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# BENZOYL PEROXIDE DECOMPOSITION ON THE SURFACE OF CARBON MATERIALS ON THE BASE OF ACTIVATED CARBON KAU

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*Stability of non-aqueous solutions and catalytic reaction of benzoyl peroxide (BP) decomposition by samples of carbon materials (CM) – apricot shell stone activated carbon KAU, its nitrogen- and oxygen-containing (N-KAU, O-KAU) modified forms, and enzyme catalase have been examined. It has been shown that catalytic activity of CMs, quantitatively estimated by Michaelis constants, is determined by the surface functional groups nature rather than by structural-sorption characteristics. The catalytic activity of nitrogen-containing CM in non-aqueous media is by an order of magnitude higher than that of enzyme catalase. Catalyst capability to decompose benzoyl peroxide decreases in a sequence N–KAU > catalase > KAU > O-KAU. A comparative analysis of the experimental data with the results of quantum chemical calculations of the bond breaking energy in the BP molecule in different media, electronic structure of model carbon nanoclusters (CNC) and energy parameters of BP decomposition reaction has been carried out. It has been shown that the O-O bond is the weakest in BP molecule in spite of the media polarity. Free radical of BP ($C_6H_5$-COO$^{\cdot}$, BP$^{\cdot}$) more easily (both kinetically and thermodynamically) interacts with nitrogen-containing graphite-like plane model CNC as compared to pristine and oxygen-containing ones. The thermodynamic and kinetic characteristics of the interaction between BP· radical and CNC surfaces are determined by their electron donor capabilities (ionization potentials).*

***Keywords:*** *KAU-type activated carbons, benzoyl peroxide, catalytic decomposition, Michaelis constants, reaction mechanism, TPD MS method, quantum chemical calculations, DFT method*

## INTRODUCTION

Carbon materials (CM) are widely used as adsorbents and catalysts in chemical and biotechnologies. They, for example, can catalyze the chemical various type reactions, so are used to accelerate the processes of reduction-oxidation and acid-basic types (halogenation, decomposition, dehydrogenation, hydrolysis, etherification *etc.*) [1].

The catalytic activity of CM depends on the structural parameters (specific surface area, porosity character) and chemical heterogeneity of the surface - heteroatoms incorporated into the carbon matrix structure [2]. Functionalization of CM surfaces by polar oxygen-containing groups (carboxylic, anhydride, lactonic, phenolic) increases their acidity and leads to hydrophilization of material that is important when carbon catalysts are used in an aqueous

media [3]. The presence of nitrogen-containing groups on the surface of CMs increases basicity of the last and improves interaction between carbon surface and acid molecules [4]. The incorporation of nitrogen atoms in the CM structure affects its catalytic properties. It has been found that nitrogen-containing carbon materials are more active in the process of $H_2S$ and $SO_2$ removal [5], the nitrogen oxides reduction [6]. High specific surface area and low cost of CM make them attractive for use in the electrocatalytic processes, including the fuel cells development [7].

Nanoporous CM can impact on a variety of biologically important processes. Studies have found that such materials can affect on enzymatic processes (hydrolysis of proteins, fats, esters, sucrose inversion, decomposition of peroxide compounds, urea *etc.*), i.e. such materials demonstrate enzyme-mimetic activity [8].

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Quantum chemical simulation of the catalytic activity of CM made it clear [9–12] that the reaction of hydrogen peroxide decomposition over surface of a carbon nanocluster (CNC) functionalized with heteroatoms O and N occurred due to the transfer of electron density from the cluster to the hydrogen peroxide molecule in the formed complexes «CNC–$H_2O_2$». In such systems the rate of decay is controlled by the ionization potential (electron work function or energy value of the highest occupied molecular orbital) of carbon cluster.

Enzymatic activity in non-aqueous media attracts much attention because it gives a number of advantages: better solubility of the substrate, possibility to change the reaction selectivity by changing environment, rather than the enzyme [13], lower risk of microbial contamination and others [14]. It was found that catalase could act as a biocatalyst in non-aqueous media, which led to the creation of enzyme electrodes for organic phase to monitor $H_2O_2$ content in non-aqueous media or in water-saturated chloroform. Use of enzymatic activity in non-aqueous media allows us to create biocatalysts for organic synthesis not only hydrogen peroxide used in cosmetics and medicines, but also other water-insoluble peroxide compounds, i.e. *tert*-butyl and cumene hydroperoxide, benzoyl peroxide (BP) and *m*-chloroperbenzoic acid [15].

Advantages of enzyme reactions in non-aqueous media make actual examination of enzymatic catalase-mimetic activity of CM in non-aqueous solutions, since the results of this research will help to create new biocatalysts based on the available resources with directed action for biotechnology and biosensorics.

The aim of this work is the experimental study of the BP solutions stability and the process of its decomposition by various modified forms of CM, comparing with the results of quantum chemical modeling of homolytic destruction of BP molecules in a vacuum and in some polar solvents, BP radical (BP·) interaction with pristine, modified and functionalized graphite-like clusters, calculations of the electronic structure of the latter, as well as activation and thermodynamic characteristics of the BP decomposition reaction.

