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THE INITIAL STAGES OF CYCLOOCTENE OXIDATION BY MOLECULAR OXYGEN IN THE PRESENCE OF *tert*-BUTYL HYDROPEROXIDE

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Received: March 26, 2007

Abstract. The initial stages of liquid-phase oxidation of cyclooctene by molecular oxygen in the presence of *tert*-butyl hydroperoxide were investigated. It was shown that radical formation is the result of bimolecular decomposition of hydroperoxide. The influence of azodiizobutyronitrile on this process was studied. The kinetic parameters of the process were calculated.

Keywords: oxidation, molecular oxygen, olefin, hydroperoxide.

1. Introduction

The liquid-phase oxidation of alkenes by molecular oxygen is a very attractive process for obtaining various oxygen containing compounds [1, 2] from economic and ecological viewpoints. The use of catalysts in this process allows to increase reaction rate and turn the process in the necessary direction and thus carry out process with high selectivity on main product [3-6]. Investigations of mechanism of catalyst action and kinetics of oxidation process are important for finding optimum conditions of obtaining the necessary products.

The oxidation processes of alkenes in the presence of heterogeneous catalysts can proceed by heterogeneous pathway on the catalyst surface or by heterogeneous-homogeneous pathway when the radicals are formed on the catalyst surface and oxidation process proceeds in volume of the reaction system. One of the methods which is used for investigation of mechanism of catalyst action is kinetic method [7], when the rate of olefin oxidation is measured in identical conditions in the presence of homogeneous initiator, heterogeneous catalyst and at simultaneous presence of initiator and catalyst. On the base of comparison of determined experimental values of oxidation rates at simultaneous presence of homogeneous initiator and heterogeneous catalyst with theoretical

calculated values it is possible to make a conclusion about the role of catalyst in the oxidation process.

The investigations of cyclooctene oxidation in the presence of d-metals borides have shown [8] that these catalysts accelerate this process in the presence of hydroperoxide. Moreover, for the purpose of establishing the mechanism of catalyst action by kinetic method it is necessary to use homogeneous initiator which does not influence the catalyst activity. It was shown in [8] that azodiizobutyronitrile meet these requirements. Therefore, for taking into accounting non-catalytic processes proceeding in the system it is necessary to have a preliminary research of the oxidation process of this olefin without the catalyst in the presence of hydroperoxide as well as the influence of azodiizobutyronitrile on this process.

In the present work the initial stages of liquid-phase cyclooctene (CO) oxidation by molecular oxygen in the presence of *tert*-butyl hydroperoxide (TBHP) and the influence of another initiator on this process – azodiizobutyronitrile (AIBN) – was investigated.

2. Experimental

Cyclooctene is a catalyst obtained from Lancaster firm which was additionally distilled. As a solvent there was used chlorbenzene which was additionally dried and distilled. Molecular oxygen was cleared before it was given into reaction mixture. It was puted through CaCl₂ and mixture CaO and NaOH.

The oxidation reaction was carried out in a thermostated glass reactor with magnetic stirrer at the oxygen pressure of 9410⁴ Pa. The oxidation rate was determined from the rate of oxygen absorption. It was established that the oxidation rate is practically independent from pressure of oxidation gas when pressure is larger than 5·10⁴ Pa.

3. Results and Discussion

The dependence of initial rate of cyclooctene oxidation (R_{O_2}) on cyclooctene and TBHP concentrations are presented in Fig. 1. It can be seen that this dependence is linear. It indicates that the reaction is first order with respect to these components.

Comparison of obtained data with classical equation of rate of radical chain oxidation of hydrocarbons (1) with the second order in peroxy radical concentration chain termination reaction [9, 10] allow to conclude that the formation of radicals in this system is the result of bimolecular decomposition of TBHP.

$$R_{O_2} = \frac{k_p}{\sqrt{k_t}} [RH] \sqrt{R_i} \quad (1)$$

where k_p – the rate constant of propagation reaction, k_t – the rate constant of chain termination reaction, RH – hydrocarbon, R_i – the rate of initiation;

In this case, equation for rate of cyclooctene oxidation in the presence of TBHP is written as:

$$R_{O_2} = \frac{k_p}{\sqrt{k_t}} [CO] \sqrt{k_{hp} [TBHP]^2} \quad (2)$$

where k_{hp} – the rate constant of radical formation reaction by decomposition of TBHP.

