



Vanadium diboride catalyzed oxidation of cyclooctene by molecular oxygen: Kinetic study

Yuriy B. Trach^{a,*}, Lidia V. Bulgakova^a, Oksana I. Makota^a, Wladimir Ya. Suprun^b, Bärbel Schulze^c, Christian B.W. Stark^c

^a Institute of Chemistry and Chemical Technologies, Lviv Polytechnic National University, 12 S. Bandera Str., 79013 Lviv, Ukraine

^b Institute of Technical Chemistry, Leipzig University, Linné str. 3, D-04103 Leipzig, Germany

^c Institute of Organic Chemistry, Leipzig University, Johannisalle 29, D-04103 Leipzig, Germany

ARTICLE INFO

Article history:

Received 22 April 2008

Received in revised form 2 December 2008

Accepted 10 December 2008

Available online 24 December 2008

Keywords:

Catalyst

Oxidation

Olefin

Molecular oxygen

Kinetics

ABSTRACT

The kinetics of the liquid-phase oxidation of cyclooctene by molecular oxygen catalyzed by VB_2 on initial stages of process was studied. The vanadium diboride was found to activate the oxidation process in the presence of hydroperoxide in the reaction system. It was shown by FTIR investigation that cyclooctene and hydroperoxide are complexed with the same catalytic center. The reaction rate depended on cyclooctene concentration with less than first order. In the investigation system the radicals are formed as a result of proceeding of two processes—noncatalytic and catalyzed by vanadium diboride bimolecular decomposition of *tert*-butyl hydroperoxide. Based on the obtained data the kinetic model of the investigated process was proposed. The equation for the reaction rate was derived from this model. This equation is allowed to describe all observed kinetic dependences.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The oxidation reaction of hydrocarbons by molecular oxygen is very attractive and significant reaction of organic synthesis and animate nature. The oxygen-containing products obtained in this reaction are widely used in industry as well as in laboratory synthesis [1–4]. The great advantage of this oxidation process is the use of ecologically clean and inexpensive oxidant—molecular oxygen.

However, direct interaction of molecular oxygen with hydrocarbons proceeds usually with low selectivity. Therefore, search for effective methods of selective transformation of hydrocarbons into main products has attracted extensive attention.

The use of catalysts in this process is one of the methods which allows to considerably increase selectivity of oxidation reaction [1,5–9]. The positive effect of catalyst action is related to influence on single stage of multi-stage oxidation process. It leads to the increase in contribution of this stage in the overall oxidation process and selectivity of products produced in this stage respectively. However, some aspects of the mechanism of this interesting and widely extended in nature reaction are still not clear.

The influence of metal diborides on the oxidation process of cyclooctene and 1-octene by molecular oxygen depends on

the nature of olefin as it was shown in [10]. Thus, in the case of vanadium diboride VB_2 the rate of the oxidation process of cyclooctene and 1-octene increased in comparison with noncatalytic process. Whereas in the case of molybdenum-containing compounds increase in oxidation rate is observed for 1-octene and decrease in oxidation rate is observed for cyclooctene. It testifies about necessity of kinetic investigation of the olefin oxidation reaction in the presence of different catalysts for the purpose to establish mechanism of catalysts influence on single stages of oxidation process as well as on the overall process [1,11,12].

The present study is designed to kinetic investigation of the cyclooctene oxidation reaction by molecular oxygen catalyzed by vanadium diboride as the most active catalyst among investigated in [10].

2. Experimental

Cyclooctene was obtained from Acros Organics and additionally distilled. As a solvent was used chlorobenzene which was additionally dried and distilled. Gaseous oxygen was used as an oxidant. *tert*-Butyl hydroperoxide (TBHP) was synthesized from *tert*-butyl alcohol and hydrogen peroxide in the presence of sulfuric acid by the procedure [13]. Vanadium diboride was commercial pure-grade reagents. Azodiizobutyronitrile (AIBN) was purified by recrystallization from ethanol.