## EXPERIMENTAL

The catalytic activity of CM based on activated carbon KAU and its modified forms

have been determined in this paper. Oxygen-containing sample O-KAU was prepared by oxidation of KAU with nitric acid [16], nitrogen-containing material N-KAU was obtained by urea impregnation of O-KAU with following heat treatment [17].

The investigated samples were characterized [18]. Their structural and adsorption parameters were obtained from nitrogen adsorption-desorption isotherms at 77 K with prior degassing at 473 K for 12 h (Autosorb-1-MP, Quantachrome). The specific surface area ($S_{BET}$) was calculated using the Brunauer–Emmett–Teller (BET) equation. The sorption volume of pores ($V_s$) was determined by measuring benzene adsorption in a desiccator [19]; elemental composition - by Prehl and Dumas methods [20, 21]. Qualitative and quantitative characterization of functional groups on the surface of CM samples was performed by Böehm titration [22].

Powdered BP (Merck KGaA, contains 25 % water) and ethyl acetate (Merck KGaA, for liquid chromatography, 99.8 %) were used. Number of solvents – ethyl acetate, acetone, tetrachloromethane, butanol, acetic acid – was used to determine the stability of peroxide in non-aqueous media. Weighed portions of BP were used to prepare solutions with desired concentrations (from 1 to 10 %). BP concentration in solution was determined by iodometric titration [23].

The kinetics of BP decomposition in non-aqueous media was measured by the volumetric method [24]. The BP decomposition was performed in a thermostated cell with stirring. The temperature of the reaction mixture was measured with an accuracy of ±0.5 K, ambient temperature with accuracy of ±1 K, the volume of gases released in the reaction, with an accuracy of ±0.01 mL. The released gas volume measurements were conducting for 120 min. Each experiment was performed using 10 mL of BP solution. Michaelis constant ($K_M$, mmol/L) was used for quantitative assessment of catalytic enzyme-mimetic activity and for the comparison of this value for pristine carbon, its modified forms and catalase. Initial reaction velocity ($V_o$) for different substrate concentrations was used to determine the Michaelis constant [25].

Analysis of the BP decomposition reaction products was done by temperature-programmed mass spectrometry (TPD-MS) [26]. 0.1 g of the

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carbon sample was added to 50 mL of 5 % BP dioxane solution. The suspension was stirred during 24 h. Than the sample was filtrated, dried and analyzed by TPD-MS method. These experiments were performed using a MX-7304A monopole mass spectrometer with electron impact ionization adapted for thermodesorption measurements. 0.1–2.0 mg of samples in molybdenum/quartz ampoule was evacuated to ~$5 \cdot 10^{-5}$ Pa at 293 K. Then the samples were heated at the rate of 0.15 K/s up to 1023 K. The volatile pyrolysis products were passed through a high-vacuum valve into the ionization chamber of the mass spectrometer, where they were ionized and fragmented by electron impact. The mass spectra were recorded (within 1–210 Da) and analyzed using a computer-based data acquisition and processing setup. Owing to the low heating rate, diffusion effects could be neglected and the intensity of the ion current could be considered proportional to the desorption rate.

BP molecules stability in different solvents was studied by theoretical modeling. Calculations were done using US GAMESS [27] by density functional theory with exchange-correlation functional B3LYP [28, 29] involving dispersion corrections [30] and the basic set 6–31G (d, p). Solvents environment was imitated in approaching of continuum solvent model (polarization continuum model) [31]. The mechanism of influence of the CM electronic structure on BP decomposition was investigated by quantum-chemical calculations of energy parameters of BP radical interaction with graphite-like plane model of CNC. The CM were modeled by following CNC: activated carbon

AC ($C_{16}H_{10}$), oxidized activated carbon O-AC ($C_{16}O_2H_8$), nitrogen-containing activated carbon N-AC ($C_{14}N_2H_{10}$). The free energy of physical adsorption ($\Delta G_{phs}$) was calculated (with appropriate thermodynamic amendments) as the difference between total energy of physically adsorbed complexes [BP$^\bullet$...CNC] and those of individual radicals BP$^\bullet$ and graphite-like CNC:

$$\Delta G_{phs} = G^0_{298} [BP^\bullet...CNC] - G^0_{298} [BP^\bullet] - G^0_{298} [CNC].$$

The activation energy was calculated as:

$$\Delta G_{act} = G^0_{298} \text{ (transition state)} - G^0_{298} \text{ (reagents)},$$

energy effect of reaction ($\Delta G_{react}$) respectively:

$$\Delta G_{react} = G^0_{298} \text{ (reaction products)} - G^0_{298} \text{ (reagents)},$$

where $G^0_{298} = E_{tot} + ZPE + G_{0 \to 298 \text{ K}}$; $E_{tot}$ − total energy of corresponding optimized structure, zero-point energy ($ZPE$) corrections, and value $G_{0 \to 298 \text{ K}}$ − impressed by calculating of Hesse matrix of each of these states.

