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LIQUID PHASE OXIDATION OF CUMENE IN THE PRESENCE OF POTASSIUM PERMANGANATE

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The kinetics of oxidation of cumene with potassium permanganate in acetonitrile was studied. It was shown that the rate of oxidation increases in a weakly acidic medium, and the kinetics of the consumption of permanganate ions taken at concentrations substantially lower than the cumene concentration is described by the first-order equation. The effective rate constant linearly depends on the concentration of cumene. It was shown that the addition of small quantities of potassium permanganate into the reaction solution (0.01 mol/L) initiates oxidation of cumene by molecular oxygen. It was proposed the mechanism of reaction, where, at the first stage, the abstraction of the H-atom from the C–H bond of cumene by the reactive Mn^{7+} containing species occurs and as a result the C-centered $Ph(CH_3)_2C\bullet$ radicals are formed. They react with oxygen and then participate in the reactions of the propagation of the chain of the process of liquid phase oxidation.

Keywords: potassium permanganate, oxidation, cumene, radicals, molecular oxygen.

Introduction

Oxidation is an important area in both chemical science and industry [1]. Oxidation products such as phenol, carboxylic acids and their anhydrides are important universal synthetic intermediates for the production of many chemicals, pharmaceuticals and functional materials, some of which are produced in millions of tons annually. For example, phenol, a product of oxidation of cumene, has a world annual consumption of 11.6 million tons [2]. In the last decades, the direct oxidation functionalization of C–H and C–C-bonds has proven to be one of the most effective methods for synthesizing complex products from simple and easily accessible source materials. Among oxidation processes these, where molecular oxygen as a "green" and accessible oxidant is used, attracts special attention due to its high atomic economy and environmentally friendly characteristics. Improvement of the processes of oxidation of petrochemical and coal-chemical origin substrates, which are realized on an industrial scale, for obtaining important oxygen-containing products remains an actual task [3–5].

Potassium permanganate ($KMnO_4$) is the most common salt, widely used in organic chemistry as an active stoichiometric oxidant [6]. It is well soluble in water and organic solvents, inexpensive and refers to "green" oxidants [7]. The mechanism of oxidation by permanganates was widely studied [8–11]. The catalysis of liquid-phase oxidation with Mn^{3+}, Mn^{2+} salts was also studied [12–15]. But the catalysis by $KMnO_4$ of the oxidation with molecular oxygen remains virtually unexplored.

It is interesting to study the catalytic action of potassium permanganate in the radical-chain oxidation process with molecular oxygen. In this case, its content in the reaction mixture will be several orders of magnitude smaller than when it acts as a stoichiometric oxidant.

Experimental Part

The process of oxidation of cumene in an inert-to-oxidation acetonitrile, in which the organic and inorganic components of our system are well dissolved was studied at 25 °C in a weakly acid medium created by the addition of

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acetic acid. The kinetics of the reactions was followed by recording the concentration of permanganate ions (MnO_4^-), determining photocolorimetrically change in optical density (D_{540}) of a band with a wavelength of 540 nm in quartz cuvettes of 5 mm thick. The studies were carried out in the region of concentrations, where no deviations from the Bouguer–Lambert–Beer law were observed. Reagents from Merck and Sigma were used as obtained.

Results and Discussion

It was established that when potassium permanganate is added to acetonitrile, there is no decrease in the optical density of the absorption band of permanganate ions at $\lambda_{max} = 540$ nm, which indicates that this solvent is inert in our conditions (Fig. 1, curve 0).