* Corresponding author.

E-mail address: yu.trach@polynet.lviv.ua (Y.B. Trach).

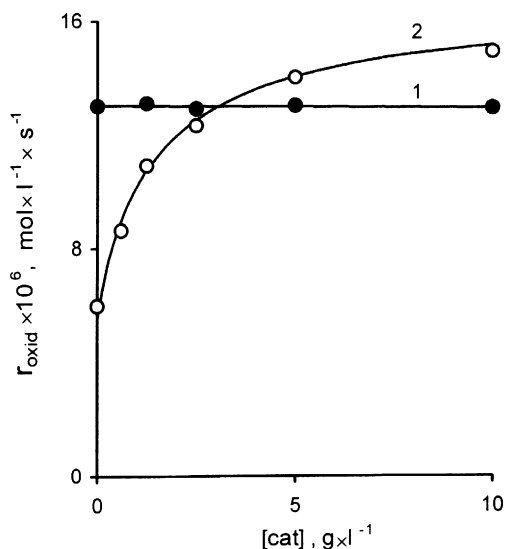


Fig. 1. Dependence of initial rate of oxidation process on content of VB_2 in the presence of (1) AIBN ($[\text{AIBN}] = 5 \times 10^{-3} \text{ mol/l}$) as well as the experimental points and theoretically calculated with Eq. (2) dependence of initial rate of oxidation process on content of VB_2 in the presence of (2) TBHP ($[\text{TBHP}] = 5 \times 10^{-2} \text{ mol/l}$, $[\text{cyclooctene}] = 6.9 \text{ mol/l}$).

The oxidation reaction was carried out in a thermostated glass reactor (25 mm diameter, 35 mm height) with a temperature-controlled jacket and magnetic stirrer. The oxygen pressure was 90 kPa, reaction temperature 80 °C. The agitation speed of magnetic stirrer was 1000 rpm which ensured the kinetically controlled regime of the process. The volume of the reaction mixture was 2 ml. Changes in the reaction mixture volume within 1–4 ml were found to exert no effect on the oxidation rate.

The oxidation rate was determined from the rate of oxygen absorption. It was established that the oxidation rate of both catalytic and noncatalytic oxidation process does not depend on the pressure of oxidation gas when partial pressure of oxygen is higher than 50 kPa. The purified and freshly distilled cyclooctene was not oxidized under reaction conditions during 2 h in the absence of homogeneous initiators (TBHP and AIBN) in the reaction system.

FT-IR spectra were used to study the catalyst before and after its interaction with cyclooctene, TBHP or reaction mixture. FT-IR spectra of the catalysts were recorded using a FTIR 1725 × (PerkinElmer) spectrophotometer in 4000–400 cm^{-1} wave number range using pressed KBr pellets.

For IR investigation the samples of catalyst were prepared by following procedure. The catalyst was added to solution of cyclooctene or TBHP in chlorobenzene (the reagents concentrations were the same as in the oxidation reaction system) or to the reaction mixture. These mixtures with catalyst were stirred at reaction temperature. After that the catalyst was separated from the mixture, pressed with KBr, degassed and IR spectrum was recorded.

3. Results and discussion

3.1. Effect of catalyst in the presence of AIBN and TBHP

The dependence of initial rate of the oxidation process of cyclooctene by molecular oxygen (r_{oxid}) on content of VB_2 in the presence of AIBN is shown in Fig. 1. It can be seen that catalyst does not influence on the process when AIBN is present in the reaction mixture.

