

The liquid-phase oxidation of olefins by molecular oxygen in the presence of metal borides and MoO₃

Yu. Trach^a, B. Schulze^b, O. Makota^{a,*}, L. Bulgakova^a

^a Lviv Polytechnic National University, S. Bandera Str. 12, U-79013 Lviv, Ukraine

^b Institute of Organic Chemistry, Leipzig University, Johannisallee 29, D-04103 Leipzig, Germany

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Abstract

The initial stages of the liquid-phase oxidation of 1-octene and cyclooctene by molecular oxygen in the presence of transition metal borides and MoO₃ are investigated. The investigated compounds influence the oxidation process only in the presence of hydroperoxide in the reaction system. The most active in this process is vanadium diboride. The molybdenum compounds activate the oxidation process of 1-octene and inhibit the oxidation of cyclooctene.

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1. Introduction

The liquid-phase oxidation of alkenes by molecular oxygen is a very attractive process from an economic and ecological point of view. It allows to obtain various valuable oxygen-containing compounds including epoxides which are initial substances for numerous different and widely used products [1–4].

The use of catalysts in this process makes it possible to increase the reaction rate, to conduct the reaction in the desired direction and in such a way to carry out the process with high selectivity on epoxide as the main product. It is important to study the mechanism of catalyst action on this process in order to optimize the process for obtaining epoxides [5–7].

In this work the influence of the transition metal borides and molybdenum oxide on initial stages of the liquid-phase oxidation of 1-octene and cyclooctene by molecular oxygen in the presence of *tert*-butyl hydroperoxide (TBHP) is investigated.

2. Experimental

Cyclooctene was purchased from Acros Organics. Commercial 1-octene of reagent pure grade was additionally purified

by distillation. *tert*-Butyl hydroperoxide was synthesized by the procedure given in Ref. [8]. Chlorobenzene used as a solvent was additionally dried and distilled.

Gaseous oxygen was used as an oxidant; prior to entering the reaction system, it was passed through a bed of soda lime and calcium chloride to remove moisture.

The catalysts were commercial chemicals of a chemically pure grade. The metal borides: TiB₂, ZrB₂, HfB₂, VB₂, NbB₂, TaB₂, CrB₂, MoB₂ were chosen as catalysts to study the influence of metal nature on oxidation process. These borides crystallized in one space group differed from each other only by unit cell parameters [9]. These compounds were also chosen to exclude a possible influence of elements ratio and crystal structure of that borides [10–12] on proceeding of the process. In addition, activity of Mo₂B and MoO₃ in that reaction was investigated.

The oxidation of 1-octene and cyclooctene by molecular oxygen and epoxidation of these olefins by TBHP was carried out in a glass reactor equipped with a magnetic stirrer and constant temperature jacket to keep the temperature constant within ± 0.1 °C.

The oxidation rate was determined from the rate of oxygen absorption. The rate of the epoxidation process of olefins by TBHP was determined from kinetic curves for TBHP consumption. The hydroperoxide content was determined by iodometric titration. The analysis of a reaction mixture on epoxide was carried out on Hewlett-Packard HP 6890 N, a capillary column DB-1 packed with dimethylsiloxane.

* Corresponding author.

E-mail address: oksanaimak@mail.ru (O. Makota).

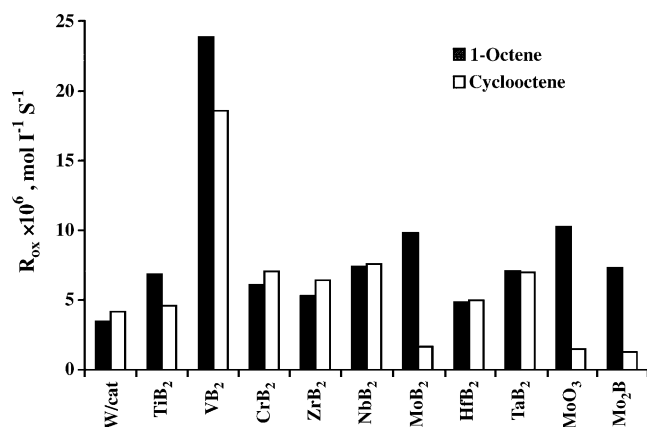


Fig. 1. Performances of borides and MoO_3 in the oxidation of 1-octene and cyclooctene by oxygen in the presence of TBHP. Reaction conditions: temperature = 353 K; [1-octene] = 5.2 mol/l; [cyclooctene] = 6.9 mol/l; [TBHP] = 0.05 mol/l; [catalysts] = 3 m²/l; oxygen pressure = 9×10^4 Pa.

3. Results and discussion

The initial rates of 1-octene and cyclooctene oxidation (R_{ox}) in the presence of TBHP and investigated metal compounds or without these compounds in the reaction system are given in Fig. 1. One can see that the oxidation rate of 1-octene in the presence of investigated compounds is higher than without them. The investigated catalysts differ substantially regarding their activity in the process. The most active are VB_2 , MoB_2 and MoO_3 whereas ZrB_2 and HfB_2 show minimum activity. The presence of MoB_2 and MoO_3 observes three-fold increase of oxidation rate of 1-octene and seven-fold increase for the case of VB_2 .

