

DECOMPOSITION OF *TERT*-BUTYL HYDROPEROXIDE
IN THE PRESENCE OF SELECTED INITIATORS AND CATALYSTS

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Abstract. *Tert*-butyl hydroperoxide decomposition in the presence of initiators (*tert*-butyl peroxide (*t*BuOO*t*Bu), azodiisobutyronitrile (AIBN)) and catalysts (Mo₂B₅, MoB, Mo₂B, MoSi₂, VB₂, VSi₂) was studied. Our experiments suggest that the introduction of radicals may reduce the catalytic activity. The mechanism of the initial stage of *tert*-butyl hydroperoxide decomposition and reaction rate equation are proposed.

Keywords: hydroperoxide, decomposition reaction, heterogeneous catalysis.

1. Introduction

Alkylhydroperoxides are highly reactive compounds, which find applications in various chemical processes [1-4]. Among them *tert*-butyl and cumene hydroperoxides are the most widely used ones in practice. These hydroperoxides show relatively high thermal stability because they start to decompose at temperatures higher than 363 K. Moreover, *tert*-butyl hydroperoxide is an organic peroxide extensively used in a number of oxidation reactions [5-7]. Heterogeneous catalysts are generally used for the decomposition of hydroperoxides, which allows starting the process at lower temperatures and alter limiting step resulting in acceleration of the oxidation significantly. In view of this, the majority of chemical reactions, including hydroperoxides, might be developed in the presence of catalysts. Nowadays there are a lot of well-known catalytic processes with hydroperoxides, for example, polymerization and oxidation of hydrocarbons or epoxidation of alkenes [6-9], which are highly widespread chemical processes and therefore have been intensively studied by many research groups.

On the other hand, the precise mechanism of the catalytic decomposition reaction of hydroperoxides is still not well understood, and hence it does not allow carrying out the chemical processes in the desired direction [10-11]. Additionally, the reason for the appearance of the induction period at the beginning of the reaction is not well established yet and furthermore the nonlinear dependence of the reaction rate on catalyst content also remains unclear.

Due to this, the present study is focused on investigating the decomposition reaction of *tert*-butyl hydroperoxide in the presence of two different initiators (*tert*-butyl peroxide and azodiisobutyronitrile) and six different heterogeneous catalysts (e.g. Mo₂B₅, MoB, Mo₂B, MoSi₂, VB₂, and VSi₂).

2. Experimental

The applied catalysts such as Mo₂B₅, Mo₂B, MoSi₂, VB₂, and VSi₂ were purchased from ALB Materials and MoB from Sigma Aldrich with chemical pure grade of 99.5 %. The solvents, chlorobenzene and toluene, were purchased from Aldrich and were dried through distillation in advance. *Tert*-butyl hydroperoxide (*t*BuOOH) was synthesized from *tert*-butyl alcohol and hydrogen peroxide in the presence of sulfuric acid by the procedure given in [12]. The *tert*-butyl peroxide (*t*BuOO*t*Bu) was purchased from Aldrich. Azodiisobutyronitrile (AIBN) was purchased from Aldrich and purified by recrystallization from ethanol.

The decomposition reaction of *t*BuOOH was carried out under argon atmosphere in a thermo-stated glass reactor equipped with a reflux condenser and a magnetic stirrer. The reaction temperature was maintained as 363 K and the content of catalyst was 10 g/l. Continuous agitation was carried out at the speed of 1000 rpm using the magnetic stirrer. The exact value of *tert*-butyl hydroperoxide concentration was determined by iodometric titration. The initial rate of *t*BuOOH decomposition was extrapolated on the basis of kinetic curves using data after the induction period.

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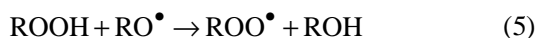
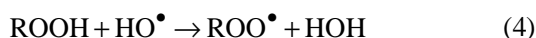
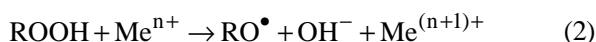
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3. Results and Discussion

The kinetic curves of *t*BuOOH consumption during the decomposition process in the presence of Mo₂B₅ as an active catalyst for *t*BuOOH decomposition [13] are shown in Fig. 1. The kinetic curves of *t*BuOOH consumption characterize the induction period for both chlorobenzene (Fig. 1, *curve* 1) and toluene (Fig. 1, *curve* 3) as solvents in the absence of an initiator.