When another homogeneous initiator—TBHP, was used instead of AIBN the character of catalyst influence on the process changed (Fig. 1). The introduction of VB_2 in the reaction system results in

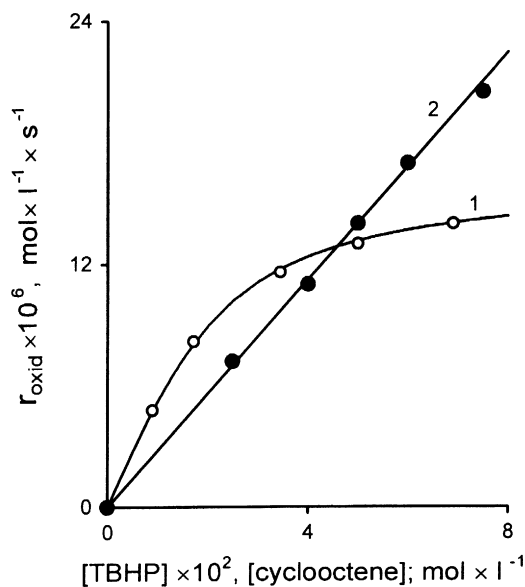


Fig. 2. The experimental points and theoretically calculated with Eq. (2) dependences of initial rate of oxidation process on (1) cyclooctene ($[\text{TBHP}] = 5 \times 10^{-2} \text{ mol/l}$) and (2) TBHP ($[\text{cyclooctene}] = 6.9 \text{ mol/l}$) concentrations. $[\text{cat}] = 5 \text{ g/l}$.

increase in the oxidation rate. This effect indicates the activated influence of VB_2 on process in the presence of TBHP. This dependence does not begin from outset of coordinates. It is result of the contribution of noncatalytic component of the oxidation process.

Comparison of vanadium diboride influence on the oxidation process in the presence of AIBN and TBHP allows to make a conclusion that this catalyst does not influence on chain propagation and chain termination stages. It suggests that the effect of VB_2 on the process deals with its participation in the stage of radical formation by TBHP decomposition.

3.2. Effect of TBHP

The effect of TBHP concentration on the initial oxidation rate of cyclooctene was studied at concentration of olefin 6.9 mol/l and catalyst loading of 0.01 g in 2 ml of reaction mixture. The results are represented in Fig. 2. One can see that the oxidation rate increases linearly with increase in TBHP concentration in the studied range. It indicates the reaction is first order with respect to this component.

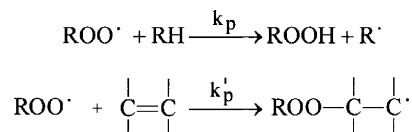
3.3. Effect of cyclooctene

The results of investigation of effect of cyclooctene concentration on initial rate of the oxidation reaction are presented in Fig. 2. It is seen that the increase in cyclooctene concentration results in nonlinear increase in initial rate of oxidation process.

This dependence differs from the typical dependence described by classical rate equation of radical chain oxidation of hydrocarbons with molecular oxygen [1,14]:

$$r_{oxid} = \frac{-d[\text{O}_2]}{dt} = \frac{k_p + k_p'}{\sqrt{kt}} [\text{RH}] \sqrt{ri} \quad (1)$$

where k_p and k_p' are the rate constants of chains propagation reactions:



