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E. N. Abdullayev[1], A. M. Mishura[1], I. A. Iermolenko[2,3], A. S. Lytvynenko[1],
M. A. Kolosov[4], E. G. Shvets[4], K. S. Gavrilenko[2,5], S. V. Kolotilov[1]

[1] L. V. Pisarzhevsky Institute of Physical Chemistry of the National Academy of Sciences of Ukraine,
31 Nauky ave., 03028 Kyiv, Ukraine
[2] Enamine Ltd., 78 Winston Churchill str., 02094 Kyiv, Ukraine
[3] Institute of Organic Chemistry of the National Academy of Sciences of Ukraine,
5 Academik Kukhar str., 02094 Kyiv, Ukraine
[4] V. N. Karazin Kharkiv National University, School of Chemistry, 4 Svobody sq., 61022 Kharkiv, Ukraine
[5] Taras Shevchenko National University of Kyiv, 12 Pavlo Skoropadskyi str., 01033 Kyiv, Ukraine

The Oxidation of Cyclic Ketones by H_2O_2 Catalyzed by Cu(II) and Fe(III) Coordination Polymers

Abstract

It has been shown that the oxidation of ketones – analogs of cyclohexanone – by hydrogen peroxide in the presence of $Cu_3(btc)_2$ (btc^{3-} = 1,3,5-benzenetricarboxylate) occurred mainly by the radical mechanism, rather than by the Baeyer-Villiger reaction mechanism, and led to a mixture of products formed due to the ring cleavage and reduction of the hydrocarbon chain length. Unlike aliphatic ketones, α-tetralone hardly underwent conversion in the reaction with H_2O_2 in the presence of HKUST-1, and the oxidation of the same ketone in the presence of $Fe_2(OH)_3(btc)$ led to the formation of a number of products; among them, 1,4-naphthoquinone was dominant.

Keywords: catalytic oxidation; cyclic ketones; hydrogen peroxide; porous coordination polymers; copper(II); iron(III)

Е. Н. Абдуллаєв[1], А. М. Мішура[1], Є. А. Єрмоленко[2,3], А. С. Литвиненко[1], М. О. Колосов[4], О. Г. Швець[4], К. С. Гавриленко[2,5], С. В. Колотілов[1]

[1] Інститут фізичної хімії ім. Л. В. Писаржевського Національної академії наук України,
просп. Науки, 31, м. Київ, 03028, Україна
[2] ТОВ НВП «Єнамін», вул. Вінстона Черчилля, 78, м. Київ, 02094, Україна
[3] Інститут органічної хімії Національної академії наук України,
вул. Академіка Кухаря, 5, м. Київ, 02094, Україна
[4] Харківський національний університет імені В. Н. Каразіна,
майдан Свободи, 4, м. Харків, 61022, Україна
[5] Київський національний університет імені Тараса Шевченка,
вул. Володимирська, 60, м. Київ, 01033, Україна

Окиснення циклічних кетонів H_2O_2, каталізоване координаційними полімерами Cu(II) та Fe(III)

Анотація

З'ясовано, що окиснення кетонів – аналогів циклогексанону – перекисом водню в присутності $Cu_3(btc)_2$ (btc^{3-} = 1,3,5-бензолтрикарбоксилат) проходило переважно за радикальним механізмом, а не за механізмом реакції Баєра-Віллігера, і призводило до суміші продуктів, що утворювалися внаслідок розщеплення кільця та зменшення довжини вуглеводневого ланцюга. На відміну від аліфатичних кетонів, α-тетралон майже не вступав у реакцію з H_2O_2 в присутності HKUST-1, а окиснення цього кетону в присутності $Fe_2(OH)_3(btc)$ призводило до утворення низки продуктів, серед яких домінував 1,4-нафтохінон.

