

Comparative evaluation of the activity of some homogeneous and polymeric catalysts for the epoxidation of alkenes by organic hydroperoxides

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Abstract

Attempts have been made to immobilize some molybdenum-containing complexes with low molecular weight organic ligands, including newly synthesized ones, on commercial ion-exchange resins. The catalytic activity of these complexes in the epoxidation reaction of cyclohexene with *tert*-butyl hydroperoxide was evaluated and compared to that of the molybdenyl acetylacetonate homogeneous catalyst as well as to some polymeric molybdenum-containing catalysts derived from ion-exchange resins and obtained previously. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Molybdenum complexes have long been known to be useful catalysts for the epoxidation of alkenes by organic hydroperoxides. The industrial implementation of this organic reaction has been achieved by the Halcon process which utilizes soluble Mo complex in order to catalyze the selective epoxidation of propylene to propylene oxide as an important precursor in the organic synthesis [1]. Since then, a number of soluble molybdenum complexes have been synthesized and employed as catalysts for the epoxidation of various alkenes and a few examples only are mentioned here in this respect [2–6]. On the other hand, the preparation of polymer-supported catalysts for the epoxidation of

alkenes has received scientific attention since the late 1970s [7–9]. The attempts to immobilize molybdenum and vanadium complexes on polymers have initially included cation-exchange resins [7,9–11], anion-exchange resins [8], cross-linked poly(ethylene oxide), polyvinylalcohol, poly(vinylpyridine) [12,13], etc. More recently, a number of chelating functional molybdenum-containing copolymers have been synthesized and employed as catalysts for the epoxidation of alkenes, mostly, cyclohexene and propylene [14–19].

In our works published recently [20,21], we reported on the catalytic epoxidation of cyclohexene and other alkenes by *tert*-butylhydroperoxide (TBHP) in the presence of some molybdenum-containing polymeric complexes. More particularly, our most recent study was focused on the estimation of the stability of the catalytically active complexes based on chelating commercial ion-exchange resins

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(polyampholites) on repeated use in the epoxidation reaction [21]. The aim of the present work was to evaluate and compare the activity of these polymeric catalysts with the well-known molybdenyl acetylacetonate ($\text{MoO}_2(\text{acac})_2$) and with other newly prepared molybdenum-containing complexes, that were proved to serve as catalysts for the epoxidation of alkenes by organic hydroperoxides.

2. Experimental

2.1. Starting materials

Cyclohexene (Fluka AG, >99.5%), TBHP (Fluka AG), sodium molybdate $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (Fluka AG), molybdic acid $\text{MoO}_3 \cdot \text{H}_2\text{O}$ (85% MoO_3 , Merck), molybdenyl acetylacetonate $\text{MoO}_2(\text{acac})_2$ (Riedel de Haen, Germany), employed directly as homogeneous catalyst and 1,2-dichloroethane (99%, Merck-Schuchardt) were commercial products. Toluene (The Oil Chemical Company, Bourgas, Bulgaria) was initially distilled and the corresponding fraction (b.p. 110–111°C) was collected and refluxed over sodium for several hours. This was finally followed by the second distillation within the same temperature range. The gas chromatography analysis (GLC) showed the purity of the final product over 99.9%. Waste polyethylene glycol fraction $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ was obtained from the Oil Chemical Company, Bourgas, Bulgaria and, according to GLC analysis, contained the following products: $n = 1$ (2.3%); $n = 2$ (15.7%); $n = 3$ (58.1%); $n = 4$ (16.9%); $n = 5$ (4.8%).

The industrial grade chelating ion-exchange resin Amberlite IRC 748 and the monofunctional weakly acidic cation exchanger Amberlite IRC 50 (Rohm&Haas, USA) which are chemically modified copolymers of styrene and divinylbenzene of macroporous (macroreticular) structure and particle diameter $\sim 300\text{--}1200\ \mu\text{m}$ [22] were employed as polymeric supports. The ion-exchange resins were initially treated by passing 500 ml 1.5 N HCl at the specific rate of $3\text{--}4\ \text{ml cm}^{-3}\ \text{h}^{-1}$ through $25\text{--}30\ \text{cm}^3$ of the polymers soaked preliminarily for 24 h in distilled water and placed into a glass column. The procedure was followed by washing with deionized water to pH 6–7 for the filtrate and drying for 24 h in air.

2.2. Catalysts preparation

Catalyst A: This novel molybdenum-containing complex has been synthesized in the Laboratory of Organoelement Compounds (the Faculty of Chemistry at the Sofia University “Sv.Kl. Okhridski”, Bulgaria) and was kindly provided to us to evaluate its versatility and activity in the epoxidation reaction.