The dependence of the initial rate of *t*BuOOH decomposition reaction on catalyst content is shown in Fig. 2. The initial reaction rate increases nonlinear with the increase in Mo₂B₅ content up to the value of 5 g/l. After that, the reaction rate practically does not depend on this parameter. This suggests that reaction order with respect to catalyst is less than one.

Taking into account the results obtained from [3, 4, 14-17], the decomposition process of hydroperoxide (ROOH) has to be described according to the following scheme where Meⁿ⁺ is an activated form of the catalyst used:



According to the scheme, the typical degradation pathways for *t*BuOOH can be summarized as mentioned in the following reaction scheme:

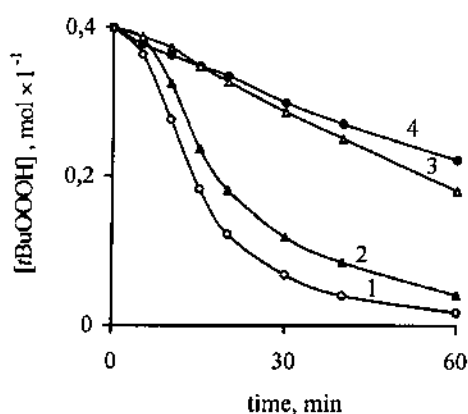
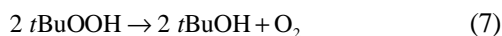
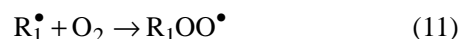
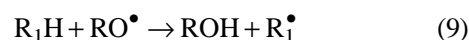
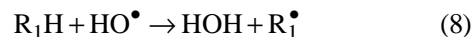


Fig. 1. *t*BuOOH decomposition at 363 K in the presence of 10 g/l Mo₂B₅ in chlorobenzene (1); in chlorobenzene with 0.02M *t*BuOO*t*Bu (2); in toluene (3); in chlorobenzene with 0.02M AIBN (4)

If a solvent (R₁H) participates in these radical reactions, the aforementioned scheme (equations (1)-(6)) can be completed with the following equations (8)-(11):



In this case the radicals R₁[•] and R₁OO[•] will additionally be present in the reaction mixture.

Most probably, one of the reasons for the existence of an induction period could be low concentration of radicals at the beginning of hydroperoxide decomposition. In that case the induction period may decrease or disappear, when an initiator, which decomposes significantly faster than *t*BuOOH, is added. To explore this further, we have investigated the influence of radicals on *t*BuOOH decomposition in the presence of some selected heterogeneous catalysts such as Mo₂B₅, MoB, Mo₂B, MoSi₂, VB₂ and VSi₂. At first, initiator *t*BuOO*t*Bu as a source of radicals was chosen. *t*BuOO*t*Bu produces *t*BuO[•] radicals, which have to be present in the reaction system of *t*BuOOH decomposition (equations (1)-(2), where *t*BuO[•] radical corresponds to RO[•] radical).

The study of the influence of *t*BuOO*t*Bu initiator on the *t*BuOOH decomposition process in the presence of catalysts Mo₂B₅ and VB₂ are shown in Figs. 1 and 3 (*curves* 1 and 2, respectively). The results obtained demonstrated that introduction of *t*BuOO*t*Bu into the reaction system does not accelerate the reaction but inhibits the catalytic decomposition of *t*BuOOH.

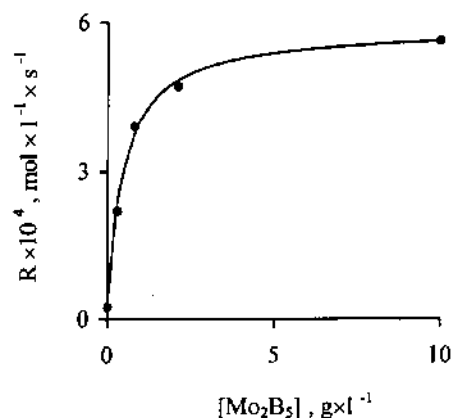


Fig. 2. Dependence of the initial rate of *t*BuOOH decomposition on the content of Mo₂B₅ at 363 K, 0.4M *t*BuOOH calculated by formula (16) (line) and experimental data (points)