Ключові слова: каталітичне окиснення; циклічні кетони; пероксид водню; пористі координаційні полімери; мідь(II); залізо(III)

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■ Introduction

Oxidation reactions have been widely used in both high-volume organic industry (for example, manufacturing of dicarboxylic acids to produce plastics) and in fine organic synthesis for the preparation of substances for pharmaceuticals (active pharmaceutical ingredients, APIs) and agrochemistry [1–3]. Many currently used methods of organic compounds oxidation involve the application of toxic catalysts based on platinum group metals [4, 5] or oxidizing agents, which contain toxic metals (chromium, manganese, osmium) and, hence, produce toxic wastes [6–8]. Residual impurities formed from reagents or catalysts can also cause contamination of the products, which is critical for the production of APIs. For example, the content of platinum metals in the substance in some cases should not exceed 10^{-6} % by weight [9]. The development of new environmentally friendly methods for the oxidation of organic compounds and studies of the pathways of such processes are the tasks of modern organic and physical chemistry.

The problem of generating large amounts of waste during oxidation can be solved using environmentally friendly oxidants, such as hydrogen peroxide, which produces water and oxygen (in the side reaction of decomposition of H_2O_2) [10, 11]. At the same time, the widespread use of hydrogen peroxide as an oxidant in organic chemistry is limited because of the formation of an unpredictable mixture of products due to multiple parallel processes and/or different mechanisms, which can occur simultaneously [11, 12]. Nevertheless, there are many examples of the successful use of H_2O_2 for the selective oxidation of organic compounds in literature. High selectivity is achieved when the reaction proceeds by a single mechanism, unlike radical oxidation. For example, the oxidation of ketones by the Baeyer-Villiger mechanism in the presence of metal-containing catalysts usually leads to lactones with high yields [13–18]. In contrast, it has been found that hydrogen peroxide can decompose in the presence of $Cu_3(btc)_2$ (btc^{3-} is 3,5-benzenetricarboxylate), forming OH radicals, which cause deep oxidation of organic molecules and the formation of a mixture of products [19]. It has been noted that ·OH radical is one of the most potent oxidants. Thus, the study of the conditions under which the oxidation reaction involving H_2O_2 proceeds by the Baeyer-Villiger or radical mechanism is a problem of high importance for selecting catalysts and determining the scope of their application.

The use of porous coordination polymers (PCP) of the 3d metals as catalysts is of particular interest since these compounds may have high catalytic performance in oxidation processes [12, 20], and their selectivity can be associated with differences in the sorption capacity of PCP with respect to reagents [21–23]. In addition, the use of PCP allows one to carry out reactions in a heterogeneous catalytic mode; this feature significantly simplifies the purification of products from the catalyst (transition metal ions) and makes possible a simple reuse of the catalyst or transfer of the reaction to the flow mode.

The aim of the study was to determine the catalytic properties of two well-known PCPs – 1,3,5-benzenetricarboxylates (btc^{3-}, also known as an anion of trimesic acid) of copper(II) (known as HKUST-1 [24]) and iron(III) [25] – in the process of cyclic ketone oxidation with hydrogen peroxide, and to determine their place among the catalysts used for the oxidation of organic compounds with hydrogen peroxide. The PCPs $Cu_3(btc)_2$ and Fe(btc) are widely used and are manufactured and distributed under trademarks Basolite® C300 and Basolite® F300, respectively. Though the synthesis of the first compound is simple and straightforward, the second one usually forms species with a high hydroxide content and corresponds to formula $Fe_2(OH)_3(btc)$. The use of these PCP made it possible to compare the catalytic activity of compounds containing metal ions with different Lewis acidity [26] and oxidative capacity [27].

The study used 1,2,3,4-tetrahydro-1-naphthalenone (I, α-tetralone) as a carbocyclic ketone. This compound is similar to industrially important cyclohexanone, but less volatile. It has a simpler NMR spectrum and can be easily analyzed by chromatography without modification. To reveal the peculiarities of oxidation of organic compounds containing several sensitive to oxidation fragments, other ketones, including ethyl 4-oxocyclohexane-1-carboxylate (**II**), *tert*-butyl 4-oxopiperidine-1-carboxylate (**III**), tetrahydro-4*H*-pyran-4-one (**IV**), were also studied (**Figure 1**).

