

Original Research Article

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NEW MOLYBDENUM-CONTAINING ORGANIC COMPLEX AS CATALYST IN THE EPOXIDATION OF STRUCTURALLY DIFFERENT ALKENES

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ABSTRACT: New molybdenum-containing organic complex based on 3, 4-dihydroxy-3-cyclobutene-1, 2-dione (squaric acid) has been synthesized and characterized by infrared (IR) spectroscopy, thermogravimetric (TGA) and elemental analyses. The molybdenum complex was prepared by one-stage interaction of squaric acid, guanidinium carbonate and molybdenum dioxy-dichloride in aqueous medium. The molybdenum-squarate complex was introduced as catalyst in the epoxidation of structurally different alkenes such as cyclohexene, 1-octene, 2,4,4-trimethyl-1-pentene, 1,5-cyclooctadiene and 1,5,9-cyclododecatriene with tert-butylhydroperoxide (TBHP). The complexes showed high activities and selectivities, comparable to those of the commercially available molybdenyl acetylacetonate($\text{MoO}_2(\text{acac})_2$).

KEYWORDS: catalytic epoxidation, alkenes, squaric acid, molybdenum-squarate complex, 3, 4-dihydroxy-3-cyclobutene-1,2-dione

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1. INTRODUCTION

Molybdenum-containing complexes have long been known as useful catalysts for the epoxidation of alkenes by organic hydroperoxides. The industrial implementation of this reaction was first achieved in the Halcon process, which utilized a soluble Mo complex and the Arco process, which made use of a heterogeneous Ti-SiO₂ catalyst to effect the epoxidation of propylene to the synthetically useful propylene oxide precursor of variety of products in the organic synthesis [1, 2]. Compared to the vast number of organic ligands employed so far for the preparation of molybdenum complexes and catalysts for the alkene epoxidation [3–7], 3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid) holds specific position. The squarate dianion possesses a squarate-planar structure (D_{4h} symmetry) and represents cyclic oxocarbon dianion stabilized by delocalization of π -electrons around the ring. Thus it appears to be particularly attractive as a template for generating self-assemblies from polarizable cations in general and organic bases in particular. Such complexes are expected to serve as efficient catalysts for various organic reactions.

2. MATERIALS AND METHODS

2.1. Starting Materials:

Squaric acid (H₂Sq), 98 % (Hulls-Marl, Germany); Guanidinium carbonate (Gua₂CO₃), purum, > 97 % (Fluka AG); MoO₂Cl₂ (Aldrich); Cyclohexene, 99 % (Merck-Schuchardt); 1-Octene, 98 % (Aldrich); 2,4,4-Trimethyl-1-pentene, 97 % (Aldrich); Cis, cis-1,5-Cyclooctadiene, > 99 % (Merck-Schuchardt); 1,5,9-Cyclododecatriene, pract. (Fluka AG); Tert-butyl hydroperoxide (TBHP), 80 % in di-tert-butylhydroperoxide (Riedel Haen AG).

2.2. Preparation of the Catalytic Molybdenum-Squarate Complex (MSqC):

2 mmol squaric acid are suspended in 10 ml of distilled water in a beaker of 50 cm³. The suspension is gradually heated to 60-70 °C while stirring until complete dissolution of squaric acid. Then 2.00 mmol Gua₂CO₃ are added in small portions to the hot solution in the cessation of evolution of carbon dioxide. The stirring was continued for about 0.5 hours under heating to maintain the substances in solution, and then 4 mmol MoO₂Cl₂ was gradually introduced in the solution. A light green suspension was obtained, which was stirred for another hour, then was cooled to room temperature. The suspension was filtered under vacuum, washed successively with distilled water, acetone and ether and dried at room temperature. Yield: 0.786 g.