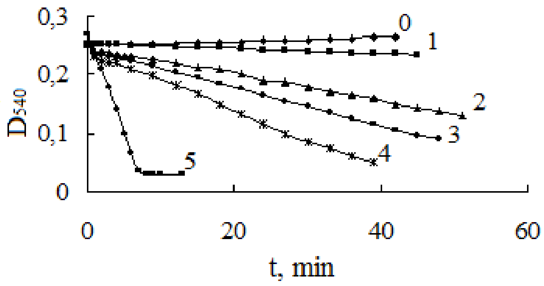

Fig. 1. The kinetics of the change in the optical density D_{540} in acetonitrile in the presence of cumene, [$C_6H_5CH(CH_3)_2$], mol/L: 0 – 0; 1 – $2.18 \cdot 10^{-2}$; 2 – $6.5 \cdot 10^{-2}$; 3 – 0.11; 4 – 0.15; 5 – 1.43 mol/L. [$KMnO_4$] = $2.67 \cdot 10^{-4}$ mol/L, [CH_3COOH] = 0.066 mol/L. λ = 540 nm, l = 5 mm

However, the addition of even small amounts (about 0.02 mol/L) in the solution of cumene causes a decrease in the optical density of D_{540}, which indicates the oxidation of cumene by permanganate. In the absence of acid, the reaction rate remains small, therefore, the reaction in solutions with additives of acetic acid, which significantly increases the rate of the process further was studied. Experimental data (Fig. 1) show that the reaction rate increases with an increase in the amount of cumene in the system.

The kinetic curves for decreasing the optical density become straight in half-logarithmic coordinates $\ln D_t/D_0 - t$: (Fig. 2) which makes it possible to calculate the effective rate constant k_{eff} of the pseudo-first-order reaction, which is a complex function of the rate constants of the individual process steps, hydrogen ion concentration and cumene concentration.

The rate constants of oxidation of cumene by potassium permanganate k_{eff} in acetonitrile are given in Table 1.

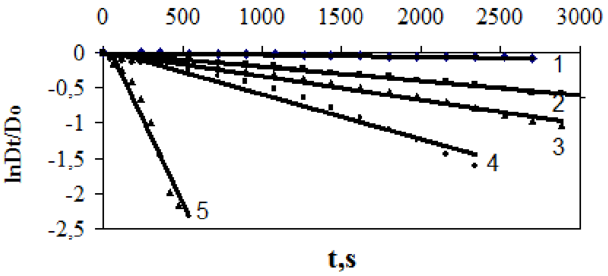

Fig. 2. Semi-logarithmic anamorphoses of absorption dependencies (D) of a solution at 540 nm on time at oxidation of cumene by $KMnO_4$ in acetonitrile. [$C_6H_5CH(CH_3)_2$], mol/L: 1 – 0.0218; 2 – 0.065; 3 – 0.11; 4 – 0.15; 5 – 1.43. [$KMnO_4$] = $2.67 \cdot 10^{-4}$ mol/L, [CH_3COOH] = 0.066 mol/L

Table 1. Dependence of the rate constant (k_{eff}) of consumption of MnO_4^- in the oxidation from the concentration of cumene in acetonitrile. 25 °C, [$KMnO_4$] = $2.67 \cdot 10^{-4}$ mol/L, [CH_3COOH] = 0.066 mol/L

[$C_6H_5CH(CH_3)_2$], mol/L	$k \cdot 10^4$, s^{-1}
0.022	0.31
0.065	2.0
0.11	3.4
0.15	6.5
1.43	46.0

The slope of linear dependence $\ln W - \ln [C_6H_5CH(CH_3)_2]$ (Fig. 3) is 1.0073, which indicates the first order on cumene in the oxidation reaction of potassium permanganate.

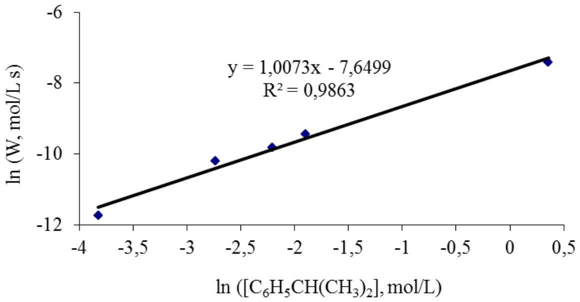

Fig. 3. Dependence of the logarithm of the rate of cumene oxidation by $KMnO_4$ in acetonitrile on the logarithm of cumene concentration. [$KMnO_4$] = $2.67 \cdot 10^{-4}$ mol/L; [CH_3COOH] = 0.066 mol/L