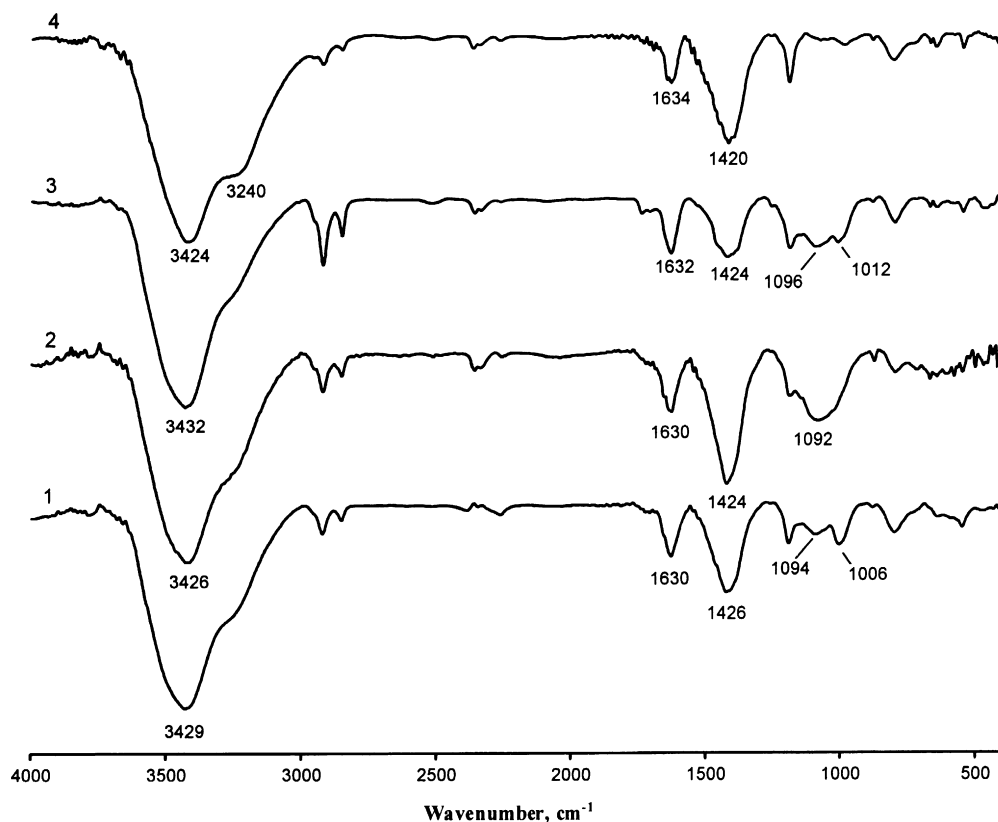
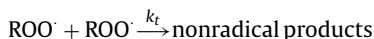


Fig. 3. IR spectra of VB_2 after interaction with reaction mixture (1), cyclooctene (2) and TBHP (3) as well as initial VB_2 (4).

k_t is the rate constant of chains termination reaction:



where RH is the organic substrate, r_i the rate of chain initiation, ROOH the hydroperoxide, R^\cdot the alkyl radical, and ROO^\cdot the peroxy radical.

In accordance with this equation the oxidation rate have to increase linearly with increase in olefin concentration. In our opinion, the nonlinear dependence r_{oxid} on cyclooctene concentration can be due to processes of complex formation of catalyst with the reagents of reaction mixture, especially with cyclooctene.

3.4. FTIR investigation

The IR spectra of vanadium diboride after interaction with reaction mixture (1), cyclooctene (2) and TBHP (3) as well as the

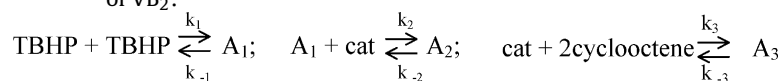
spectrum of initial VB_2 (4) are presented in Fig. 3. One can see that spectra have intense absorption peaks near 1420, 1634, 3240 and 3424 cm^{-1} . The broad absorption band at around 3424 and 3240 cm^{-1} is due to stretch mode vibration of water molecules and –OH bonds as well as at around 1634 and 1420 cm^{-1} is due to the bending mode vibration of water molecules and –OH bonds respectively [15–17].

The absorption peaks in the range of 1006–1096 cm^{-1} is appeared in the IR spectra 1–3 (Fig. 3) in compare with spectrum 4 of initial VB_2 . The absorption band in the range of 1092–1096 cm^{-1} can be attributed to absorption of C–O group which is formed in a result of interaction of TBHP and cyclooctene with surface of vana-

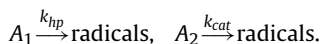
dium diboride [18]. The absorption band of C–O group in spectra 1–3 has the same value (1094, 1092 and 1096 cm^{-1} for spectra 1, 2 and 3). It allows to conclude that TBHP as well as cyclooctene complexing with the same catalytic center. Therefore the increase in cyclooctene concentration will lead to replacement of TBHP by cyclooctene in catalytic active complex of radical formation. As a result, the rate of radical formation in the result of catalytic decomposition of TBHP will be decreased as it was observed experimentally.