Catalyst B: 15 g (0.093 mol) molybdic acid and 28 g (0.190 mol) polyethylene glycol waste fraction were mixed into 100 ml distillation flask which was connected to cooled Liebig condenser and receiving flask. The mixture was heated with stirring at temperature of 180–200°C for 4–5 h until the distillation of the fraction boiling at 95–105°C was completed. The resulting black solid was rinsed thoroughly with ether, filtered and dried under vacuum to constant weight, to obtain black powderish product.

Polymeric catalyst C: 0.4 g (0.95 mmol) of the catalyst A were dissolved in 20 ml 1,2-dichloroethane placed in a small round-bottomed flask. The latter was connected to a reflux condenser and then 0.2 g Amberlite IRC 50 cation exchanger, dried preliminarily under vacuum, were added. The mixture was stirred with heating under reflux for 24 h. Then the mixture was cooled, the treated polymer was filtered, rinsed consecutively with 1,2-dichloroethane and ether and dried under vacuum at 50–60°C to constant weight.

Polymeric catalyst D: 3.35 g (10.3 mmol) $\text{MoO}_2(\text{acac})_2$ were added to $120\ \text{cm}^3$ toluene in a round-bottomed flask equipped with reflux condenser. The suspension was heated with stirring under reflux for 30 min and then 1.5 g Amberlite IRC 748 in hydrogen form, dried preliminarily under vacuum at 70°C, were added. The mixture was refluxed with stirring for another 24 h. Finally, the modified ion-exchange resin was filtered, washed with acetone to the absence of dissolved molybdenum in the filtrate and dried under vacuum at 70°C to constant weight [21].

Polymeric catalyst E: 18.2 g (0.075 mol) $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ were dissolved in 400 ml deionized water. Then, concentrated nitric acid was added dropwise to the solution until pH value of ca. 3.5 was reached. Next, 2.8 g air-dried ion-exchange resin Amberlite IRC 748 in hydrogen form were introduced and this was followed by a vigorous shaking of the mixture for 24 h at room temperature. The ion exchanger so modified was filtered and washed with deionized

water to neutral reaction. Finally, after consecutive washing with ethanol and ether, the polymer was dried in vacuo at 70°C to constant weight [21].

2.3. Catalytic epoxidation

For the typical experimental procedure, an amount of the catalyst, equivalent to 0.033 mmol Mo and 6.6 ml (0.065 mol) cyclohexene were placed into a three-necked 12 cm³ thermostated glass reactor fitted with a reflux condenser, thermometer and a septum cap. The mixture was stirred for 5 min at 79°C and then 1 ml (ca. 0.010 mol) anhydrous TBHP was added. No solvent was used in the epoxidation reaction; an excess of cyclohexene reactant was placed in the reaction mixture instead. The reaction was monitored at certain time intervals to determine the current concentration of TBHP and was left to proceed until its nearly complete conversion. At this point, a sample for the GLC determination of the reaction products was collected. In some cases, the catalyst was removed from the reaction solution, evacuated and placed in the reactor with fresh reactants. This process was repeated up to several times with the same catalyst sample, following the same pattern of collecting samples and the reaction products analyses.

2.4. Analyses

Gas-liquid chromatographic (GLC) analyses of the products obtained from the epoxidation reaction were performed on a SIGMA 2000 instrument (Perkin-Elmer, Norwalk, CT, USA) equipped with a flame ionization detector. Data handling was provided by Chromatographics 2 Data System (Perkin-Elmer). The chromatograph was fitted with Permaphase DMS (polydimethylsiloxane) fused-silica capillary column (50 m × 0.25 mm). The oven temperature was 70°C and nitrogen (30 psi) was the carrier gas. GLC analysis was combined with both the titrimetric determination of alkene oxide in non-aqueous medium [23] and standard hydroperoxide iodometric method.

The concentration of the functional groups in the initial (i.e., non-modified) ion-exchange resins was determined by back titration in accordance with the method described elsewhere [24]. Colorimetric methods for molybdenum analysis of the modified cation exchangers were adopted, based on the formation of

colored complexes with thiocyanate [25]. The molybdenum content in catalyst B was evaluated by thermal gravimetric analysis (TGA) using OD-102 instrument (MOM, Hungary) at heating rate of 10°C/min over the temperature range 20–800°C in air. This was combined with the elemental microanalysis on the Carlo Erba instrument (Italy). The standard infrared (IR) spectra of the polymeric catalysts as well as the homogeneous catalyst B were recorded as KBr pellets on a Specord 75 IR spectrometer (Germany).

