrer, at 50-70°C in the presence of the heterogeneous catalysts MoO_3 , $CoMoO_4$, $MnMoO_4$, and Ag_2MoO_4 (at a concentration of 5-100 g/liter) in a medium of CX. Experiments in which tertiary butyl hydroperoxide, t-BuOOH, was added were carried out in the presence of Ag_2MoO_4 , $MnMoO_4$, and MoO_3 , and without any heterogeneous catalyst, in an atmosphere of Ar or O_2 . Experiments on the decomposition of cyclohexene hydroperoxide (CXHP) were carried out in the presence of $MnMoO_4$ (50°C) and Ag_2MoO_4 (70°C) in a medium of CX under argon. The decomposition of ethylbenzene hydroperoxide (EBHP) in chlorobenzene under argon at 90°C was investigated in the presence of Ag_2MOO_4 . The initial concentration of CXHP was



Fig. 1. The effect of metal molybdates on the decomposition of hydroperoxides in CX (1-3, 5) and in chlorobenzene (4) in an atmosphere of argon: 1) CXHP, $Ag_2MoO_{\perp} = 50$ g/liter, $60^{\circ}C$; 2) CXHP, $Ag_2MoO_{\perp} = 80$ g/liter, $70^{\circ}C$; 3) t-BuOOH, $Ag_2MoO_{\perp} = 5$ g/liter, $70^{\circ}C$; 4) EBHP, $Ag_2MoO_{\perp} = 90$ g/liter, $90^{\circ}C$; 5) CXHP, $MnMoO_{\perp} = 100$ g/liter, $50^{\circ}C$.

Fig. 2. Kinetics of oxygen absorption (1, 1')and buildup of CXHP (2, 2'), cyclohexenone (3, 3'), cyclohexenol (4, 4'), and cyclohexene oxide (5, 5') in the oxidation of CX in the presence of MnMoO₄ (figures with dash) and Ag₂MoO₄ (figures without dash) at 70°C.

about 10^{-2} mole/liter. The products of the oxidation of CX and of the decomposition of CXHP were determined by GLC. The surface areas of the heterogeneous catalysts was determined by the BET method via the thermal desorption of argon

Catalyst	MoO3	CoMoO ₄	MnMoO4	Ag ₂ MoO ₄
Surface, m ² /g	0,2	11,0	5,0	0,6

DISCUSSION OF RESULTS

In the presence of MoO₃, almost all the hydroperoxide formed reacts with CX, giving equimolar quantities of cyclohexenol and the olefin oxide, with a very small amount of cyclohexenone (Table 1). A similar picture is observed with $COMOO_4$ as catalyst: the concentration of hydroperoxides is relatively small and the ratio W(alcohol)/W(oxide) = 1. The quantity of alcohol is three times greater than that of ketone, whereas in the formation of radicals in the liquid phase, and in the second-order recombination of peroxide radicals, this ratio should be close to unity [1]. Hence, in the presence of $CoMoO_4$, as with MoO_3 , epoxidation of CX by the hydroperoxide occurs.

The ratio W(alcohol)/W(ketone) = 1 is also observed in the case of MnMoO₄ and Ag_2MoO_4 . For these catalysts, a considerable increase in the yield of alcohol over the yield of olefin oxide is characteristic, i.e., despite the presence of Mo in the catalyst, catalytic epoxidation by hydroperoxide is almost absent. The absence of catalytic epoxidation in these systems is supported by experiments in which t-BuOOH is added to the initial CX (Table 2). Whereas in the presence of MoO₃, CX oxide is the main product of the reaction of t-BuOOH (in an atmosphere of argon), in the presence of MnMoO₄ and Ag_2MoO_4 under analogous conditions, no oxide is detected. Oxidation of CX with t-BuOOH added initially in the presence of MnMoO₄ and Ag_2MoO_4 yields mainly CXHP as the preferred product. When hydroperoxide is absent in the initial cyclohexene ([ROOH] \leq 10⁻³ mole/liter) no oxidation takes place, and it commences only on the addition of CXHP. CXHP decomposes in the presence of MnMoO₄ (Fig. 1, curve 5) at a considerable rate (1.6·10⁻⁴ mole/liter·sec), being con-



Fig. 3. Effect of concentration of $MnMoO_4$ on the initial rate of absorption of O_2 (1) and formation of CXHP (2), cyclohexenone (3), cyclohexenol (4), and cyclohexene oxide (5) in the oxidation of CX at 50°C.