Found energy minima and transition states were tested in accordance with the Marrel-Leydler theory by additional calculation of Hesse matrix, allowing us to evaluate thermodynamic (free energy of physical ($\Delta G_{phs}$) and chemical ($\Delta G_{chs}$) sorption) and kinetic characteristics of this reaction (free activation Gibbs energy $\Delta G_{act}$) at 298 K [32].

## RESULTS AND DISCUSSION

BP destruction was studied for a series of CM, which differ by structural-sorption characteristics, surface chemistry - presence of heteroatoms in the structure (Table 1 and Table 2) [18].

**Table 1.** Structural-sorption characteristics and elemental composition of the investigated CM

| Carbon materials | $V_s$, cm³/g | $S_{BET}$, m²/g | Elemental composition, (wt. %) | | | |
|---|---|---|---|---|---|---|
| | | | C | H | O | N |
| KAU | 0.50 | 1070 | 99.4 | 0.2 | 0.1 | 0.3 |
| O-KAU | 0.85 | 1850 | 96.3 | 1.1 | 2.1 | 0.5 |
| N-KAU | 0.90 | 1470 | 89.2 | 2.3 | 6.3 | 2.2 |

It has been found that for studied CM structural-adsorption characteristics differ: sorption pore volume $V_s$ – from 0.50 to 0.90 cm³/g and specific surface area $S_{BET}$ – from 1070 to 1850 m²/g (Table 1). Results of

elemental analysis of carbon samples have been shown that during the oxidation number of oxygen atoms increases in 20-fold. The results of titration (Table 2) demonstrated that the surface groups had mainly acid character. Total number

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of acid groups after carbon material oxidation increased in 20 times too. Phenolic, lactone and carboxyl groups prevail on the carbon materials surface. They can be involved in catalytic processes. The basic surface groups were defined in N-KAU sample due to the presence of

nitrogen atoms in carbon structure. The content of nitrogen atoms is the smallest for KAU – 0.3 %, nitric acid oxidation doubles their number in carbon structure, and functionalization of O-KAU by urea impregnation (formation of N-KAU) allow to introduce *N*-atoms up to 2.2 %.

**Table 2.** The content of surface groups on CM

| Carbon materials | Concentration of functional groups, mmol/g | | | | |
|---|---|---|---|---|---|
| | **Carboxylic** | **Lactonic** | **Phenolic** | **Sum of acidic groups (SEC\*)** | **Basic groups** |
| KAU | 0.04 | 0.06 | 0.02 | 0.12 | 0.00 |
| O-KAU | 0.84 | 0.20 | 1.39 | 2.43 | 0.00 |
| N-KAU | 0.00 | 0.45 | 0.05 | 0.50 | 1.90 |

\* static exchange capacity

Solvents can affect on the stability of BP [33, 34]. For differentiation of the processes of BP decomposition in solution and on a solid surface, stability of peroxide solutions in acetone, ethyl acetate, carbon tetrachloride, butanol and glacial acetic acid was studied. It was found that during two hours BP decomposed on: 0 % in ethyl acetate; 0.14 % in acetone; 0.23 % in carbon tetrachloride; 1.37 % in butanol; 1.90 % in glacial acetic acid. BP solution in ethyl acetate exhibited the highest stability. Hence, this solvent was chosen as optimal for investigation of BP catalytic decomposition [18].

Calculation of the Michaelis constants was done on the base of kinetic data for the initial reaction velocity ($V_0$) at different BP concentrations ($C$). A plot of $V_0$ on $C$ in double inverse Lineweaver–Burk coordinates ($1/V_0 = A \cdot 1/C + B$) was built according to the obtained results. Michaelis constants were calculated as the value $K_M = A/B$. As an example, Fig. 1 shows the Lineweaver–Burk dependence for the sample O-KAU. The results of the linear

equations coefficients in inverse coordinates and Michaelis constants calculation for all the systems are listed in Table 3.

Obtained from dependencies, the coefficients of determination ($R^2$) have been within 0.90–0.98 so indicating a good accuracy of Michaelis constants calculation. Analysis of the $K_M$ values allows us to place the investigated catalysts by their capability to decompose BP in followed order:
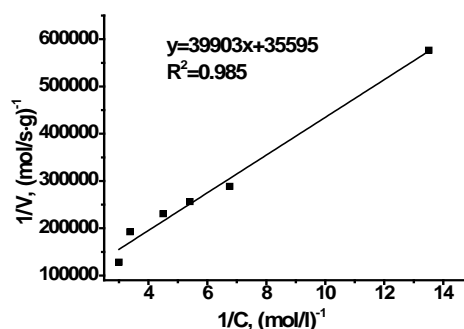
N-KAU > catalase > KAU > O-KAU.