Similar to 1-octene, the oxidation of cyclooctene is activated by TiB_2 , ZrB_2 , HfB_2 , VB_2 , NbB_2 , TaB_2 , CrB_2 . However, in the case of molybdenum-containing compounds the oxidation rate is lower than the rate of noncatalytic process. It demonstrates an inhibition effect of molybdenum compounds on the process of cyclooctene oxidation.

One can assume that the inhibition influence of MoB_2 , Mo_2B and MoO_3 on the oxidation process of cyclooctene may result from their participation in a chain termination reaction. In this case in the presence of another initiator, for example, azodizobutyronitrile (AIBN), in the reaction system compounds of molybdenum also have to inhibit the oxidation process. However, as Table 1 data show these compounds do not influence the oxidation process of cyclooctene in the presence of AIBN. It can indicate that the investigated molybdenum compounds do not take part in the chain termination reaction.

Table 1

The initial rate of cyclooctene oxidation by O_2 in the presence of AIBN without and in the presence of molybdenum-containing compounds in the reaction system

	Without catalyst	MoB_2	MoO_3	Mo_2B
R_{ox} (mol l ⁻¹ s ⁻¹)	5.3	5.3	5.6	5.6

Reaction conditions: temperature = 353 K; [cyclooctene] = 6.9 mol/l; [AIBN] = 2.5×10^{-3} mol/l; [catalysts] = 3 m²/l; oxygen pressure = 9×10^4 Pa.

In our opinion the reason of a different influence of Mo-containing compounds and compounds not containing molybdenum can be explained by various stabilities of complexes these catalysts formed with components of the reaction system: 1-octene, cyclooctene and *tert*-butyl hydroperoxide.

Taking into account that the investigated oxidation system has the same composition as the system of hydroperoxide epoxidation: catalyst, olefine, hydroperoxide, one can speculate that the composition of complexes is also identical. The hydroperoxide epoxidation process of olefins in the presence of molybdenum compounds occurs via the formation of catalyst–olefine–hydroperoxide complex [13–16]. This triple complex is not active in a chain propagation reaction. Increasing the stability of catalyst–olefine–hydroperoxide complex leads to a decrease in amount of both, the catalyst–hydroperoxide complex and free hydroperoxide, responsible for radicals' formation in the reaction system.

In the case of the oxidation process of cyclooctene the rate reduction is obviously due to formation of more stable catalyst–cyclooctene–TBHP complex in comparison with catalyst–octene–TBHP complex.

In Ref. [17] it was shown that with an increase of olefine concentration in the epoxidation process of 1-octene by *tert*-butyl hydroperoxide in the presence of MoB_2 the reaction rate also increased up to the saturation point after which the epoxidation rate did not practically depend on the 1-octene concentration. It is connected with practically total linkage of the catalyst in a primary complex with olefine which further reacts with hydroperoxide with formation of epoxide. That is the reason why the process rate practically does not change with the further increasing amount of 1-octene.

When the complex of catalyst with cyclooctene and also the triple catalyst–cyclooctene–TBHP complex are more stable than the same complexes with 1-octene the independence of the epoxidation rate from olefine concentration should be observed at smaller concentration of cyclooctene.

Fig. 2 illustrates that the independence of the epoxidation rate (R_{ep}) from olefine concentration in a case of cyclooctene

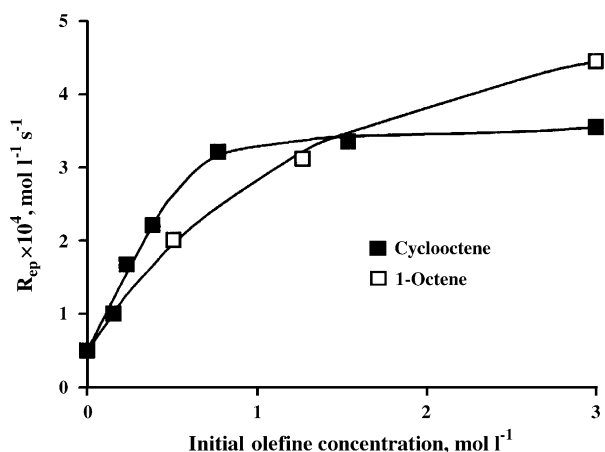


Fig. 2. Effect of olefine concentration on initial epoxidation rate of 1-octene and cyclooctene by TBHP in the presence of MoB_2 . Reaction conditions: temperature = 353 K; [TBHP] = 0.5 mol/l; [catalyst] = 3 m²/l.

in comparison with 1-octene is observed at smaller olefine concentration.

These data verify that catalyst–cyclooctene–hydroperoxide complex is more stable than catalyst–octene–hydroperoxide complex. Therefore, in system containing cyclooctene the concentration of catalyst–hydroperoxide complex and free hydroperoxide which show activity in reaction of radicals' formation is lower and as a result the oxidation rate is also lower.

4. Conclusion

Thus, the given results show that TiB_2 , ZrB_2 , HfB_2 , VB_2 , NbB_2 , TaB_2 , CrB_2 activate oxidation process of 1-octene and cyclooctene. MoB_2 , Mo_2B and MoO_3 activate the oxidation process of 1-octene and inhibit the oxidation of cyclooctene. It can be due to the greater stability of catalyst–cyclooctene–hydroperoxide complex in comparison with catalyst–octene–hydroperoxide complex.

Further details on the mechanism of this interesting process are still under investigation.

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