Fig. 4. Effect of concentration of Ag_2MoO_4 on initial rate of absorption of O_2 (1) and formation of CXHP (2) in the oxidation of CX at 70°C.

verted into alcohol and ketone, the rate of formation of ketone being twice that of alcohol. An analogous ratio of the rates of formation of alcohol and ketone is observed in the oxidation of CX in the presence of $MnMoO_4$ (Figs. 2 and 3). These results, together with the way in which the initial rate of oxygen absorption and formation of products depends on the concentration of $MnMoO_4$ (see Fig. 3), support the following mechanism:

 $RH + O_{2} \rightarrow R' + IIO_{2}'$ $R' + O_{2} \rightarrow RO_{2}'$ $RO_{2}' + RH \rightarrow ROOH + R'$ $nROOH + S \rightleftharpoons |nROOH - S| - | \xrightarrow{\rightarrow} RO' + RO_{2}' + H_{2}O + S$ $RO_{2}' + RO_{2}' \rightarrow R'COR'' + ROH + O_{2}$ $nRO_{2}' + S \rightarrow ROH + R'COR'' + O_{2}$

Thus, the catalytic function of $MnMoO_4$ in the oxidation of CX is connected with radical decomposition of CXHP on its surface. The existence of a limit to this dependence would seem to be connected with linear chain termination on the surface of the $MnMoO_4$.

In the case of Ag_2MoO_4 , the chief product of the reaction is characteristically CXHP (see Tables 1 and 2 and Fig. 2); the composition of the products does not vary with time (as can be seen from Table 1), in distinction from other combounds of Mo. It is observed that Ag_2MoO_4 has no effect on the decomposition of hydroperoxides (see Fig. 1, curves 1-4), which shows that reaction (1) is not involved. As with $MnMoO_4$, after complete purification of the original olefin from hydroperoxide ([ROOH] $\leq 10^{-3}$ mole/liter) oxidation of CX does proceed, and commences only on addition of CXHP. The initial rates of absorption of O_2 and of formation of CXHP increase with increased concentration of Ag_2MoO_4 (Fig. 4). These results indicate that the mechanism proposed for the action of Ag must comprise reaction (3) supplemented by reaction (2) for decomposition of hydroperoxide. Consequently, the oxidation-reduction cycle of the catalyst is laid down by reactions (2) and (3).

The formation of CXHP proceeds in the surface layer according to the reaction

 $| O_2 \dots S \dots ROOH | + RH \rightarrow 2ROOH + S$

almost without the formation of radicals in the liquid phase. Thus, the catalytic function of Ag_2MoO_4 under the conditions of oxidation of CX is associated with simultaneous activated absorption of both O_2 and hydroperoxide on its surface. The elementary events of chain propagation and termination take place in the surface layers.

CONCLUSIONS

1. Under the conditions of low-temperature oxidation of cyclohexene, cobalt(II) molybdate catalyzes the epoxidation of the double bond by the cyclohexene hydroperoxide which is formed.

2. The catalytic function of manganese(II) molybdate is connected with radical breakdown of hydroperoxide on its surface. Parallel with this radical breakdown, molecular decomposition of hydroperoxide takes place on the surface with the formation of cyclohexanone. As well as taking part in chain initiation, manganese molybdate also participates in the radical breakdown stage.

3. The catalytic function of silver molbydate is associated with mutual activated absorption of oxygen and hydroperoxide on its surface. Formation of hydroperoxide takes place in the surface layers without giving rise to radicals in the liquid phase.

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OXIDATION OF ETHANOL BY OZONE AND ANALYSIS OF PROBABLE STRUCTURE OF ACTIVATED COMPLEX

V. V. Shereshovets, N. Ya. Shafikov,G. S. Lomakin, A. I. Ivanov,I. R. Akhunov, O. A. Ponomarev,and V. D. Komissarov

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In previous studies [1, 2] using the kinetic isotope effect, it was shown that the limiting stage in the reaction of O_3 with ethanol is rupture of an α -CH bond. With the aim of studying the mechanism of this stage, we have applied quantum-chemical calculations in the present work as a means for analyzing possible models of the activated complex; also, within the framework of transition-state theory, we have estimated the values of the preexponential factor. The data are compared with results obtained from kinetic studies of the reaction in various solvents.

EXPERIMENTAL

The kinetics of the reaction of O_3 with C_2H_5OH (ROH) were studied at 11-50°C under static conditions, following the O_3 consumption in the liquid phase spectrophotometrically [3]. As solvents, we used 1,2-dichloroethane, a binary mixture of CCl_4 and 1,2-dichloroethane, and CH_3COOH . All of the solvents were purified by treatment for 10-15 min with an O_3-O_2 mixture, after which they were distilled. The experiments were performed in a thermostated quartz cell (volume 10 ml, optical path length 2 cm). The solution of O_3 in the particular solvent was prepared directly in the cell; after determining the O_3 concentration, the ROH solution was introduced. It was established in special experiments that under these conditions, the consumption of O_3 in reactions with products from the oxidation of ROH, and also the consumption of ROH in reaction with such a solvent as acetic acid, can be neglected.

The initial concentrations of the reactants (M) were as follows: $[ROH]_0 \sim 3 \cdot 10^{-3}$ to $3 \cdot 10^{-2}$, $[0_3]_0 \sim 5 \cdot 10^{-5}$ to $2 \cdot 10^{-3}$.

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