3. Results and discussion

3.1. Preparation and characterization of the catalysts

Some basic characteristics of the molybdenum-containing complexes used as catalysts for the epoxidation reaction are shown in Table 1. The high molybdenum content in the complexes synthesized with low-molecular weight ligands (catalysts A and B) was indeed not surprising. On the other hand, the catalyst E had the highest amount of molybdenum sorbed among the polymeric complexes, due to the conditions such as the favorable combination of the polyampholite structure and polar aqueous medium employed for its preparation.

Catalyst A: The procedures for synthesis and characterization of this compound suggested the presence of MoO₂Cl₂ fragment attached by coordination bond to certain chelating low-molecular ligand functional groups and will be described in detail elsewhere [26].

Catalyst B: Elemental analysis data and determination of the molybdenum content indicated the molecular formula of the product close to C₆H₈O₆Mo. The comparison of IR spectrum of the complex with that of waste polyethylene glycol fraction showed the presence of strong absorption bands at 960 cm⁻¹ (Mo=O) and 720–750 cm⁻¹ in the molybdenum-containing complex, whereas no such bands were observed in the “blank” sample. Some changes in the intensities of the absorption bands at 1110–1120 cm⁻¹ (C–O–C) and 1060–1070 cm⁻¹ (C–O–H) and shift towards higher wavenumbers for the latter were also observed, indicating the formation of complexes with the oxomolybdenum fragments. Unfortunately, attempts to immobilize the molybdenum complex B

Table 1
Some basic characteristics of the molybdenum-containing catalysts and their precursors

Type of catalyst	Ligand functional groups or substrates involved	Functional groups content in the ion-exchangers (mmol g ⁻¹)	Ion-exchange capacity (IEC) towards 0.1N NaOH (mequiv g ⁻¹)	Molybdenum content in the catalyst (mmol g ⁻¹)	Solubility in the reaction medium under the experimental conditions
MoO ₂ (acac) ₂		–	–	3.066	Good
A	–	–	–	2.370	Good
B	HO(CH ₂ CH ₂ O) _n H (n = 1–5)	–	–	3.788	Good
C		11.1	11.1	0.104	Insoluble
D		3.5	4.8	0.680	Insoluble
E		3.5	4.8	1.550	Insoluble

on the ion-exchange resins employed, to obtain the corresponding heterogeneous polymeric catalyst were unsuccessful.

Polymeric catalysts C, D and E: As discussed in our recent work [21], the modification of Amberlite IRC 748 with $\text{MoO}_2(\text{acac})_2$ in organic medium to prepare catalyst D was accompanied by the complete ligand exchange. The lowest molybdenum content for the newly prepared heterogenized catalyst C (calculated polymer ligand/metal ion ratio of approximately 110) is considered to result from the probable molecular structure of the immobilized homogeneous complex and the polymer functional groups. Perhaps the unchanged MoO_2Cl_2 fragment, attached by coordination bond to the ligand groups did not effectively interact with the carboxylic groups of the Amberlite IRC 50 polymer support under the selected experimental conditions. Thus, the possibility of complete ligand exchange was difficult to be proved with the heterogenized complex C. The probable structure of the coordination center involving the polymeric matrix of the chelating ion-exchange resin Amberlite IRC 748 and the molybdenum-containing species (catalysts D and E) was discussed previously [21].

3.2. Catalytic epoxidations

The yields in the reactions were expressed as $Y = (C_{\text{ox}}/C_0) \times 100$ where, C_{ox} and C_0 (mol l^{-1}) are the concentration of epoxide formed and the initial concentration of TBHP, respectively. The selectivity with respect to the TBHP reacted, calculated by the ratio $S = 100 C_{\text{ox}}/(C_0 - C)$, where C is the final TBHP concentration, was found to be, in most cases, 95–100%. The catalytic activity was evaluated by the turnover number, i.e., the maximum reaction rate observed with respect to TBHP per minute per active site of the catalyst and was, accordingly, expressed in appropriate units (e.g., $\text{mol TBHP reacted mol}^{-1} \text{Mo min}^{-1}$). An excess of cyclohexene with respect to TBHP (molar ratio of 6–7) was used in order to obtain high TBHP conversions and selectivities with respect to cyclohexene oxide, as established by most of the authors, studying the catalytic epoxidation of alkenes with organic hydroperoxides [1–21]. No inert solvent was employed, since the objective of work was to estimate the catalytic activity, selectivity and versatility under more

“severe” conditions (i.e., higher concentrations of both reactants).