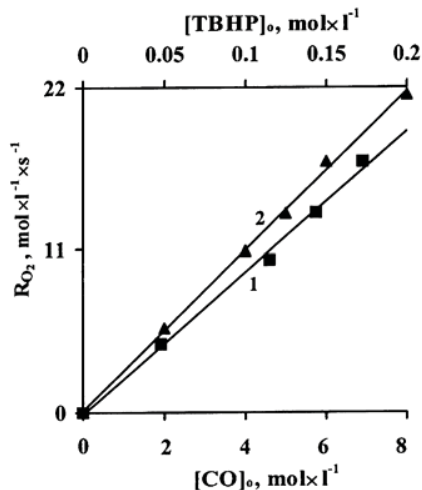


Fig. 1. The dependence of R_{O_2} on initial cyclooctene (1) ($[TBHP]_0 = 0.15$ mol/l) and TBHP (2) ($[CO]_0 = 6.9$ mol/l) concentrations. $T = 363$ K

The rate constant of bimolecular reaction of radical formation k_g was calculated from equation (2) taking into account the linear dependence of oxidation rate on the initial TBHP and cyclooctene concentration (Fig. 1) and parameter $k_p/\sqrt{k_t}$ from [11]. The rate constant is equal to $6.0 \cdot 10^{-5}$ l·mol⁻¹·s⁻¹.

When both TBHP and AIBN are introduced into the reaction mixture at the same time, the oxidation rate must be described by the equation:

$$R_{O_2} = \frac{k_p}{\sqrt{k_t}} [CO] \sqrt{R_{AIBN} + k_{hp} [TBHP]^2} \quad (3)$$

or linear dependence of $R_{O_2}^2$ on $[TBHP]^2$:

$$R_{O_2}^2 = \frac{k_p^2}{k_t} [CO]^2 R_{AIBN} + \frac{k_p^2}{k_t} [CO]^2 k_{hp} [TBHP]^2 \quad (4)$$

where R_{AIBN} – the initiation rate on account of AIBN decomposition.

Fig. 2 illustrates the dependences of $R_{O_2}^2$ on $[TBHP]^2$ for different R_{AIBN} . One can see that dependence is linear but tangent of angle of lines inclination is nonconstant, which must be concluded from equation (4), and increased with the increases of R_{AIBN} . It indicates that in this system it is necessary to take into account the induced decomposition of hydroperoxide [10].

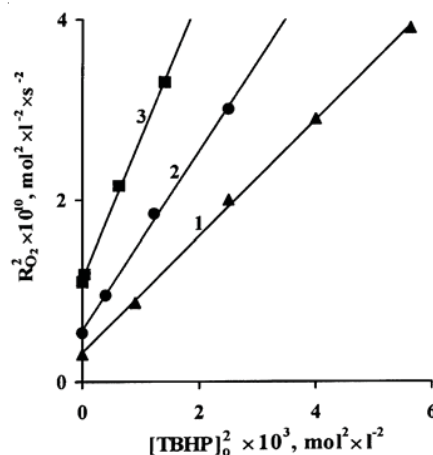


Fig. 2. The dependence of $R_{O_2}^2$ on $[TBHP]^2$ for different values of R_{AIBN} , mol l⁻¹·s⁻¹: 1 – $2.5 \cdot 10^{-7}$; 2 – $5.0 \cdot 10^{-7}$; 3 – $7.3 \cdot 10^{-7}$

In this case, the oxidation rate should be expressed by the equation:

$$R_{O_2} = \frac{k_p}{\sqrt{k_t}} [CO] \times \sqrt{R_{AIBN} + k_{hp} [TBHP]^2 + k_i [TBHP]^2 R_{AIBN}} \quad (5)$$

or linear dependence of $R_{O_2}^2$ on $[TBHP]^2$:

$$R_{O_2}^2 = \frac{k_p^2}{k_t} [CO]^2 R_{AIBN} + \frac{k_p^2}{k_t} [CO]^2 \times (k_{hp} + k_i R_{AIBN}) [TBHP]^2 \quad (6)$$

where k_i – the rate constant of AIBN-induced decomposition of TBHP.