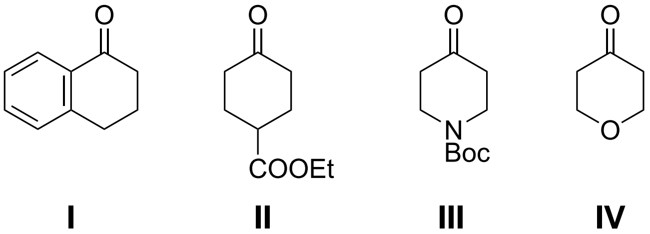


Figure 1. Ketones studied in this work

Materials and methods

$Cu_3(btc)_2$ and $Fe_2(OH)_3(btc)$ were obtained by anodic dissolution of the corresponding metals in a solution of 1,3,5-benzenetricarboxylic acid. The method of obtaining $Cu_3(btc)_2$ was described earlier [28]. $Fe_2(OH)_3(btc)$ was obtained by modification of the known method [29]. Two preliminarily cleaned iron rods with a diameter of 2 mm were immersed in a beaker with the electrolyte (0.5 g Bu_4NBF_4 and 0.2 g H_3btc in 20 mL of ethanol) and 3 F of electricity per 1 mol of trimesic acid was passed through the solution at a temperature of 32 °C and a current density of 3.8 A dm^{-2}. The contact area of iron with the electrolyte was 107 mm^2, current – 40 mA, electrolysis time – 2.2 h. During the reaction, the air was blown through the electrolyte with a peristaltic pump throughout the electrolysis and for an additional 2.5 h after its completion. The reaction mixture was then stirred for 12 h. A beige precipitate fell out during the process, which gradually turned light red. After the process, the precipitate was filtered off, washed with water, and dried at 70–80 °C. The CHN analysis: calculated for $Fe_2(OH)_3(btc)(H_2O)_{1,3}$: $C_9H_{8.6}O_{10.3}Fe_2$, %: C 27.50; H 2.20; found C 27.60; H 2.52.

Powder diffraction patterns of the coordination polymers were measured using a DRON-3M X-ray diffractometer, Cu-Kα radiation in the range of angles 2θ = 5–80° with a step of 2θ = 0.05°. The transmission electron microscopy studies were performed using a PEM-125K SELMI microscope with an accelerating voltage of 100 kV. Test samples in the form of alcohol suspensions were applied to copper mesh covered with a film of amorphous carbon and then dried. The CHN analysis was performed using a CarloErba 1106 instrument. Nitrogen adsorption isotherms were measured by the volumetric method using a Sorptomatic 1990 instrument. Optical micrographs were obtained using an XY-B2 trinocular microscope (Ningbo Sunny Instruments Co., Ltd., PRC) equipped with the attached PowerShot G6 Canon camera in the mode of illumination of the sample, the light source was a lamp built into the microscope. The composition of the reaction mixtures in the ketone oxidation processes was determined by ^{1}H NMR (a Bruker Advance 400 spectrometer), gas chromatography with mass spectrometric detection (an Agilent 7890 A chromatograph) and in individual experiments with mass spectrometry (a Shimadzu GCMS QP-2020 instrument using a column type HP-5 and a direct sample inlet (DI) into the ion source).

Mass spectra of mixtures were obtained by the direct introduction of samples into an ion source (DI) on a Shimadzu GCMS QP-2020 instrument (ionization energy 70 eV). In addition to DI, an attempt was made to chromatographically separate mixtures of reaction products followed by the mass spectrometric detection of individual substances (GCMS) using a Shimadzu GCMS QP-2020 instrument, the carrier gas was helium (99.999% vol.), the sample solvent – ethyl acetate, the sample volume – 1 µL, the injector temperature – 150 °C. Column: the stationary phase was 5% diphenylpolysiloxane, 95% dimethylpolysiloxane; the length – 30 m; the inner diameter – 0.25 mm; the thickness of the stationary phase film – 0.25 µm. Column temperature control: the initial temperature was 35 °C; the initial isotherm time – 1 min; the temperature gradient – 15 °C min^{-1}; the final temperature – 200 °C; the time of the final isotherm – 5 min (the detector temperature – 200 °C; the ionization energy – 70 eV). The NIST 17.0 database was used to assign mass spectra.