3.5. Kinetic model

Taking into account the obtained experimental results and the data of our previous investigations [19–21], we may propose the next model of radical formation process in the initial stages oxidation reaction of cyclooctene by molecular oxygen in the presence of VB_2 :



The radicals are formed in the following reactions:

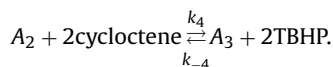


As it follows from the model, in the investigation reaction system the formation of two complexes between catalyst and reactants takes place: catalyst–2TBHP and catalyst–2cyclooctene. Other complexes are also formed in the reaction system, but they are not kinetically displayed in the investigated oxidation process and thereby they are not included into the kinetic model.

Based on the data of IR investigation and according to the above model the increase in olefin concentration leads to the increase in

A_3 complex amount. Consequently, more amount of catalyst is ligated in complex A_3 which is nonactive in radical formation reaction. As a result, the amount of complex A_2 , which is active in radical formation reaction, is decreased, and the rate of oxidation process is also decreased as observed experimentally.

In order to show by mathematic the decrease in the amount of A_2 complex and the increase in the amount of A_3 complex when concentration of cyclooctene in reaction mixture increased, in the kinetic model we introduce the stage [19]:



Taking the kinetic model into consideration and assuming that $k_4 \gg k_{-4}$, the rate of chain initiation in investigated system can be expressed:

$$\begin{aligned} r_i &= k_{hp}[A_1] + k_{cat}[A_2] \\ &= \frac{k_1[\text{TBHP}]^2}{k_{-1} + k_{hp} + k_2[\text{cat}]} \left(k_{hp} + \frac{k_{cat}k_2[\text{cat}]}{k_{-2} + k_{cat} + k_4[\text{cyclooctene}]^2} \right) \end{aligned}$$

If to assume that the reactions of radical formation are determining stages of the oxidation process then

$$k_{-1} + k_2[\text{cat}] \gg k_{hp} \quad \text{and} \quad k_{-2} + k_4[\text{cyclooctene}]^2 \gg k_{cat}$$

In this case:

$$\begin{aligned} r_i &= k_{hp}[A_1] + k_{cat}[A_2] \\ &= \frac{k_1[\text{TBHP}]^2}{k_{-1} + k_2[\text{cat}]} \left(k_{hp} + \frac{k_{cat}k_2[\text{cat}]}{k_{-2} + k_4[\text{cyclooctene}]^2} \right) \end{aligned}$$

Substituting this equation into the classical equation (1) we obtain the equation which describes the rate of cyclooctene oxidation by molecular oxygen in the presence of VB_2 and TBHP in the reaction mixture:

$$\begin{aligned} r_{oxid} &= \frac{k_p + k'_p}{\sqrt{k_t}} [\text{cyclooctene}][\text{TBHP}] \\ &\quad \times \sqrt{\frac{k_1}{k_{-1} + k_2[\text{cat}]} \left(k_{hp} + \frac{k_{cat}k_2[\text{cat}]}{k_{-2} + k_4[\text{cyclooctene}]^2} \right)} \end{aligned}$$

or

$$\begin{aligned} r_{oxid} &= \frac{k_p + k'_p}{\sqrt{k_t}} [\text{cyclooctene}][\text{TBHP}] \\ &\quad \times \sqrt{\frac{K_1}{1 + (k_2/k_{-1})[\text{cat}]} \left(k_{hp} + \frac{k_{cat}K_2[\text{cat}]}{1 + (k_4/k_{-2})[\text{cyclooctene}]^2} \right)} \end{aligned} \quad (2)$$

where $K_1 = k_1/k_{-1}$, $K_2 = k_2/k_{-2}$.