2.3. Catalytic Epoxidations:

Epoxidation is carried out by the reaction of 6.5-7.5 ml of an alkene with 1 ml of TBHP in the presence of 0.033 mmol MSqC, which are vigorous stirring vigorous stirring for certain period of

time in batch laboratory reactor of 12 cm³ at 70°C. For evaluation of the applicability of the MSqC as a catalyst, the reaction is carried with an excess of alkene in terms of TBHP (molar ratio 6-7), without the addition of an inert solvent. These conditions were chosen to evaluate the catalytic activity at the "more realistic" conditions of high initial concentrations of the starting reagents.

2.4. Analytical Methods:

FT-IR, elemental analysis, TGA, GLC, GLC/MS

3. RESULTS AND DISCUSSION

3.1. Suggested Structure of the Molybdenum-Squarate Complex:

Molybdenum-containing organic complex based on 3, 4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid) has been characterized characterized by infrared (IR) spectroscopy, thermogravimetric (TGA) and elemental analyses.

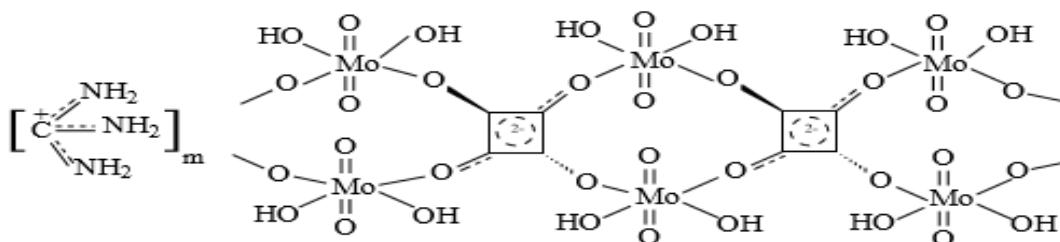
FT-IR spectra:

- fundamental vibrations, characteristic for squarate dianion (1500 -1550;1090 – 1100 cm⁻¹, (ν(C-O)+ν(C-C));
- characteristic absorption bands at 900 - 950 cm⁻¹ (cis MoO₂) and 500 – 600 cm⁻¹ (Mo–O-bond with organic ligand).

Elemental analysis data, proving the inclusion of guanidine fragment;

Hydrothermal instability of the MSqC above 120 – 130°C (unlike the thermal stability in air, 200 – 210°C).

The result of all analysis is characteristic for similar complexes of oligomeric type with completely amorphous structure and attached Mo-fragment to the organic ligand:



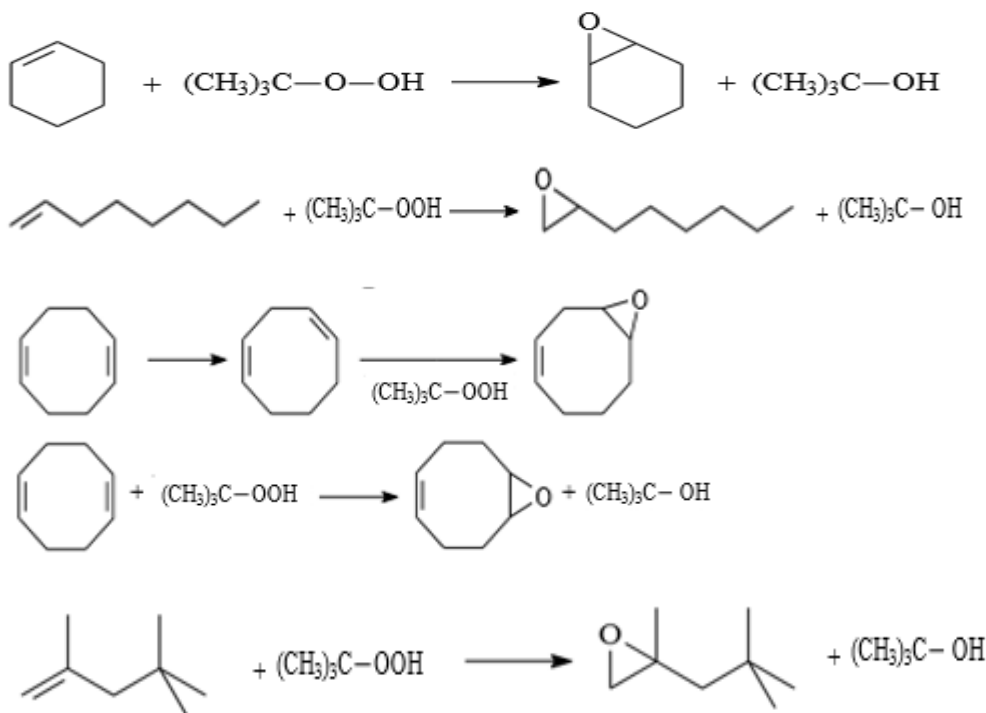
3.2. Catalytic Epoxidations.