It is supposed, that the first stage of oxidation with potassium permanganate of organic substrates is the abstraction of the hydrogen atom from their C–H or O–H bonds [16–18]. Taking into account the proposed in the work [19] participation of various reactive species in the oxidation of permanganate in an acidic medium, the following reactions can be assumed in the mechanism of oxidation of potassium permanganate:

$$MnO_4^- + H^+ = HMnO_4$$

$$HMnO_4 + H^+ = H_2MnO_4^+$$

$$H_2MnO_4^+ = H_2O + MnO_3^+$$

Depending on the medium, there may be different reactive species and, respectively, the following reactions:

$$MnO_4(-) + HR \rightarrow HOMnO_3(-) + R^\bullet$$

$$HOMnO_3 + HR \rightarrow (HO)_2MnO_2 + R^\bullet$$

$$(HO)_2MnO_2(+) + HR \rightarrow (HO)_3MnO(+) + R^\bullet$$

In the process of oxidation of cumene with potassium permanganate to abstract the hydrogen atom from the C–H bond can MnO_4^- (in a neutral or alkaline medium), and in an acidic medium one of its protonated forms, for example, $H_2MnO_4^+$. This is confirmed by the results of quantum-chemical calculations performed for oxidation reactions with potassium permanganate of N-hydroxyphthalimide, where the rise of reaction rate in an organic solvent is observed with an increase in the concentration of acid in it [20].

The action of potassium permanganate in radical-chain processes was investigated on example of liquid-phase oxidation of cumene (RH) with molecular oxygen (Fig. 4).

The kinetics of oxidation was studied by gas volumetric measuring absorbing oxygen. The amount of oxygen absorbed was measured at a constant temperature (40 °C) and constant partial pressure of oxygen (760 mm Hg). The frequency of the reactor shaking, which provides the reactions in the kinetic mode, was determined in special experiments.

The rates of cumene oxidation with molecular oxygen were calculated by the tangent of the slope of the kinetic curve of oxygen absorption.

The effect of the presence of potassium permanganate on the oxidation of cumene by molecular oxygen in an acetonitrile medium was investigated.

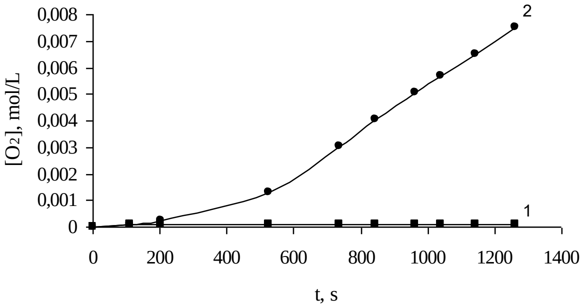

Fig. 4. The kinetics of oxygen absorption when oxidation of cumene in absence of $KMnO_4$ (1), and with $KMnO_4$ (2). $[C_6H_5CH(CH_3)_2]$ = 1.76 mol/L, [ACN] = 14.2 mol/L, $[KMnO_4]$ = 0.013 mol/L

The data in Figure 4 show that under the chosen conditions (40 °C, oxygen pressure 760 mm Hg) in the absence of permanganate, the reaction practically does not occur, no oxygen absorption is observed. The addition of small (0.013 mol/L) amounts of permanganate to the reaction medium results in the oxidation proceeding at a rate of $9.7 \cdot 10^{-6}$ mol/(L·s). The fact that oxygen is absorbed in the course of oxidation can be explained by the formation of radicals in the reaction medium in the reaction of permanganate with cumene.