In the area where catalyst content is more than 5 g l^{-1} (area where the oxidation rate slightly depend on catalyst content) this equation can be expressed:

$$\begin{aligned} r_{oxid} &= \frac{k_p + k'_p}{\sqrt{k_t}} [\text{cyclooctene}][\text{TBHP}] \\ &\quad \times \sqrt{\frac{K_1}{(k_2/k_{-1})} \left(\frac{k_{cat}K_2}{1 + (k_4/k_{-2})[\text{cyclooctene}]^2} \right)} \end{aligned}$$

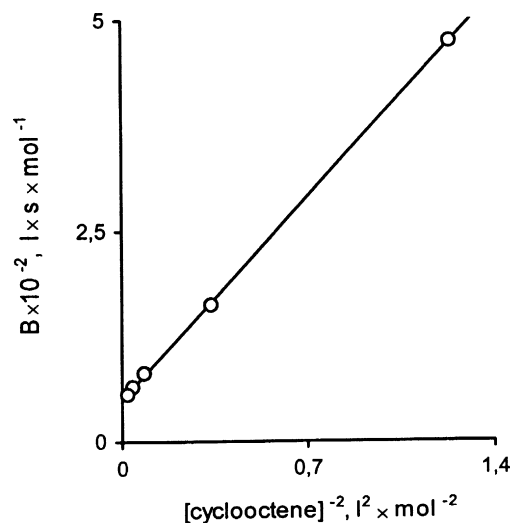


Fig. 4. Dependences of B on $[\text{cyclooctene}]^{-2}$.

This equation can be written in the next linear form for dependence of rate on olefin concentration:

$$\begin{aligned} &\frac{\left(\left((k_p + k'_p)/\sqrt{k_t} \right) [\text{TBHP}] \right)^2}{r_{oxid}^2} \\ &= \frac{(k_2/k_{-1})(k_4/k_{-2})}{k_{cat}K_1K_2} + \frac{k_2/k_{-1}}{k_{cat}K_1K_2} \frac{1}{[\text{cyclooctene}]^2} \end{aligned}$$

As it can be seen from Fig. 4, this dependence, where

$$B = \frac{\left(\left((k_p + k'_p)/\sqrt{k_t} \right) [\text{TBHP}] \right)^2}{r_{oxid}^2}$$

is indeed linear. In order to find the value of B we used value $(k_p + k'_p)/\sqrt{k_t} = 2.1 \times 10^{-3} \text{ l}^{0.5} \text{ mol}^{-0.5} \text{ s}^{-0.5}$ presented in [22]. From this dependence we calculated the constants ratio k_4/k_{-2} , which is equal $14.5 \times 10^{-2} \text{ l}^2 \text{ mol}^{-2}$.

To estimate others constants Eq. (2) can be written as

$$\begin{aligned} D &= \frac{r_{oxid}^2 (1 + (k_2/k_{-1})[\text{cat}])}{\left(\left((k_p + k'_p)/\sqrt{k_t} \right) [\text{cyclooctene}][\text{TBHP}] \right)^2} \\ &= k_{hp}K_1 + \frac{K_1k_{cat}K_2}{1 + (k_4/k_{-2})[\text{cyclooctene}]^2} [\text{cat}] \end{aligned}$$

With the purpose to find the constants ratio k_2/k_{-1} we have substituted in the expression for D the value k_2/k_{-1} , in the case of which the correlation coefficient of linear dependence in coordinates D on $[\text{cat}]$ was maximal (Fig. 5).

The calculated optimal value k_2/k_{-1} was found to be 0.42 l g^{-1} at correlation coefficient 0.99. From the dependence shown in Fig. 5, using $K_1 = 0.81 \text{ mol}^{-1}$ presented in [23] the constants $k_{hp} = 7.5 \times 10^{-5} \text{ s}^{-1}$ and $k_{cat}K_2 = 2.2 \times 10^{-3} \text{ l g}^{-1} \text{ s}^{-1}$ were also estimated.