**Fig. 1.** Lineweaver–Burk dependence for O-KAU sample

**Table 3.** The coefficients of linear equations in inverse Lineweaver–Burk coordinates, Michaelis constants and coefficients of determination ($R^2$) for the investigated catalysts

| Catalysts | $A$, (g/L)·s | $B$, (g/mol)·s | $K_M$, mmol/L | $R^2$ |
|---|---|---|---|---|
| Catalase | 2529 | 7318 | 346 | 0.966 |
| KAU | 5103 | 10687 | 477 | 0.905 |
| O-KAU | 39917 | 35608 | 1121 | 0.985 |
| N-KAU | 10 | 547 | 18 | 0.898 |

Thus, the carbon KAU and its oxidized form O-KAU have been shown a weak catalytic activity in comparison with those of nitrogen-containing sample N-KAU and native catalase. Presence of nitrogen atoms in CM increases their catalytic activity while oxygen atoms reduce it. In addition, enzyme-mimetic catalase activity of nitrogen-containing carbon exceeds in order the activity of native catalase in non-aqueous media. The obtained result is important, because it indicates ways to create effective enzyme-mimetic catalysts based on cheap raw materials.

It has been found that the catalytic activity (changing values of $K_M$) of the investigated CM in the BP decomposition reaction does not correlate with their structural and sorption parameters ($S_{BET}$, $V_s$) (Table 1), but depends on the presence of heteroatoms (O, N) in the CM structure, the nature and amount of oxygen-containing surface groups. As it is seen in Tables 1–3, substitution of carbon atoms by nitrogen atoms in the sample N-KAU leads to increasing catalytic activity, whereas oxidation (increasing SEC, which characterizes the total amount of surface oxygen-containing groups [35–41]) significantly reduces the catalytic capability of the sample O-KAU in BP decomposition. Similar dependence was observed in [11, 12, 41] in the study of $H_2O_2$ decomposition by modified carbon materials with nitrogen- and oxygen-containing surface groups. This gives us reason to believe that, as in paper [39], the catalytic activity of samples KAU and N-KAU in PB decomposition reaction by carbons with SEC < 1.0 mmol/g is determined exclusively by their electron donor properties. The mechanism of $H_2O_2$ decomposition in such systems is determined, evidently, by enthalpy factor (ionization potential, electron work function, magnitude of the energy of the highest occupied molecular orbital $E_{HOMO}$ of CM, and strength of prereaction «CM-BP» complexes).

A significant reduction of catalytic activity ($K_M = 1121$ mmol/L) of oxygen-containing O-KAU is due to both a decrease in its electron donor capability [37, 38] and presence of surface oxygen-containing groups with partical properties [39, 40]. During carbon oxidation, as shown in Table 2, mainly carboxylic and phenolic groups are formed on its surface, which can make quite stable H-complexes with peroxide molecule (for the $H_2O_2$ molecule it was proved in papers [9, 11]) and thus exclude the

participation of carbon in the decomposition reaction. So, with high probability we can say that the catalytic activity of BP decomposition by oxygen-containing CM depends on both the formation of reactive complexes «CM...PB», where destruction of PB molecules and inhibition of the BP degradation process occur by the formation of H-complex «Oxidized CM…BP». In such systems BP decomposition process is evidently determined by entropy factor.

It should be noted that the enzymatic catalytic activity of the nitrogen-containing carbon N-KAU in nonaqueous medium is in one order greater than that of native catalase (Table 3). It could be used for design of effective enzyme-like carbonaceous catalysts for biotechnology and biosensorics.

Optimization of the spatial structure and calculated energy parameters of BP molecules and of all possible products derived due to bond rupture has been provided by method RSM/B3LYP-D3/6-31G (d, p). In particular, the homolytic break of the O-O bond (Fig. 2 *a*, pos. 1) forms two free radicals *PhCOO•* (BP•), its molecular mass being 121 a.m.u. In turn, BP• through C-C bond (Fig. 2 *b*, pos. 4) can decay onto phenyl radical Ph• (77 a.m.u.) with the release of molecule $CO_2$ (44 a.m.u.). BP molecule can also decay by breaking O-C bond (Fig. 2 *a*, pos. 2) and forms two free radicals PhCOOO• and PhCO•, their relative molecular masses are 137 and 105 a.m.u., respectively. The first one can decay onto $O_2$ and free radical PhCO•. It is also possible a rupture of C-C bond (Fig. 2 *a*, pos. 3). There it may be formed phenyl radical Ph• and radical PhCOOOCO• (165 a.m.u.). The latter, like the previous one, may decompose with rupture of O-O bond (Fig. 2 *c*, pos. 5) so forming radical PhCOO• and $CO_2$ molecule.

The results of calculation are shown in Table 4. It has been estimated that regardless of the media calculation, the O-O bond in the molecule BP (Fig. 2 *a*, pos. 1) is broken most lightly, resulting in formation of two radical PhCOO•. C-C bond between the carboxyl group and benzene ring (Fig. 2 *a*, pos. 3) is much stronger. O-C bond is the strongest (Fig. 2 *a*, pos. 2); it connects O-atom of peroxide group and C-atom of carboxyl group. It should be noted that radical PhCOOOCO• (Fig. 2) generally fails to be localized because the

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optimization of the structure of this radical is happening with increase in interatomic distance of O-O bond (pos. 5) to the value of over 2.5 A. This means the bond rupture, resulting in formation of PhCOO$^\bullet$ radical and $CO_2$ molecule.