The molybdenum-squarate complex was tested as catalyst in the epoxidation of structurally different alkenes such as cyclohexene, 1-octene, 2,4,4-trimethyl-1-pentene, 1,5-cyclooctadiene and 1,5,9-cyclododecatriene with tert-butylhydroperoxide (TBHP). Reaction of alkenes epoxidation is represented below:

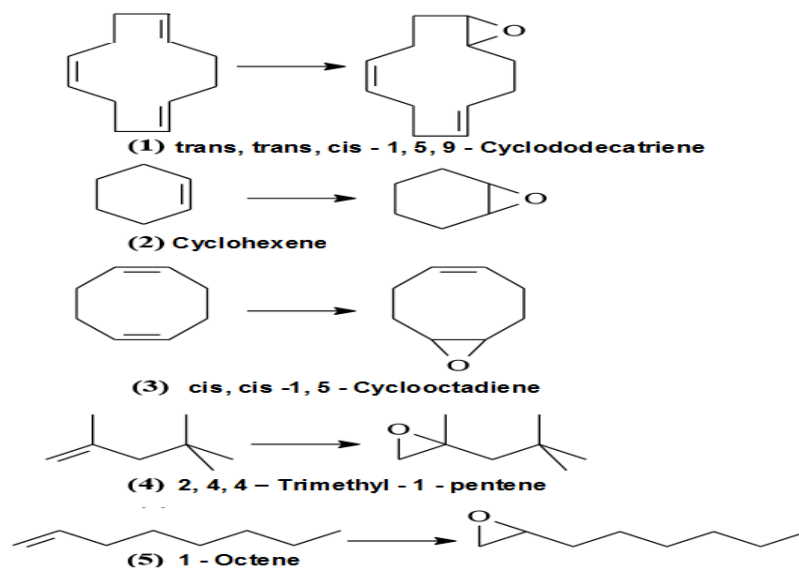
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3.3. Comparison of the Reactivity of Structurally-Different Alkenes:



After the series of experiments with structurally-different alkenes we have found the following order of epoxidation reactivity:

trans, trans, cis-1,5,9-cyclododecatriene (1) > cyclohexene (2) > cis, cis-1,5-cyclo-octadiene (3) > 2,4,4-trimethyl-1-pentene (4) > 1-octene (5)

3.5 Basic Parameters Evaluated: To determine the catalytic efficiency and productivity of the resulting molybdenum complex were calculated following parameters:

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TBHP Conversion: $x = (C_0 - C)/C_0 \cdot 100$ [%];

Alkene Epoxide Yield: $Y = (C_{ox}/C_0) \cdot 100$ [%];

C_0 : initial TBHP concentration [mol/l];

C : final TBHP concentration [mol/l];

C_{ox} : concentration of the alkene epoxide formed [mol/l];

TOF_{50%} - turnover frequency at 50 % conversion of TBHP: the reaction rate observed with respect to the alkene epoxide (AE) per minute per active site of the catalyst at 50 % TBHP conversion [mol AE.mol⁻¹Mo.min⁻¹];

Catalytic productivity (P) (integral parameter): the moles of principal reaction product (AE) formed per minute per active site of the catalyst by the end of the reaction (in most cases, at 90 – 100 % conversion of TBHP), [mol AE.mol⁻¹Mo.min⁻¹]. Reaction conditions: temperature 79°C; alkene: 6.5 – 7.5 ml; TBHP: 1 ml; catalyst amount corresponding to 0.033 mmol Mo; laboratory reactor volume: 12 cm³. The experimental results obtained from the experiments were shown in Tables 1 and 2 and of Figures 1 and 2. Catalytic activities and selectivities of MSqC were compared to those of the commercially available molybdenyl acetylacetonate (MoO₂(acac)₂).

