

Catalytic Properties of Some Molybdenum Complexes in the Epoxidation Reaction of Olefins with Hydroperoxides

J. SOBCZAK and J. J. ZIÓŁKOWSKI

Institute of Chemistry, University of Wrocław, 50-383 Wrocław, Poland

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*Catalytic properties of $H_2[Mo_2O_4(Ox)_2(H_2O)_2] \cdot 3H_2O$, $Mo(CO)_6$, $MoO_2(acac)_2$, $MoO(OH)_3$, MoO_2 (*t*- $C_6H_{11}O_2$) $_2$ and $Mo(V)$ acetylacetonate in the epoxidation reaction of cyclohexene with cumene hydroperoxide were investigated.*

Kinetic studies for the model reaction at a molar ratio of cyclohexene : cumene hydroperoxide : Mo catalyst = 1:1:0.002 at 85°C and 90°C in nitrobenzene and benzene were carried out. $H_2[Mo_2O_4(Ox)_2(H_2O)_2] \cdot 3H_2O$ shows the highest catalytic selectivity owing to its electronic structure.

Introduction

Among many preparation methods of the epoxide which employ complexes of transition metals as catalysts, the most thoroughly examined one has recently been the epoxidation reaction of olefins by means of organic hydroperoxides^{1–14}.

The most active catalysts in those reactions appeared to be the complex molybdenum compounds, in particular: $Mo(CO)_6$ ^{1,5,6}, molybdenum naphthenate,^{3,15} molybdenum resinate^{9,10}, $MoO_2(acac)_2$ ^{2,5} and others, especially those readily soluble in the reaction medium.

In spite of the fact that the reactions between olefins and organic hydroperoxides catalyzed by molybdenum compounds were dealt with in a number of papers, the mechanism and kinetics of such reactions are, however, still not fully explained. Some light on this problem was shed by Sheldon^{5,6}, Sapunov *et al.*¹⁴, who suggest that the epoxidation reaction of olefins proceeds through an intermediate which is most probably the molybdenum complex with a hydroperoxide and olefin. Some authors believe that initially a molybdenum complex with hydroperoxide is formed and then coordinated to the olefin^{26,5,6,16}, whereas others suggest a reverse sequence^{26,14}. It seems, however, unquestionable that the molybdenum complex is modified during the epoxidation process and is converted into some type of compounds, *viz.*, molybdenum(VI) diol complexes^{5,6,17}.

The purpose of the present work was to obtain additional information on the mechanism and structure of

the active molybdenum complex used as a catalyst in this reaction.

Experimental

Materials and Procedures

Cumene hydroperoxide (Koch-Light Laboratories Ltd), stabilized with sodium carbonate, was purified from the stabilizer and dried over $MgSO_4$.

Cyclohexene (Fluka AG, Buchs SG) was distilled before use.

Molybdenum Compounds

$Mo(CO)_6$ (Merck-Schuchardt), $MoO_2(acac)_2$ ¹⁸, molybdenum(V) acetylacetonate were prepared by dissolving molybdenum(V) hydroxide in acetylacetonate. $MoO_2(trans-C_6H_{11}O_2)_2$ ⁵, $MoO(OH)_3$ ⁹, MoO_3 (POCh-Gliwice), $H_2[Mo_2O_4(Ox)_2(H_2O)_2] \cdot 3H_2O$ were prepared by our own method from the reaction between molybdenum(V) hydroxide and oxalic acid in aqueous solution.

The epoxidation reaction was carried out under nitrogen in a glass reactor fitted with a magnetic stirrer and reflux condenser. The reactor was fed with the catalyst, solvent and olefin and then the mixture was treated with the hydroperoxide solution at a suitable temperature. The reaction time was measured since the hydroperoxide was introduced into the reaction system.

The reaction was carried out in a 50 ml volume. 5 ml cyclohexene (50 mmol) and about 50 mmol cumene hydroperoxide in nitrobenzene or benzene solution were used. 2×10^{-3} mol of catalyst was added per mol of olefin and hydroperoxide.

Analytical Determinations

Conversion of cumene hydroperoxide was monitored by iodometric titration.

Cyclohexene and epoxycyclohexane were determined by means of gas chromatographic methods in a 1 m column filled with W-DMCS Chromosorb with a liquid SE-30 phase of about 2.5% with 0.03% PEG-20000 added.

Electronic absorption spectra were recorded by means of a Cary 14 spectrophotometer.