Kinetic curves of TBHP consumption in the presence of various catalysts are shown in Fig. 1. As might be expected, for the homogeneous catalysts $\text{MoO}_2(\text{acac})_2$, A and B, nearly complete TBHP conversion was reached within shorter reaction times as compared to the catalytic reaction in the presence of the heterogenized polymer complexes. The highest activity, close to that of $\text{MoO}_2(\text{acac})_2$ among the synthetic complexes was observed with the novel homogeneous catalyst A. Some induction period within the range of 10–30 min was observed with the polymeric catalysts D and E, indicating that in the presence of the heterogeneous complexes the initial formation of the catalytically efficient complex Mo(VI)/TBHP occurred more slowly [20].

The kinetic curves of TBHP consumption in the presence of the novel catalyst C prepared by immobilizing the homogeneous catalyst A on Amberlite IRC 50 cation-exchange resin are shown in Fig. 2. This heterogenized complex showed the highest activity among the polymer catalysts (Table 2). Several consecutive epoxidation runs in the presence of the same catalyst sample were conducted, to estimate its stability on multiple recycling. Following some initial “activation” during the first run, however, some loss in the catalytic activity, probably due to Mo leaching with the repeated use was observed in the third run (Fig. 2). As discussed in our previous work [21], the polymeric catalysts D and E showed better stability on multiple recycling.

The commercial homogeneous $\text{MoO}_2(\text{acac})_2$ catalyst had the highest activity, followed by the newly synthesized catalyst A (Table 2). The ratios between the activities of the homogeneous catalysts on one hand, and the corresponding polymeric ones obtained by their immobilization on the ion-exchange resins, on the other (the pairs of catalysts $\text{MoO}_2(\text{acac})_2$ and D; A and C, respectively), were found to be different. In the case of $\text{MoO}_2(\text{acac})_2$ and the corresponding heterogenized complex (catalyst D), the result was close to that reported previously [20]. The reason for this might be that the complete ligand exchange, taking place during the treatment of Amberlite IRC 748 with $\text{MoO}_2(\text{acac})_2$ in non-aqueous solution [21] resulted in the formation of the less efficient

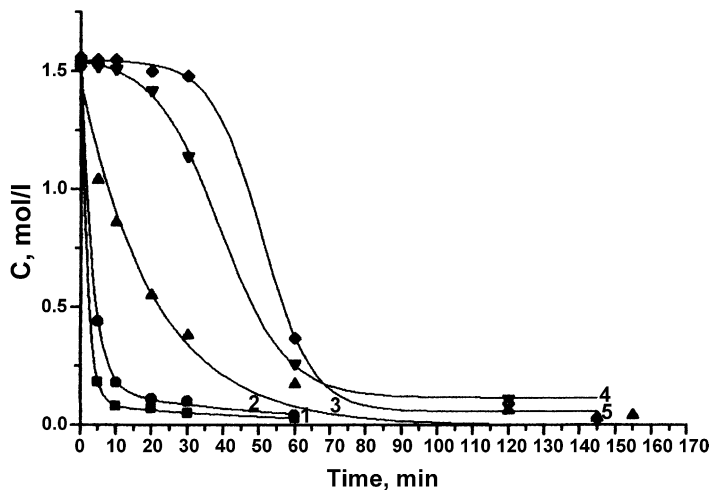


Fig. 1. Kinetic curves of TBHP consumption for the epoxidation of cyclohexene in the presence of various catalysts. C_0 : 1.520–1.560 mol l⁻¹; temperature: 79°C; cyclohexene: 65.6 mmol; TBHP: 9.9 mmol; catalyst: 0.033 mmol. (1) MoO₂(acac)₂; (2) catalyst A; (3) catalyst B; (4) catalyst E; (5) catalyst D.