Ketone oxidation experiments were performed according to the method similar to that described in the literature [11]. A portion of the appropriate PCP and a portion of a ketone (concentrations of reaction mixtures are indicated in the *Results and discussion* section) were added to the solution obtained by mixing acetonitrile with aqueous hydrogen peroxide. In most cases the solutions were prepared by mixing 40 mL of acetonitrile with 7 mL of 35% aqueous solution of H_2O_2 (d = 1.1 g cm^{-1}); the solution obtained contained 1.7 M H_2O_2 and 5.9 M water. The resulting suspension was stirred at 25 °C for 24 h on a magnetic stirrer. After standing for a certain time, 50 mL of 1.1 M aqueous Na_2SO_3 solution was added to the reaction mixture, the organic compounds were extracted with ethyl acetate (2 portions of 75 mL), the extracts were dried over sodium sulfate, and the solvents were removed on a rotary evaporator under reduced pressure. The reaction products were analyzed as described above.

■ Results and discussion

The powder diffraction pattern of the HKUST-1 sample obtained in this work was similar to the diffraction pattern of the hydrated form of copper(II) benzenetricarboxylate $Cu_3(btc)_2(H_2O)_3 \cdot xH_2O$ [30]. In contrast, there were no distinct reflections on the diffraction pattern of the coordination polymer $Fe_2(OH)_3$(btc), which was a sign of a disordered structure. The results obtained are in good agreement with the literature – copper(II) 1,3,5-benzenetricarboxylate is almost always characterized by a well-defined crystalline structure, while iron(III) 1,3,5-benzenetricarboxylate, according to X-ray diffraction, is usually referred to as a material with low crystallinity or even amorphous one [31].

The TEM studies showed that the HKUST-1 sample mainly consisted of particles of *ca.* 0.5 μm size (**Figure 2**, *a*). The particle size of $Fe_2(OH)_3$(btc), determined by optical microscopy, was 0.7–0.8 μm (**Figure 2**, *c*). Particles of $Fe_2(OH)_3$(btc) were unstable in the electron beam of TEM.

According to nitrogen adsorption data, HKUST-1 was characterized by the value of $S_{BET} = 1435$ m² g⁻¹, the volume of micropores according to the Dubinin-Radushkevich equation V_{DR} was equal to 0.533 cm³ g⁻¹ [28]. In the case of $Fe_2(OH)_3$(btc) the value of S_{BET} was 520 m² g⁻¹, the volume of micropores according to the Dubinin-Radushkevich equation was $V_{DR} = 0.196$ cm³ g⁻¹. The distribution of pores by size was calculated using the Saito-Foley method, the sample $Fe_2(OH)_3$(btc) had dominating pores size with a diameter of 1.0 nm, and there were pores with a diameter of 1.2–1.4 nm. The values of S_{BET} and