For confirmation the assumptions about the processes proceeding in the investigated reaction system the theoretical dependences of the initial oxidation rate on the catalyst content and concentrations of TBHP and cyclooctene with the use of the determined rate constants were calculated with Eq. (2). As it can be seen from Figs. 1 and 2 the theoretically calculated dependences are in excellent agreement with experimental points.

Taking into account the obtained experimental results and the literature data [1], the early stages of oxidation process of cyclooctene in the presence of TBHP catalyzed by VB_2 can be described by the scheme which is presented in Fig. 6.

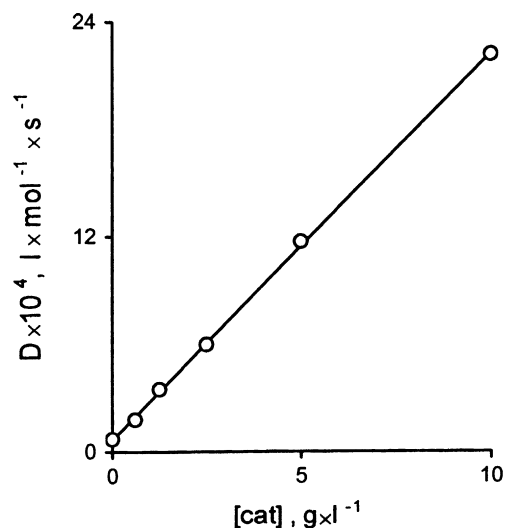


Fig. 5. Dependences of D on content of VB_2 .

4. Conclusions

The kinetics of initial stages of the liquid-phase oxidation of cyclooctene by molecular oxygen catalyzed by VB_2 has been reported for the first time. It was shown that catalyst does not influence on the process in the presence of AIBN in the reaction system. In the presence of TBHP the radicals are formed in a result of noncatalytic and catalyzed by VB_2 bimolecular decomposition of *tert*-butyl hydroperoxide. The effect of *tert*-butyl hydroperoxide, cyclooctene and catalyst on the reaction rate was investigated. The reaction is first order with respect to hydroperoxide and less than first order with respect to VB_2 and cyclooctene.

The IR investigation demonstrated that after interaction of vanadium diboride with reaction components in the IR spectra of catalyst the absorption peak at around 1094 cm^{-1} was appeared which can be attributed to absorption of C–O group.

Based on the obtained results the kinetic model of the initial stages of oxidation process has been proposed. The equation of oxidation rate which quantitatively described the obtained experimental dependences has been evaluated from this model.

Acknowledgments

The work was supported by Deutscher Akademischer Austausch Dienst (DAAD) and Fundamental Researches State Found of Ukraine (Grant of President of Ukraine).