Results and Discussion

Studies on the Catalytic Activity of Molybdenum Compounds

The catalytic activity of various molybdenum compounds was examined in a model epoxidation reaction of cyclohexene with cumene hydroperoxide at a molar ratio of cyclohexene:cumene hydroperoxide:catalyst = 1:1:0.002.

The results of studies on this reaction in nitrobenzene as solvent at 85°C in the presence of various molybdenum compounds are presented in Table I.

With the catalysts listed in Table I (except with MoO₃) all solutions became brown during the reaction. The active form of the catalyst is most probably identical in all reactions. The electron spectra of these solutions exhibit a distinct band at about 22800 cm⁻¹.

For H₂[Mo₂O₄(Ox)₂(H₂O)₂]·3H₂O as a catalyst, after cyclohexene and epoxy-cyclohexane were distilled off under reduced pressure from the reaction mixture and a fresh portion of the olefin and hydroperoxide

was introduced, the reaction was found to proceed further but at a lower rate. This is an evidence that the active form of the catalyst was preserved in the reaction system. The lower rate of epoxidation may be explained as due to the inhibiting effect of cumyl alcohol which was left in the reaction mixture after removal of cyclohexene and epoxy-cyclohexane.

Kinetic and Epoxidation Mechanism

Kinetic measurements of the epoxidation reaction of cyclohexene with cumene hydroperoxide were carried out at 90°C in the presence of the most active and selective molybdenum catalysts. The epoxidation reaction was carried out in nitrobenzene, but with some catalysts the reaction was also carried out in benzene for comparison. The catalytic effectiveness of the molybdenum catalysts under investigation is presented in Table II.

The data in Table II show that the most effective and selective catalyst in nitrobenzene solution is the oxalate complex of molybdenum(V), H₂[Mo₂O₄(Ox)₂(H₂O)₂]·3H₂O. The catalytic activity of this complex in benzene solution is considerably lower (Figure 1). This is because the oxalato complex causes decomposition of cumene hydroperoxide very slowly while in

TABLE I. Epoxidation of Cyclohexene with Cumene Hydroperoxide in Nitrobenzene at 85°C.^a

Catalyst ^b	Reaction Time (min)	Hydroperoxide Conversion (%)	Cyclohexene Conversion (%)	Selectivity per Used		Reaction Yield (%)
				Cyclohexene (%)	Hydroperoxide (%)	
MoO ₂ (acac) ₂	280	76.2	70.8	56.4	52.4	39.9
MoO ₂ (acac) ₂ ^c	280	63.2	90.9	19.7	28.3	17.9
Mo(V) Acetylacetonate	265	82.2	81.4	63.6	63.0	51.8
H ₂ [Mo ₂ O ₄ (Ox) ₂ (H ₂ O) ₂]·3H ₂ O ^e	260	71.3	68.2	75.2	71.9	51.3
MoO ₃ ^d	1200	—	—	—	—	—
Mo(OH) ₃ ^{d, e}	475	77.9	88.3	52.7	59.7	46.5

^a 50 mmol cyclohexene + 50 mmol cumene hydroperoxide + 0.1 mol in nitrobenzene (solution volume 50 ml), nitrogen atmosphere. ^b Acac = acetylacetonate, Ox = oxalate. ^c Oxygen atmosphere; the reaction products were found to contain considerable amounts of cyclohexanediol-1,2. ^d Heterogeneous system, molybdenum compound incompletely dissolved. ^e The system is initially heterogeneous.

TABLE II. Epoxidation Reaction of Cyclohexene with Cumene Hydroperoxide Catalyzed by Molybdenum Compounds in Nitrobenzene at 90°C.

Catalyst	Time (min)	Hydroperoxide Conversion (%)	Cyclohexene Conversion (%)	Selectivity per Used		Reaction Yield (%)
				Cyclohexene (%)	Hydroperoxide (%)	
Mo(CO) ₆	330	82.6	85.0	67.8	69.7	57.6
MoO ₂ (acac) ₂	400	87.3	81.2	60.1	55.9	48.8
MoO ₂ [t-C ₆ H ₈ O ₂] ₂	440	81.2	82.4	69.9	70.9	57.6
H ₂ [Mo ₂ O ₄ (Ox) ₂ (H ₂ O) ₂]·3H ₂ O	350	73.6	70.5	96.5	92.4	68.0