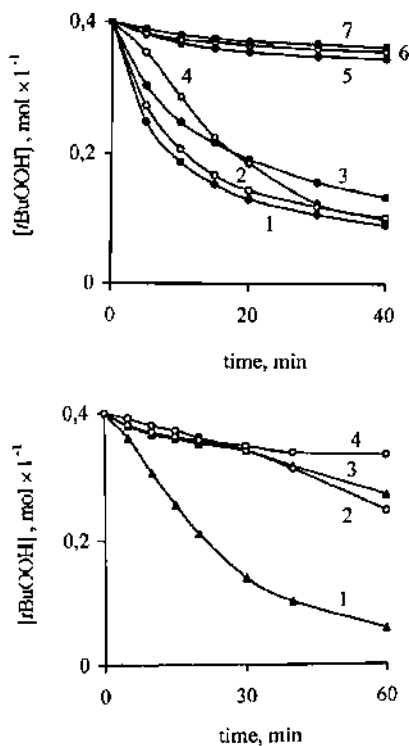


Fig. 4. *t*BuOOH decomposition in chlorobenzene at 363 K in the presence of 10 g/l Mo₂B (1, 3) and 10 g/l MoSi₂ (2, 4); 3, 4 – with 0.02M AIBN

In subsequent experiments, the influence of another initiator, *e.g.* AIBN, on the process of *t*BuOOH decomposition in the presence of not only Mo₂B₅ (Fig. 1, curves 1, 4) and VB₂ (Fig. 3, curves 1, 3) but also MoB, Mo₂B, MoSi₂ and VSi₂ (Figs. 4, 5) was studied. The results obtained show that instead of expected increase, a significant decrease in the rate of *t*BuOOH decomposition was observed. Moreover, in the case of Mo-containing catalysts this influence is stronger compared to that of V-containing catalysts. Therefore, it inhibits the radical formation of the catalytic decomposition of *t*BuOOH.

The non-catalytic decomposition of *t*BuOOH in the presence of initiators *t*BuOO*t*Bu and AIBN was also investigated (Fig. 3, curves 5-7). Both *t*BuOO*t*Bu and AIBN accelerate the non-catalytic decomposition of *t*BuOOH, and that is in agreement with the aforementioned scheme (Eq. (1)). Thus, the inhibition of *t*BuOO*t*Bu and AIBN on the catalytic decomposition of *t*BuOOH (Eqs. (2)-(3)) most probably is due to an interaction of the appearing radicals with the catalyst. Consequently, it leads to the formation of a less active form of catalyst.

Based on the results obtained, it seems logical to assume that the induction period of the catalytic reaction of *t*BuOOH decomposition in the absence of initiators *t*BuOO*t*Bu or AIBN will increase when chlorobenzene is replaced with toluene, which is more active in

Fig. 3. *t*BuOOH decomposition at 363 K in the presence of 10 g/l VB₂: in chlorobenzene (1); in chlorobenzene with 0.02M *t*BuOO*t*Bu (2); in chlorobenzene with 0.02M AIBN (3); in toluene (4) and in the absence of the catalyst: in chlorobenzene with 0.02M AIBN (5); in chlorobenzene with 0.02M *t*BuOO*t*Bu (6); in chlorobenzene (7)

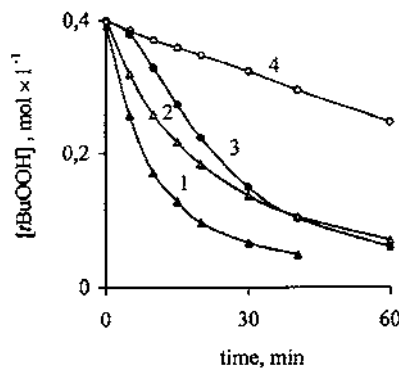
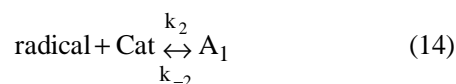
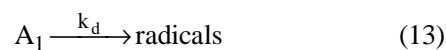
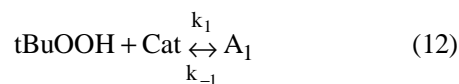
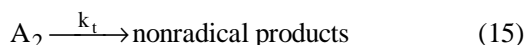


Fig. 5. *t*BuOOH decomposition in chlorobenzene at 363 K in the presence of 10 g/l VSi₂ (1, 2) and 10 g/l MoB (3, 4); 2, 4 – with 0.02M AIBN

H-abstraction reactions (Eqs. (8)-(10)) [2]. Therefore, in the presence of toluene, as compared to chlorobenzene, the amount of R₁[•] radicals in the reaction mixture seems to be higher. Experimental results presented in Fig. 1 (curves 1, 3) and Fig. 3 (curves 1, 4) show that the induction period is considerably longer when toluene is used instead of chlorobenzene. It additionally confirms the inhibition influence of the radicals on the reaction of catalytic decomposition of *t*BuOOH.