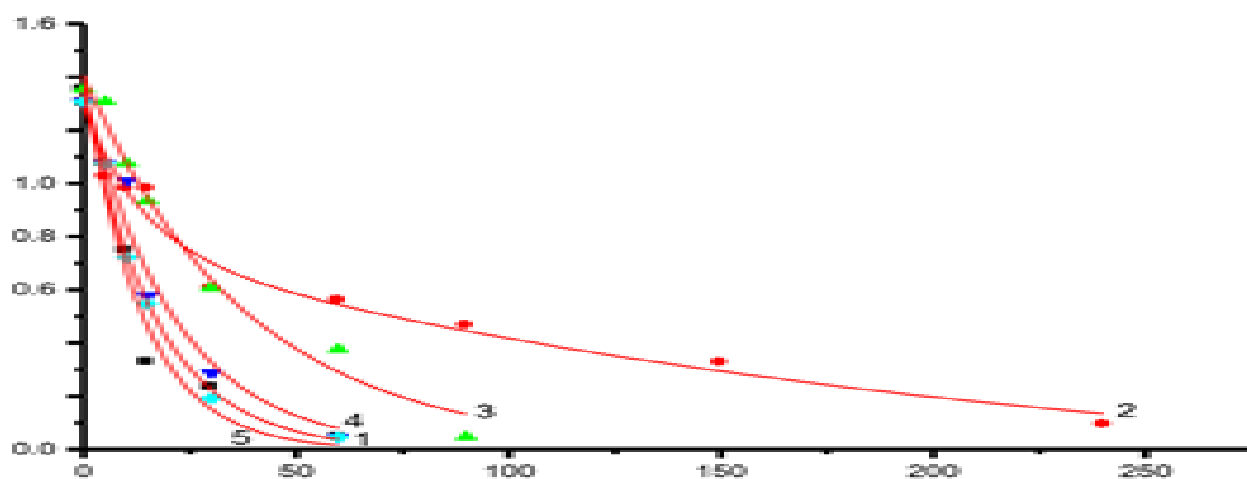


Fig. 1. Kinetic curves for the TBHP consumption in the epoxidation of various alkenes in the presence of the molybdenum-squarate complex as a catalyst. (1) cyclohexene; (2) 1-octene; (3) 2,4,4-trimethyl-1-pentene; (4) 1,5-cyclooctadiene; (5) 1,5,9- cyclododecatriene.