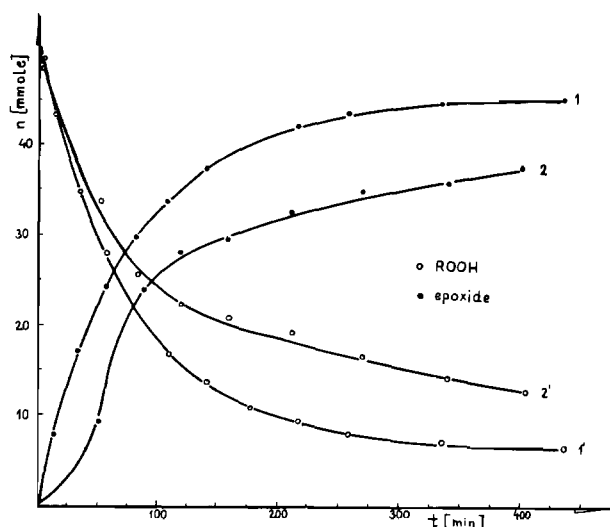


Figure 1. Reaction of cumene hydroperoxide with cyclohexene in benzene at 90°C catalyzed by $\text{Mo}(\text{CO})_6$ (curves 1, 1') and $\text{H}_2[\text{Mo}_2\text{O}_4(\text{ox})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (curves 2, 2').

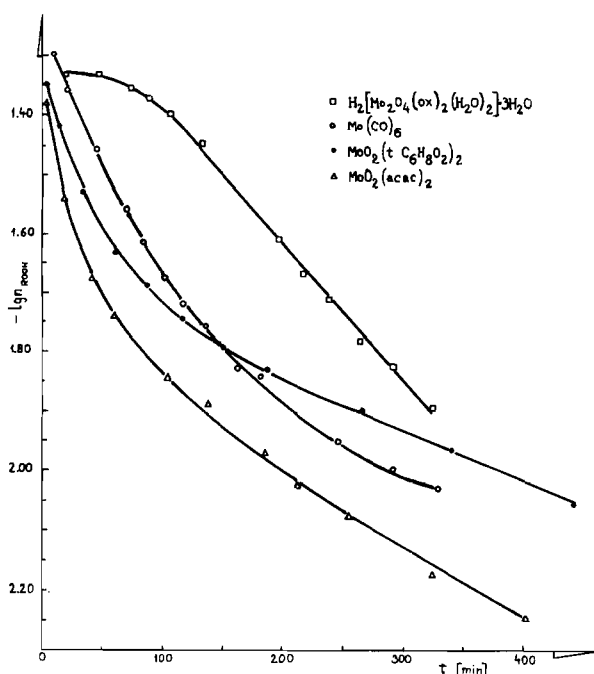


Figure 2. Reaction of cumene hydroperoxide with cyclohexene in nitrobenzene at 90°C catalyzed by molybdenum compounds.

nitrobenzene at 86°C the hydroperoxide undergoes full decomposition after about 35 min.

The kinetic curves describing the decomposition of cumene hydroperoxide by the compounds listed in Table II are presented in Figure 2, which shows that

only in the epoxidation reaction catalyzed by $\text{H}_2[\text{Mo}_2\text{O}_4(\text{Ox})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ is the decomposition of cumene hydroperoxide a first-order reaction. The kinetic curves of cyclohexene conversion and epoxy cyclohexane production do not exhibit a rectilinear dependence for the catalysts given in Table II in the semilogarithmic scale. For the molybdenum(V) oxalato complex, $\text{H}_2[\text{Mo}_2\text{O}_4(\text{Ox})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$, kinetic studies were made over the temperature range 70–90°C. The decomposition of cumene hydroperoxide over this temperature range is a first order reaction. The rate constants are provided in Table III, and $\log k$ vs. $1/T$ is plotted in Figure 3. The curve consists of two nearly straight lines. This fact may indicate that the reaction proceeds according to a mechanism in which the homolytic decomposition of the hydroperoxide by the molybdenum complex competes with the epoxidation reaction of an olefin⁵. From the diagram shown in Figure 3 the activation energy of cumene hydroperoxide decomposition was calculated and the following values were obtained:

TABLE III. Rate Constants for the Decomposition of Cumene Hydroperoxide in the Epoxidation of Cyclohexene Catalyzed by $\text{H}_2[\text{Mo}_2\text{O}_4(\text{Ox})_2(\text{H}_2\text{O})_2]$.