Thus, when breaking C-C bond (pos. 3) it can be formed three BP decomposition products: $CO_2$ molecule, PhCOO$^\bullet$ radical and Ph$^\bullet$ radical, which may engage in interaction with CM.
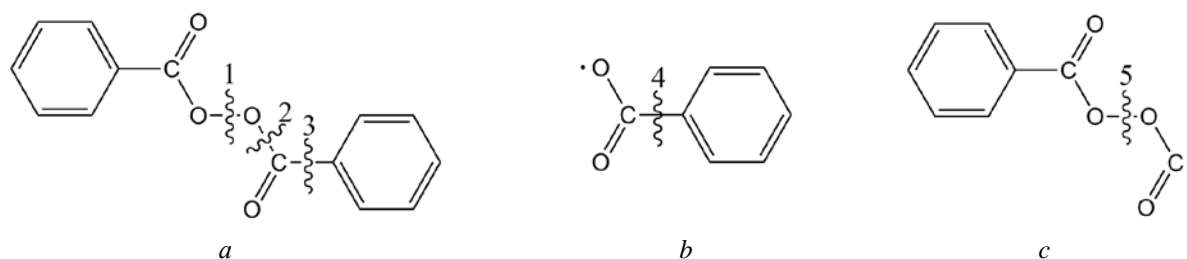


**Fig. 2.** Possible ruptures of covalent bonds of BP (*a*) and respective products of its decomposition (*b, c*) by homolytic mechanism

**Table 4.** Break energy of bonds in BP molecule in different media

| Media | Dielectric constant | Dipole moment | Break energy, kJ/mol | | | |
|---|---|---|---|---|---|---|
| | | | 1 (O-O) | 2 (O-C) | 3 (C-C) | 4 (C-C) |
| Ethyl acetate | 6.1 | 1.81 | 92.55 | 319.5 | 120.6 | 22.4 |
| Acetone | 20.9 | 2.84 | 96.71 | 326.2 | 123.1 | 25.7 |
| Carbon tetrachloride | 2.2 | 0 | 101.3 | 329.7 | 123.7 | 25.9 |
| Butanol | 17.1 | 1.66 | 104.5 | 327.9 | 136.8 | 22.6 |
| Acetic acid | 6.19 | 1.74 | 114.9 | 335.6 | 147.2 | 20.5 |
| Vacuum | | | 105.5 | 392.2 | 123.5 | 18.2 |

The results of quantum-chemical calculations are confirmed by experimental TPD MS spectra (Fig. 3), where the presence of BP components decomposition is visible with masses 122, 105, 77, 44 a.m.u. The absence of a peak with mass 165 a.m.u. in TPD spectra is explained theoretically via predicted thermodynamic instability of the corresponding radical (Fig. 2 *c*).

The catalytic activity of CNC, simulated for the surface of CM, was connected with its electron donor properties via calculation of the ionization potentials (*I*p, eV). Based on the elemental composition, structural and adsorption characteristics, and the nature of surface groups of studied CM (Tables 1 and 2), it is practically impossible to imagine definite structures of both O-containing (O-CM) and N-containing (*N*-CM) model nanoclusters. The experimental data [18] show that oxidation of CM (functinalization of

surfaces with polar oxygen-containing groups – carboxylic, anhydridic, lactonic) results in decrease in the catalytic activity, whereas introducing of nitrogen atoms into carbon matrix increases their catalytic activity in the reaction of BP decomposition. Nevertheless, it should be noted that the electron donor capability of model CNC containing both nitrogen and oxygen atoms ($C_XN_mO_nH_Y$) is strongly dependent on the number and relative positions of heteroatoms and can be more or less than the ionization potential of pure carbon one [41]. The structure of pure carbon graphite-like cluster is simulated for by a polyaromatic structure ($C_{16}H_{10}$) including four aromatic rings (relative calculated ionization potential $I$p = 5.246 eV). Oxidation with nitric acid and modifying the surface with oxygen-containing groups (carboxylic, carbonylic, lactonic) or interaction of CM with a nitrogen-containing reagent can result in the formation of

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oxygen-containing ($C_{16-p}O_nH_{10-q}$), nitrogen-containing ($C_{16-p}N_mH_{10-q}$) or mixed doped ($C_{16-p}N_mO_nH_{10-q}$) graphite-like nanoclusters, where $m$, $n$, $p$, $q$ are integers from 0 to 6. Their structures and ionization potentials are shown in Fig. 4.
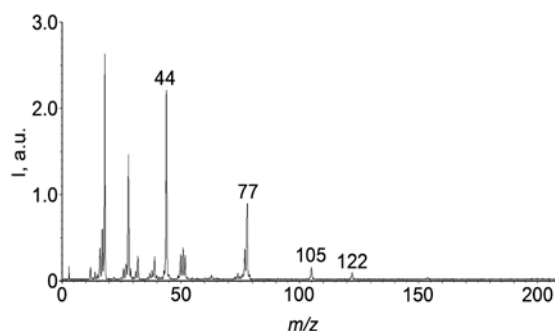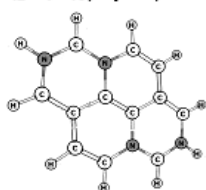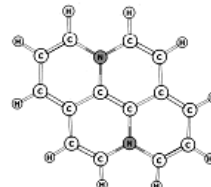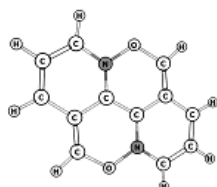