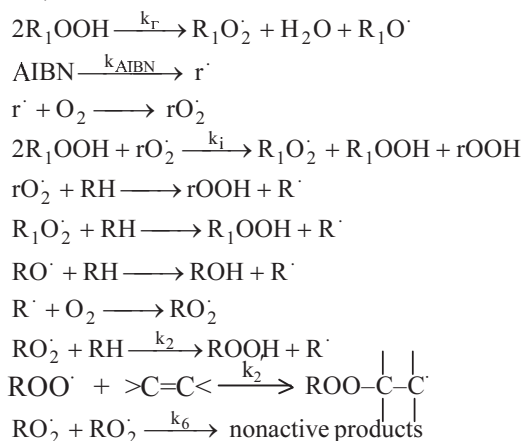
As it is concluded from Eq.6, tangent of angle of lines inclination ($\text{tg } \alpha$) of R_{O_2} dependence on $[TBHP]^2$ dependence must increase linearly with the increases of R_{AIBN} :

$$\text{tg } \alpha = \frac{k_p^2}{k_t} [\text{CO}]^2 k_{hp} + \frac{k_p^2}{k_t} [\text{CO}]^2 k_i R_{AIBN} \quad (7)$$

It is proved experimentally (Fig. 3) and it allows to calculate the rate constant of AIBN-induced decomposition of TBHP k_i , which is equal $10.84 \cdot 10^2 \text{ l}^2 \cdot \text{mol}^{-2}$.

The theoretical dependence of R_{O_2} on R_{AIBN} has been calculated in Eq. 5 using obtained constant values as presented in Fig. 3. It can be seen, that experimental obtained data of oxidation rate are practically consistent with the ones calculated in Eq. 5.

Taking into account the obtained experimental results and the data taken from literature [9, 10], we may propose the scheme of oxidation process of cyclooctene (RH) in the presence of TBHP (R_1OOH) and AIBN (see Scheme 1):



Scheme 1

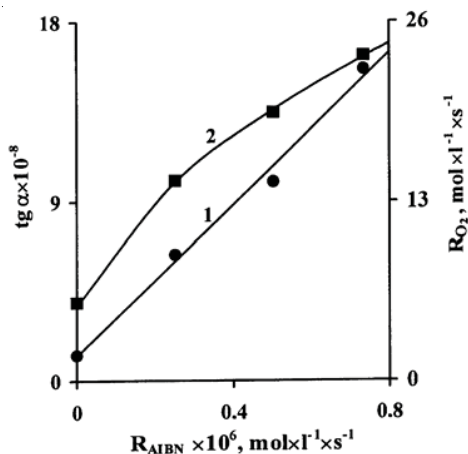


Fig. 3. The dependence of $\text{tg } \alpha$ on R_{AIBN} (1) as well as the theoretical curve and experimental points of dependence on R_{AIBN} ($[TBHP]_0 = 0.05 \text{ mol/l}$) (2). $[\text{CO}]_0 = 6.75 \text{ mol/l}$, $T = 363 \text{ K}$

4. Conclusion

Thus, the obtained results show that the formation of radicals on the initial stages of process of cyclooctene oxidation by molecular oxygen in the presence of TBHP is the result of bimolecular decomposition of hydroperoxide. Introduction of TBHP and AIBN into the reaction mixture at the same time leads to AIBN-induced decomposition of TBHP.

The influence of heterogeneous catalysts on this process is still under investigation.

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ПОЧАТКОВІ СТАДІЇ ОКИСНЕННЯ ЦИКЛООКТЕНУ МОЛЕКУЛЯРНИМ КИСНЕМ У ПРИСУТНОСТІ ГІДРОПЕРОКСИДУ ТРЕТБУТИЛУ

Анотація. Досліджено початкові стадії рідиннофазного окиснення циклооктену молекулярним киснем у присутності гідропероксиду третбутилу. Показано, що зародження радикалів відбувається внаслідок бімолекулярного розпаду гідропероксиду. Вивчено вплив на цей процес азодиізобутиронітрилу. Розраховано кінетичні параметри процесу.

Ключові слова: окиснення, молекулярний кисень, олефін, гідропероксид.