Therefore, the results obtained in the investigation of the cumene oxidation with potassium permanganate and the action of permanganate in the oxidation of cumene by molecular oxygen indicate that a known scheme of radical-chain liquid phase oxidation can be used to describe the kinetics of the process:

$$RH \xrightarrow{Mn(+7)} R^\bullet \qquad W_i$$

$$R^\bullet + O_2 \rightarrow ROO^\bullet \qquad k_0$$

$$ROO^\bullet + RH \rightarrow R^\bullet + ROOH \qquad k_p$$

$$2ROO^\bullet \rightarrow \text{molecular products} \qquad k_t$$

At the first stage of cumene oxidation by potassium permanganate radicals are formed that subsequently initiate the chain oxidation process, which leads to the formation of hydroperoxide, and Mn^{7+} may be reduced further to Mn^{3+} or Mn^{2+}, as evidenced by the complete discoloration of the solution. The ions of Mn^{3+} and Mn^{2+} are effective catalysts for the radical decomposition of hydroperoxide formed by the Haber–Weiss mechanism.

Conclusions

The oxidation of cumene with potassium permanganate in acetonitrile has been studied. It is shown that the addition of small amounts of potassium permanganate to the reaction solution (0.01 M) initiates the oxidation of cumene with molecular oxygen. A reaction mechanism was proposed: the H-atom is abstracted from the C–H bond of cumene by the active Mn^{7+} containing species at the first stage and C-centered $Ph(CH_3)_2C^{\bullet}$ radicals are formed. They react with O_2, and then $ROO^{\bullet}$ participate in the reactions of the chain liquid phase oxidation. Summarizing, one can expect high efficiency of using systems based on permanganate to catalyze the liquid phase oxidation of organic substrates with molecular oxygen due to the combination of the initiating role of Mn^{7+} containing species with subsequent catalyzing action of the formed Mn^{3+} or Mn^{2+} ions.

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Рідиннофазне окиснення кумолу в присутності перманганату калію

Л. І. Опейда, Ю. М. Гринда, О. Ю. Хавунко, А. Г. Матвієнко

Вивчено кінетику окиснення кумолу перманганатом калію в ацетонітрилі. Показано, що швидкість окиснення збільшується в слабокислому середовищі, а кінетика витрати перманганат-іонів, взятих при концентраціях значно нижчих, ніж концентрація кумолу, описується рівнянням першого порядку. Спостережувана константа швидкості лінійно залежить від концентрації кумолу. Показано, що додавання невеликих кількостей перманганату калію в реакційний розчин (0,01 моль/л) ініціює окиснення кумолу молекулярним киснем. Було запропоновано механізм реакції, в якому на першому етапі відбувається відрив Н-атома від С–Н-зв’язку кумолу активними частинками перманганат-іонів, і внаслідок цього утворюються С-центровані $Ph(CH_3)_2C\bullet$ радикали. Вони реагують з киснем, а потім беруть участь у реакціях продовження ланцюга окиснення рідкої фази.

Ключові слова: перманганат калію, окиснення, кумол, радикали, молекулярний кисень.

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Жидкофазное окисление кумола в присутствии перманганата калия

Л. И. Опейда, Ю. Н. Грында, О. Ю. Хавунко, А. Г. Матвиенко

Изучена кинетика окисления кумола перманганатом калия в ацетонитриле. Показано, что скорость окисления увеличивается в слабокислой среде, а кинетика расходования перманганат-ионов, взятых при концентрациях значительно более низких, чем концентрация кумола, описывается уравнением первого порядка. Наблюдаемая константа скорости линейно зависит от концентрации кумола. Показано, что добавление небольших количеств перманганата калия в реакционный раствор (0,01 моль/л) инициирует окисление кумола молекулярным кислородом. Было предложено механизм реакции, в котором на первом этапе происходит отрыв Н-атома от С–Н связи кумола активными частицами перманганат-ионов, и в результате образуются С-центрированные $Ph(CH_3)_2C\bullet$ радикалы. Они реагируют с кислородом, а затем участвуют в реакциях продолжения цепи окисления жидкой фазы.

Ключевые слова: перманганат калия, окисление, кумол, радикалы, молекулярный кислород.