**Fig. 3.** Experimental TPD MS spectrum of thermal decomposition of BP

**Nanoclusters ($C_{16-p}N_mH_{10-q}$) and ($C_{16-p}N_mO_nH_{10-q}$) with $Ip < Ip$ ($C_{16}H_{10}$):**



$1$-$C_{12}N_4H_{10}$; Ip=2,425 eV    $2$-$C_{12}N_3O_1H_9$; Ip =2,748 eV    $3$-$C_{10}N_3O_5H_5$; Ip=3,344 eV

$4$-$C_{14}N_4O_2H_{10}$; Ip=3,241 eV    $5$-$C_{12}N_2O_2H_8$; Ip = 3,589 eV    $6$-$C_{14}N_2H_{10}$; Ip=3,108 eV

**Nanoclusters ($C_{16-p}N_mH_{10-q}$) and ($C_{16-p}N_mO_nH_{10-q}$) with $Ip > Ip$ ($C_{16}H_{10}$):**



$7$-$C_{15}N_1O_5H_5$; Ip=7,037 eV    $8$-$C_{13}N_2O_5H_4$; Ip=6,057 eV    $9$-$C_{12}N_2O_6H_4$; Ip=5,932 eV
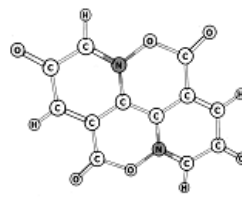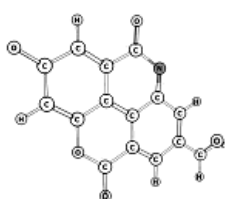
$10$-$C_{14}O_6H_4$; Ip=7,334 eV    $11$-$C_{16}O_2H_8$; Ip=6,370 eV    $12$-$C_{16}N_1O_4H_7$; Ip=5,791 eV
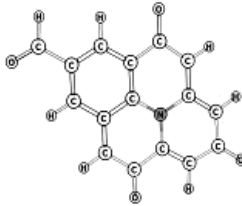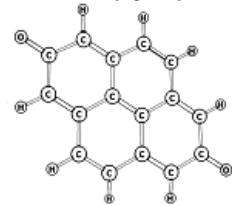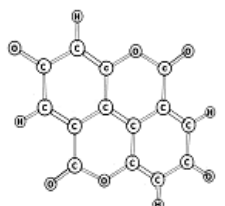
**Fig. 4.** Structures and ionization potentials Ip of nanoclusters ($C_{16-p}N_mH_{10-q}$), ($C_{16-p}O_nH_{10-q}$) and ($C_{16-p}N_mO_nH_{10-q}$)

It is seen that the structures (1–6) provide nanoclusters ($C_{16-p}N_mH_{10-q}$) and ($C_{16-p}N_mO_nH_{10-q}$), where the ionization potential $Ip < Ip_{(C16H10)} = 5.246$ eV. N,O-containing nanoclusters (2–5) have higher electron donor capability - their average value of $Ip = 3.08\pm0.33$ eV, and this is very close to the value $Ip(6) = 3.108$ eV for structure $C_{14}N_2H_{10}$. The structures (7–12) provide nanoclusters ($C_{16-p}O_nH_{10-q}$) and ($C_{16-p}N_mO_nH_{10-q}$), where $Ip > Ip_{(C16H10)}$. N,O- and O-containing nanoclusters of such types have lower electron donor capability – their average value $Ip = 6.42\pm0.51$ eV, and this is very close to the value $Ip(11) = 6.370$ eV for structure $C_{16}O_2H_8$. Therefore, in order to examine thermodynamic and kinetic characteristics of the interaction between free radical BP· (PhCOO·) and graphite-like planes of various CM, we selected nanoclusters $C_{16}H_{10}$, $C_{16}O_2H_8$ and $C_{14}N_2H_{10}$, respectively.

It has been found that the interaction of graphite-like planes with radical PhCOO· occurs in two stages. Firstly, a physically adsorbed complex is formed; at the second stage a chemical bond is formed between the reactants after overcoming the energy barrier of transition state (Fig. 5). In the complex of transition state the radical is coordinated to graphite-like planes through an O-atom. The obtained thermodynamic ($\Delta G_{phs}$, $\Delta G_{chs}$) and kinetic ($\Delta G_{act}$) characteristics of interaction between radical and CNC are presented in Table 5.