New results allow to explain the regularity of hydroperoxides catalytic decomposition reactions, in our case the nonlinear dependence of the initial rate of *t*BuOOH decomposition on catalyst content (Fig. 2). The increase in the catalyst content in the reaction system results in the increase of the quantity of radicals (Eqs. (2), (3)) which interact with catalyst, which in turn leads to the formation of a less active form of catalyst. Therefore, the beginning of *t*BuOOH catalytic decomposition process can be described through a simplified scheme:





According to the above mentioned scheme (Eqs. (12)-(15)) when steady state approximation is used and when it is assumed that $k_1 \gg k_d$ and $k_2 \gg k_t$ (decomposition of complex A_1 (Eq. (13)) and radical termination (Eq. (15)) are the limiting stages of the process) the initial rate of *t*BuOOH decomposition can be described by the following formula:

$$R = \frac{k_d K_{c1} [t\text{BuOOH}][\text{Cat}]}{1 + \frac{k_d}{k_t} K_{c1} [t\text{BuOOH}][\text{Cat}]} = \frac{a[\text{Cat}]}{1 + b[\text{Cat}]} \quad (16)$$

where $K_{c1} = k_1/k_{-1}$ – the equilibrium constant of complex A_1 formation.

According to formula (16), at specific catalyst content there is a moment where an increase in the rate of *t*BuOOH decomposition is hampered. This fact might be explained by the formation of a less active form of catalyst due to the interaction between the appearing radicals and catalyst. That is why the further increase in the catalyst content does not result in the increase in the reaction rate, i.e. the reaction rate ceases to be dependent on the catalyst content. Dependence of the initial rate of *t*BuOOH decomposition on the catalyst content was calculated by formula (16) using the values of constants $a = 11.8 \cdot 10^{-4}$ mol/(s·g) and $b = 2.1$ l/g, previously determined by a linear dependence of $1/R$ on $1/[\text{Cat}]$. The calculated dependence and experimental points are in good agreement (Fig. 2). Thus, the proposed formula (16) might describe the dependence of the initial rate of *t*BuOOH decomposition on the catalyst content.

4. Conclusions

Tert-butyl hydroperoxide decomposition in the presence of heterogeneous catalysts Mo_2B_5 , MoB , Mo_2B , MoSi_2 , VB_2 , and VSi_2 and *tert*-butyl hydroperoxide and azodiisobutyronitrile as source of radicals was studied for the first time. Two different types of initiators and six different types of Mo- and V-containing catalysts were investigated. Results revealed that the rate of *t*BuOOH decomposition strongly depends upon the nature of initiator, type of solvent and the kind of catalyst applied. Surprisingly, the promotional effect of initiators on the *t*BuOOH decomposition could only be noticed in the absence of catalysts, whereas in the presence of catalysts, initiators have shown inhibitive effects due to their interaction with catalyst components. In other words, the interaction between the radicals and catalyst components has shown clear impact on the decomposition of *tert*-butyl hydroperoxide. In fact, such interaction leads to the formation of a less active form of the catalysts and thereby inhibits the rate of *t*BuOOH decomposition. Therefore, the

choice of initiator and the type of catalyst must be carefully chosen to enhance the rate of *t*BuOOH decomposition.

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РОЗКЛАД ТРЕТ-БУТИЛГІДРОПЕРОКСИДУ У ПРИСУТНОСТІ ВИБРАНИХ ІНІЦІАТОРІВ ТА КАТАЛІЗАТОРІВ

Анотація. Вивчено розклад трет-бутилового гідропероксиду в присутності ініціаторів (трет-бутилпероксид (*t*BuOO*t*Bu), азодіізобутиронитрил (AIBN)) та каталізаторів (Mo_2B_5 , MoB , Mo_2B , MoSi_2 , VB_2 , VSi_2). Показано, що введення радикалів може зменшити каталітичну активність. Запропоновано механізм початкової стадії розкладу трет-бутилового гідропероксиду та рівняння швидкості реакції.

Ключові слова: гідропероксид, реакція розкладу, гетерогенний каталіз.