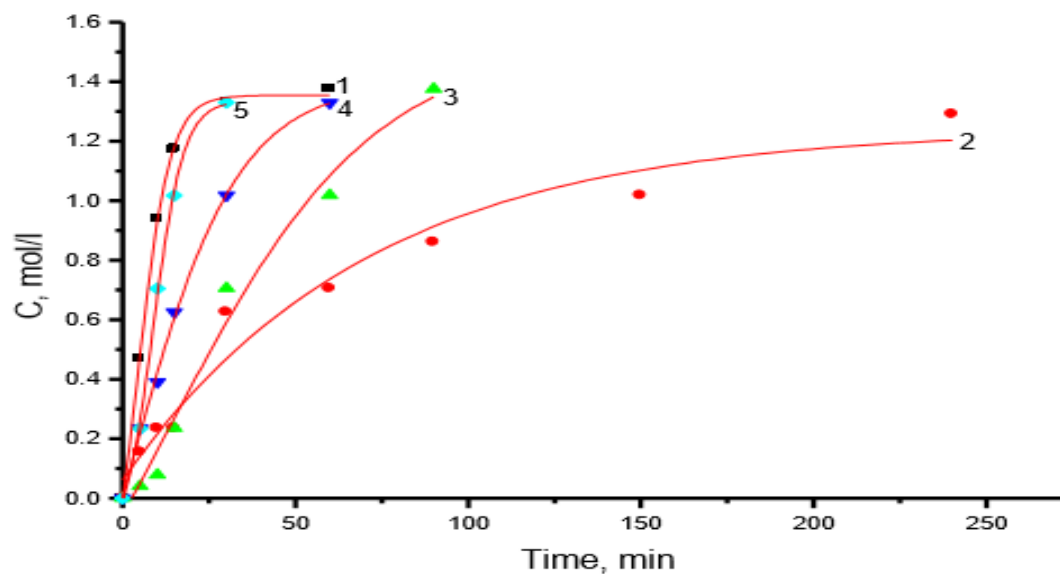


Fig. 2. Kinetic curves for the alkene epoxide accumulation in the epoxidation of various alkenes in the presence of the molybdenum-squarate complex as a catalyst. (1) cyclohexene; (2) 1- octene; (3) 2,4,4-trimethyl-1-pentene; (4) 1,5-cyclooctadiene; (5) 1,5,9-cyclododecatriene.

Table 1. Evaluation of the Catalytic Activity of the Molybdenum-Squarate Complex (MSqC) for the Epoxidation Reaction

Catalyst	Alkene	TBHP conversion, (%)	Reaction Time, min	Alkene epoxide (AE) final yield (%)	Time for 50 %TBHP conversion, $t_{50\%}$ min)	TOF _{50%} , (mol AE / mol MSqC min)	Catalytic Productivity, P (mol AE / mol MSqC min)
MScC	Cyclohexene	96.6	60	101.5	11.8	14.5	11.1
MoO ₂ (acac) ₂	Cyclohexene	96.5	30	104.0	3.6	9.1	10.7
MScC	1-Octene	92.8	240	98.6	38.5	2.1	1.5
MoO ₂ (acac) ₂	1-Octene	96.4	240	101.1	40	2.7	2.0

Table 2. Catalytic Activities of the Molybdenum-Squarate Complex and MoO₂(acac)₂ in the Epoxidation of Cyclohexene and 1-Octene with TBHP

Alkene	TBHP conversion (%)	Reaction Time, (min)	Alkene epoxide (AE), final yield, (%)	Time for 50 % TBHP conversion, t _{50%} , (min)	TOF _{50%} , (mol AE / mol MSqC min)	Catalytic productivity, P, (mol AE / mol MSqC min)
1,5,9 - Cyclododecatiene	96.5	30	101.7	9.6	20.0	11.7
Cyclohexene	96.6	60	101.5	11.8	14.5	11.1
1,5 - Cyclooctadiene	96.5	60	101.6	15.8	8.4	5.8
2,4,4 - Trimethyl-1-pentene	96.6	90	101.5	30.3	5.6	4.0
1-Octene	92.8	240	98.6	38.5	2.1	1.5

Possible Explanations for the High Catalytic Activity of the Newly Synthesized Molybdenum-Squarate Complex:

Both the steric and electronic factors contribute to the decreasing order of reactivity observed. the amorphous oligomeric structure; - inclusion of fragments with highly delocalized and symmetric structures such as guanidinium counterion and aromatic squarate anion as ligands in the complex, due to the one-pot procedure for the interaction of H₂Sq, Gua₂CO₃ and MoO₂Cl₂. The potential of squarate as ligand with respect to the MoO₂ fragments is therefore fully utilized, due to the relatively weak electrostatic interactions with the positively-charged delocalized guanidinium cation

4. CONCLUSION

The molybdenum-squarate complex prepared by the one-pot procedure of reaction of squaric acid, guanidinium salt and molybdenum dioxydichloride has very good performance as a catalyst for the epoxidation of structurally different alkenes. Its catalytic activity for the epoxidation reaction even with the least reactive 1-octene is close to that of the commercial molybdenyl acetylacetonate.

CONFLICT OF INTEREST

The authors have no conflict of interest.

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