Mo(V) active centres predominantly [14]. The smaller difference in the catalytic activity between the homogeneous and heterogeneous catalysts A and C, respectively, suggests somewhat different structure of the catalytically active complex for the latter, perhaps involving Mo(VI) from MoO₂Cl₂ fragment, partly coordinated to the low-molecular ligand. The

homogeneous catalyst B, containing polyethylene glycol ligands showed “intermediate” activity between that of the “low-molecular weight” and polymeric catalysts. The lower observed activity of the polymeric catalysts D and E, apart from the likely predominant Mo(V) species, is also believed to result from the higher molybdenum content, rendering the polymeric

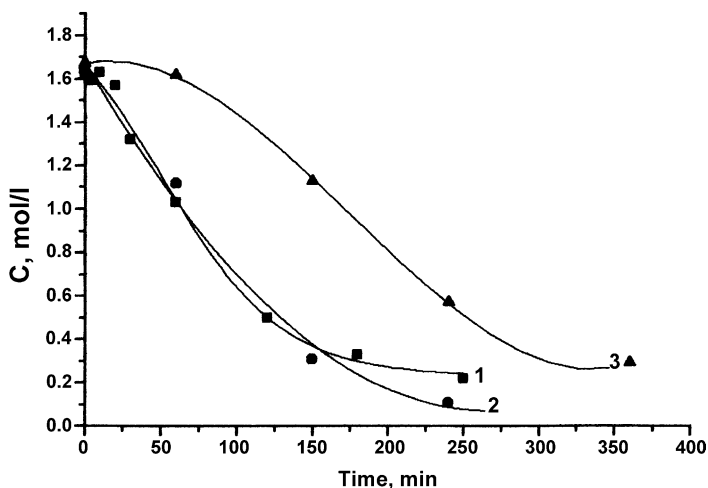


Fig. 2. Kinetic curves of TBHP consumption in the presence of catalyst C under the experimental conditions of Fig. 1: (1) “fresh” catalyst, 0.0051 mmol; (2) catalyst after single use in the epoxidation reaction, 0.005 mmol; (3) catalyst after two epoxidation experiments, 0.0041 mmol.

Table 2
Comparative evaluation of the activities of the epoxidation catalysts

Type of catalyst	TBHP conversion (%), reaction time (min)	Final yield of 1,2-epoxycyclohexane (%)	Turnover number A (mol TBHP mol ⁻¹ Mo min ⁻¹)	Catalytic activity ratios, $A_{\text{hom}}/A_{\text{het}}$
MoO ₂ (acac) ₂ ^a	100.0 (60)	100.0	62.2	
A ^a	96.8 (60)	91.2	53.0	$A_{\text{MoO}_2(\text{acac})_2}/A_{\text{D}} = 13.0$
B ^a	98.7 (155)	96.0	22.6	
C ^b	86.5 (250)	91.5	32.8	
D ^a	98.1 (145)	97.2	4.8	$A_{\text{A}}/A_{\text{C}} = 1.6$
E ^a	95.4 (160)	101.7	6.6	

^a Amount of catalyst, corresponding to 0.033 mmol Mo introduced.

^b Amount of catalyst, corresponding to 0.0051 mmol Mo.

matrix more “rigid” and thus retarding the formation of intermediate heterogenized complex. In all cases, GLC analysis showed 1,2-epoxycyclohexane as the major reaction product, followed by the unreacted excess of cyclohexene and *tert*-butylalcohol under the conditions of nearly complete TBHP conversion. In some cases (catalyst E), small amounts of 2-cyclohexene-1-ol and 2-cyclohexene-1-one (up to 3–4%), accompanied by 1,2-epoxycyclohexane yield somewhat higher than 100% (Table 2) were detected; the reason for this was discussed in detail in our previous work [21].

4. Conclusion

The catalytic activity of the newly synthesized molybdenum-containing complex with organic ligands (catalyst A) in the epoxidation of cyclohexene by TBHP was found to be close to that of the molybdenyl acetylacetonate commercial product. Also, molybdenum complex based on MoO₃ and waste polyethylene glycol fraction from the commercial production of ethylene oxide and ethylene glycols was prepared and its activity as homogeneous catalyst was found to be comparable to that of the rest of the catalysts studied. Attempts to immobilize these synthetic homogeneous catalysts on ion-exchange resins were made, with the novel catalyst A being partly successful. The resulting heterogenized complex showed the highest activity among the polymeric catalysts studied herein. However, further increase of the molybdenum content in this polymer complex and an improvement of its stability on multiple recycling by changing the

experimental conditions of immobilization, are deemed necessary. The activity of these catalysts was compared to that of other polymeric catalysts based on commercial ion-exchange resins and studied by us previously. The ratios between the activities of the homogeneous catalysts molybdenyl acetylacetonate and the novel catalyst A on one hand, and the corresponding polymeric catalysts obtained by their immobilization on commercial ion-exchange resins, on the other, were found to be different. This indirectly suggests some difference in the structure of the catalytically active complexes and the mechanisms of catalytic action.

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