Temperature °C	$k \times 10^{-3}$ (min^{-3})
70	1.01
75	2.01
80	2.86
86	3.94
90	4.96

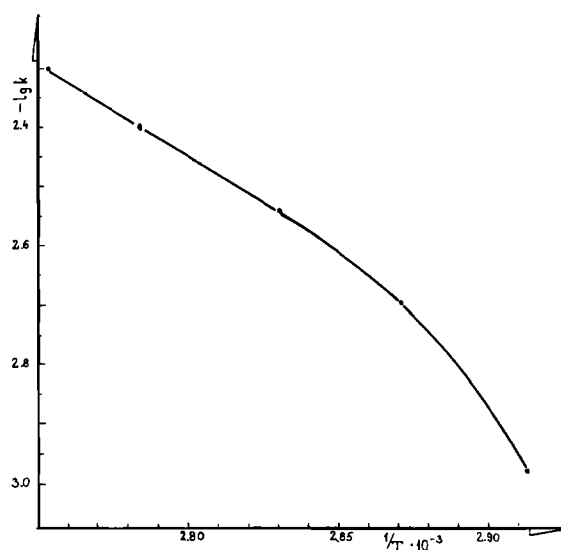


Figure 3. Plot of $\log k$ vs. $1/T$ for cumene hydroperoxide decomposition during the epoxidation of cyclohexene catalyzed by $\text{H}_2[\text{Mo}_2\text{O}_4(\text{ox})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$.

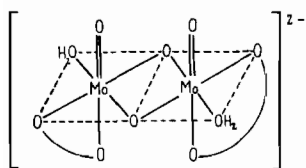


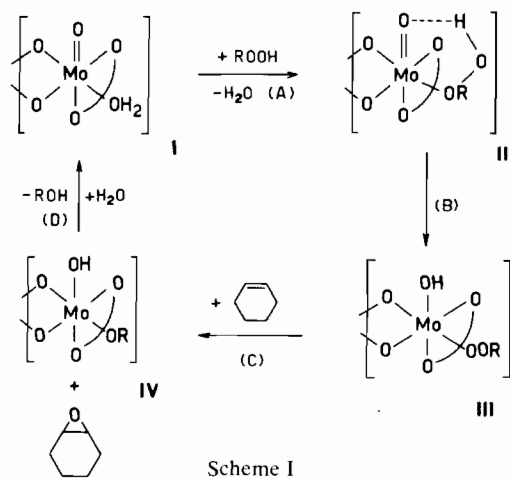
Figure 4. Structure of $[\text{Mo}_2\text{O}_4(\text{ox})_2(\text{H}_2\text{O})_2]^{2-}$ ion²⁰.

13.9 ± 0.8 Kcal/mol and *ca.* 24.0 Kcal/mol over the temperature ranges 80–90°C and 70–80°C, respectively.

A high selectivity of the epoxidation reaction of cyclohexene catalyzed by $\text{H}_2[\text{Mo}_2\text{O}_4(\text{Ox})_2(\text{H}_2\text{O})_2]$ (Table II) indicates that the structure of this molecule is very close to that of the active complex.

The oxalato complex $\text{H}_2[\text{Mo}_2\text{O}_4(\text{Ox})_2(\text{H}_2\text{O})_2]$ is a dimer whose structure is presented in Figure 4.²⁰

The epoxidation reaction starts with no initiation time if cyclohexene is introduced prior to the start of hydroperoxide decomposition. It means that the molybdenum hydroperoxide complex formation precedes the epoxidation process (Scheme I).



Scheme I

Contrary to other molybdenum complexes in lower oxidation states, the hydroperoxide is most readily coordinated to the oxalato complex by replacing the H_2O molecule (Scheme I, path A).

The entry of a hydroperoxide into the co-ordination sphere of Mo(V) (structure II) results in an increase of the electrophilic properties of oxygens from the peroxy group and facilitates their interaction with olefin 6a (path B, C) towards the epoxide formation. In the active complex the molybdenum appears most

probably in the oxidation state VI (structure [III]). This oxidation state of Mo is stabilized during the epoxidation process in which, beside the epoxide, a less active Mo(VI) complex with cumyl alcohol is formed (structure [IV]). Under the epoxidation conditions this complex may be reactivated (path D) also by the splitting off of the cumyl alcohol molecule reconverted into initial form (structure [I]).

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