As shown in the Table 5, the structure of physically sorption complex (PhCOO·... $C_{14}N_2H_{10}$) is most durable, because this system has the most negative value of physical adsorption energy $\Delta G_{phs}$. Chemisorption of PhCOO· radical on graphite-like plane occurs due to the formation of activated (transition) state (PhCOO·...CNC); a radical is coordinated with the nanocluster plane by one of the O-atoms from COO-fragment (Fig. 6). Trustworthiness of existence of transition states is confirmed by presence of a single imaginary vibrational mode $iv_{tv}$ (Table 5), which characterizes the direction of displacement of coordinates of atomic nuclei at the transition from starting materials to the reaction products. The absolute value $iv_{tv}$ is associated with the value of the steepness of the energy barrier on the surface for potential energy of reacting system.

**Table 5.** Thermodynamic – free energy physical ($\Delta G_{phs}$) and chemical ($\Delta G_{chs}$) adsorption and kinetic – Gibbs activation free energy ($\Delta G_{act}$) interaction characteristics of BP· radical with CNC

| CNC | Ionization potential, eV | $\Delta G_{phs}$, kJ / mol | $\Delta G_{act}$, kJ / mol | $\Delta G_{chs}$, kJ / mol | $K_M = A/B$, mmol/L | $Iv_{tv}$, cm$^{-1}$ |
|---|---|---|---|---|---|---|
| $C_{14}N_2H_{10}$ | 3.108 | -18.7 | 4.8 | -5.30 | 18 | 342.4 |
| $C_{16}H_{10}$ | 5.246 | -13.5 | 37.6 | -6.60 | 477 | 418.5 |
| $C_{16}O_2H_8$ | 6.370 | -12.0 | 35.9 | -6.67 | 1121 | 76.9 |
| | X | Y1 | Y2 | Y3 | Y4 | |
| $R^2$ (Y$_i$ = a$_i$ + b$_i$X) | 0.983 | 0.854 | 0.912 | 0.927 | | |



physically sorbed complex

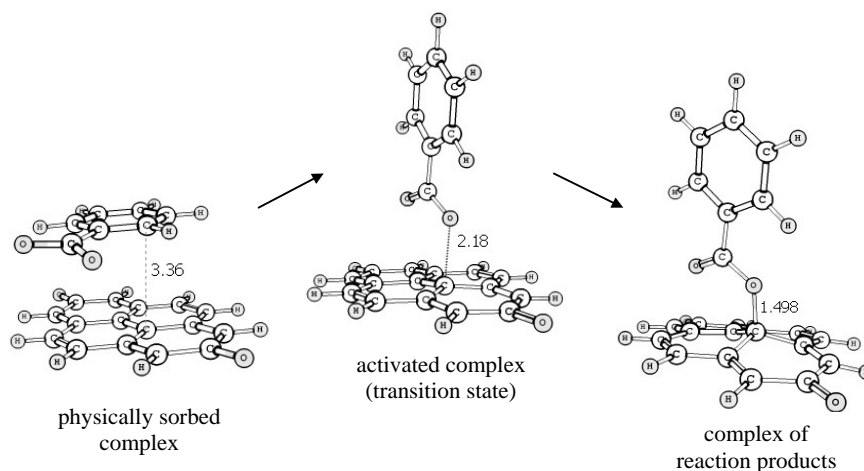activated complex (transition state)

complex of reaction products

**Fig. 5.** Scheme of interaction between BP· and O-CNC

The results of quantum chemical calculations show that under normal conditions the easiest chemical adsorption of radical PhCOO$^{\bullet}$ is on the N-containg nanocluster, as this requires the lowest activation energy ($\Delta G_{act} = 4.8$ kJ/mol), while for adsorption on the pure carbon or O-containing nanoclusters the value $\Delta G_{act}$ is higher for 31–35 kJ/mol. Table 5 also shows that the thermodynamic effect of chemisorption on N-containg nanocluster has the highest value (–5.3 kJ/mol), in comparison with the same values for other nanoclusters. This means that desorption of PhCOO$^{\bullet}$ radical occurs most easily from the surface of nitrogen-containing CM (for example, catalyst N-KAU) and, perhaps, it easy regenerate from the products of decomposition and takes part of the next acts of chemosorption.

It should be noted that thermodynamic ($\Delta G_{phs}$, $\Delta G_{chs}$) and kinetic ($\Delta G_{act}$) features ($Y_i$) of BP$^{\cdot}$ radical interaction with various type CNC in solvents of various nature are defined by their electronic donor capability (ionization potential, $X$), as evidenced by very significant correlation coefficient $R^2$ of the linear dependences $Y_{i = 1,2,3} = a_i + b_i X$. Hence, we can assume that the mechanism of BP destruction in non-aqueous solutions on the CM surface is identical to the mechanism of hydrogen peroxide degradation in aqueous solution [25, 37, 38, 41].

## CONCLUSIONS

The stability of non-aqueous solutions of BP and its catalytic decomposition by the samples of carbon materials modified with nitrogen- and oxygen-heteroatoms as well as by native enzyme catalase have been studied. It has been shown that the catalytic activity of CM quantitatively assessed by Michaelis constants is determined by the nature of surface functional groups of the carrier rather than by its structural and sorption characteristics.