References

- [1] E.T. Denisov, I.B. Afanas'ev, *Oxidation and Antioxidants in Organic Chemistry and Biology*, CRC, Taylor and Francis, Boca Raton, FL, 2005.
- [2] A.K. Yudin, *Aziridines and Epoxides in Organic Synthesis*, Wiley-VCH, Weinheim, Germany, 2006.
- [3] K. Weissermel, H.-J. Arpe, *Industrial Organic Chemistry*, Wiley-VCH, Weinheim, Germany, 2003.
- [4] M. Haruta, *Nature* 437 (2005) 1098.
- [5] S. Liu, J. Xiao, *J. Mol. Catal. A: Chem.* 270 (2007) 1.
- [6] R.M. Lambert, F.J. Williams, R.L. Cropley, A. Palermo, *J. Mol. Catal. A: Chem.* 228 (2005) 27.
- [7] T. Punniyamurthy, S. Velusamy, J. Iqbal, *Chem. Rev.* 105 (2005) 2329.
- [8] Y. Moro-oka, W. Ueda, K.-H. Lee, *J. Mol. Catal. A: Chem.* 199 (2003) 139.
- [9] R. Burch, M.J. Hayes, *J. Mol. Catal. A: Chem.* 100 (1995) 13.
- [10] Yu. Trach, B. Schulze, O. Makota, L. Bulgakova, *J. Mol. Catal. A: Chem.* 258 (2006) 292.
- [11] D.G. Blackmond, *Angew. Chem. Int. Ed.* 44 (2005) 4302.
- [12] I. Chorkendorff, J.W. Niemantsverdriet, *Concept of Modern Catalysis and Kinetics*, Wiley-VCH, Weinheim, Germany, 2003.
- [13] N.A. Milas, D.M. Surgenor, *J. Am. Chem. Soc.* 68 (1946) 205.
- [14] L.R.C. Barclay, K.U. Ingold, *J. Am. Chem. Soc.* 103 (1981) 6478.
- [15] P. Judeinstein, R. Morineau, J. Livage, *Solid State Ion.* 51 (1992) 239.
- [16] B.M. Reddy, I. Ganesh, *J. Mol. Catal. A: Chem.* 169 (2001) 207.
- [17] B.M. Reddy, G.K. Reddy, K.N. Rao, A. Khan, I. Ganesh, *J. Mol. Catal. A: Chem.* 265 (2007) 276.
- [18] A.A. Davydov, A.A. Budneva, *React. Kinet. Catal. Lett.* 20 (1982) 107.
- [19] Yu.B. Trach, O.I. Makota, M.V. Nikipanchuk, I.Yu. Pyrig, R.G. Makitra, *Petr. Chem.* 43 (2003) 424.
- [20] Yu.B. Trach, O.I. Makota, *Petr. Chem.* 45 (2005) 327.
- [21] Yu.B. Trach, L.V. Bulgakova, *Ukr. Chem. J.* 69 (5) (2005) 38.
- [22] B.I. Chernyak, M.V. Nikipanchuk, G.M. Mishchenko, Yu.B. Trach, I.Yu. Pyrig, *Kinet. Catal.* 41 (2000) 457.
- [23] E.T. Denisov, *Zh. Fiz. Khim.* 38 (1964) 2085.

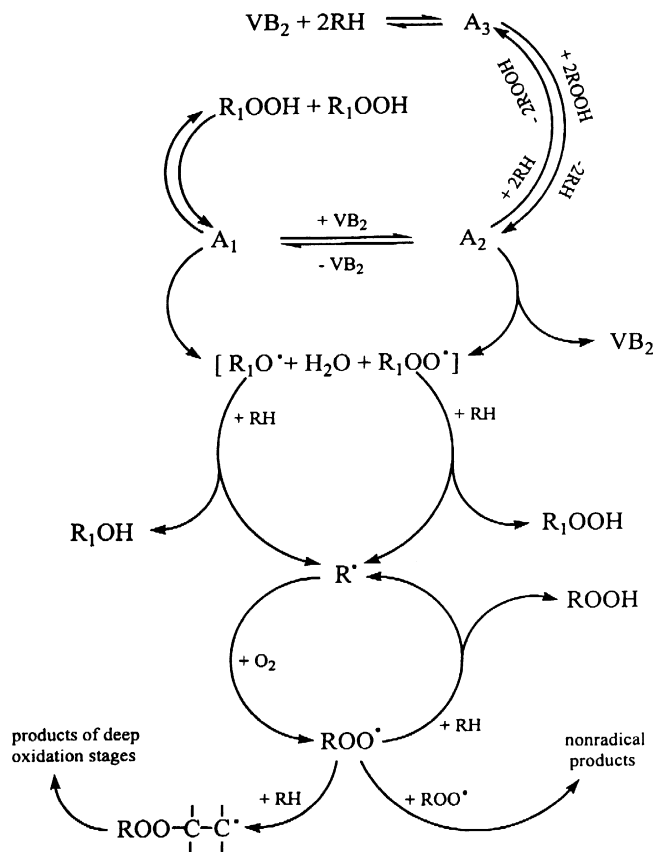


Fig. 6. Scheme of the early stages of oxidation process of cyclooctene (RH) in the presence of TBHP (R_1OOH) catalyzed by VB_2 .