It has been found that the catalytic activity of nitrogen-containing carbon materials in non-aqueous media is in order higher than that of enzyme catalase that gives opportunities to prepare efficient enzyme-like catalysts based on cheap raw materials of carbonaceous type. The capability of catalysts to decompose BP was ordered in the following row:

N-KAU > catalase > KAU > O-KAU.
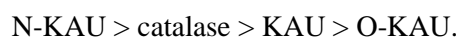
A comparative analysis has been carried out of the obtained experimental data with the results of quantum chemical calculations of the rupture energy of bonds in the molecule BP in different media, electronic structure of simulated CNC and energy parameters of peroxide decomposition. It has been found that in the molecule BP, regardless of the media polarity, the O-O bond is the weakest.

It has been shown that BP$^{\cdot}$ radical ($C_6H_5$-COO$^{\cdot}$) most easily interacts with N-containing carbon nanocluster (N-CNC), in comparison with the pure CNC and O-containing one (O-CNC). It has been also found that thermodynamic ($\Delta G_{phs}$, $\Delta G_{chs}$) and kinetic ($\Delta G_{act}$) characteristics of BP$^{\cdot}$ radical ($C_6H_5$-COO$^{\cdot}$) interaction with the surface of CM is determined by its electron donor capability (ionization potential).

# Розкладання пероксиду бензоїлу на поверхні вуглецевих матеріалів на основі активованого вугілля КАУ

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Досліджено стабільність неводних розчинів та каталітичну реакцію розкладання пероксиду бензоїлу (ПБ) зразками вуглецевих матеріалів (ВМ) – активованого вугілля з кісточок абрикоса КАУ, його азот- та кисеньвмісними (N-КАУ, О-КАУ) модифікованими формами і ензимом каталазою. Показано, що каталітична активність ВМ, кількісно оцінена за константами Міхаеліса, визначається природою поверхневих функціональних груп носія, а не його структурно-сорбційними характеристиками. Встановлено, що каталітична активність азотвмісних ВМ у неводному середовищі на порядок вища, ніж у ензиму каталази. Здатність каталізаторів розкладати пероксид бензоїлу зменшується в послідовності N–КАУ > каталаза > КАУ > О-КАУ. Проведено порівняльний аналіз одержаних експериментальних даних з результатами квантовохімічних розрахунків енергії розриву зв'язків в молекулі ПБ в різних середовищах, електронної будови модельних вуглецевих нанокластерів (ВНК) та енергетичних параметрів реакції розкладання пероксиду. Встановлено, що в молекулі ПБ, незалежно від полярності середовища, найслабшим є зв'язок О-О. Визначено, що термодинамічні і кінетичні характеристики взаємодії радикала ПБ ($C_6H_5$-СОО˙, ПБ·) з поверхнею модельних ВНК (чисто вуглецевих, азот- та кисеньвмісних) визначаються їхньою електронодонорною здатністю (потенціалом іонізації).

*Ключові слова: різновиди активованого вугілля КАУ, пероксид бензоїлу, каталітичне розкладання, константи Міхаеліса, механізм реакції, метод ТПД МС, квантово-хімічні розрахунки, DFT-метод*

# Разложение пероксида бензоила на поверхности углеродных материалов на основе активированного угля КАУ

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Исследованы стабильность неводных растворов и каталитическая реакция разложения пероксида бензоила (ПБ) образцами углеродных материалов (УМ) - активного угля из абрикосовых косточек КАУ, его модифицированными азот- и кислородсодержащими формами (N-КАУ, О-КАУ), энзимом каталазой. Показано, что каталитическая активность углеродных материалов, количественно оцененная по константам Михаэлиса, определяется природой поверхностных функциональных групп носителя, а не его структурно-сорбционными характеристиками. Установлено, что каталитическая активность азотсодержащих УМ в неводной среде на порядок выше, чем у энзима каталазы. Способность катализаторов разлагать ПБ уменьшается в последовательности N–КАУ> каталаза > КАУ > О-КАУ. Проведен сравнительный анализ полученных экспериментальных данных с результатами квантовохимических расчетов энергии разрыва связи в молекуле ПБ в разных средах, электронного строения модельных углеродных нанокластеров (УНК) и энергетических параметров реакции разложения ПБ. Установлено, что в молекуле БП, независимо от полярности среды, самой слабой является связь О-О. Показано, что свободный радикал ПБ ($C_6H_5$-СОО˙, ПБ·) легче (и кинетически, и термодинамически) взаимодействует с азотсодержащей графитоподобной плоскостью модельного УНК, чем с поверхностью исходного и функционализированного гетероатомами кислорода нанокластеров. Установлено, что термодинамические и кинетические характеристики взаимодействия ПБ· с поверхностью УНК определяются их электронодонорной способностью (потенциалом ионизации).

*Ключевые слова: разновидности активированного угля КАУ, пероксид бензоила, каталитическое разложение, константы Михаэлиса, механизм реакции, метод ТПД МС, квантово-химические расчеты, DFT-метод*

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