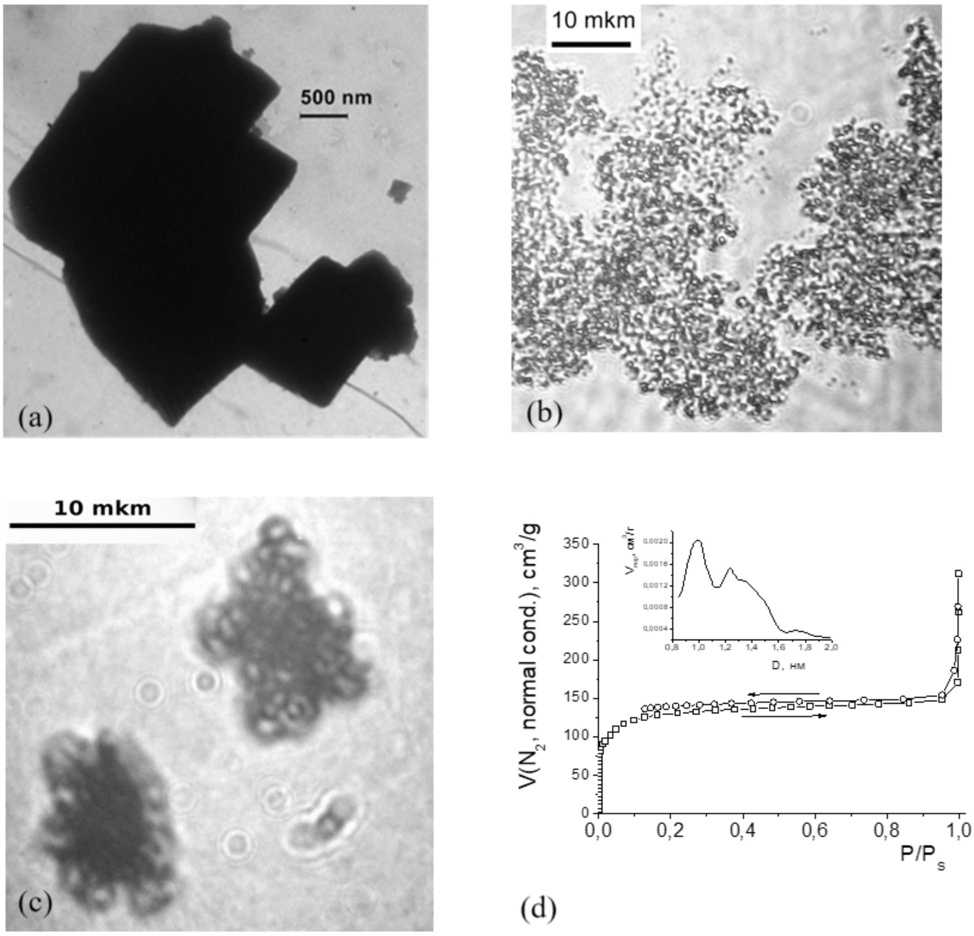


Figure 2. Images of HKUST-1 obtained by TEM (**a**) and optical microscopy (**b**), the image of $Fe_2(OH)_3$(btc), obtained by optical microscopy (**c**) and nitrogen adsorption isotherm of PCP $Fe_2(OH)_3$(btc) (**d**)

V_{DR} for HKUST-1 were close to the upper limit of the range of sorption characteristics typical for these PCPs [24], and in the case of $Fe_2(OH)_3(btc)$ S_{BET} and V_{DR} were significantly lower than the values published for similar compounds [31].

At room temperature, α-tetralone (**I**) was not oxidized by hydrogen peroxide in the presence of HKUST-1 (0.1 M of a ketone, 1.7 M of H_2O_2, $1.5 \cdot 10^{-2}$ M of HKUST-1) as the organic mixture after the experiment contained almost pure starting ketone (hereinafter the "effective concentration" of PCP in the reaction mixture is given as the ratio of the amount of PCP expressed in moles per 1 mol of a metal ion to the volume of the solution. The PCP is suspended as a fine solid). The interaction of **I** with hydrogen peroxide in the presence of HKUST-1 for 3 h at 55 °C also did not lead to the formation of a significant amount of oxidation products: according to the gas chromatography and NMR methods, the reaction mixture contained more than 97% of the initial ketone **I**, and among the minor oxidation products a lactone resulting from the Baeyer-Villiger oxidation could be identified.

Upon the oxidation of **I** (0.14 M) with hydrogen peroxide (1.7 M) in the presence of $Fe_2(OH)_3(btc)$ (1×10^{-3} M) at 25 °C in 5 h, *ca.* 5–8% of quinone was found in the results of two experiments, while about 90% of the initial ketone **I** remained unchanged. At the same time, the formation of several products was detected by gas chromatography. These products could be attributed to the lactone or the products of the compound **I** hydroxylation in the aromatic core, the yield of each of these products did not exceed 2%. Increasing the reaction time to 24 h had little effect on the formation of oxidation products.

The oxidation of organic compounds in the presence of PCPs occurs on the metal ions located in pores and on the outer surface of the catalyst particles. Clearly, not all metal ions are accessible to a substrate in this case. In order to compare the outcome of the oxidation process with the one that occurred in homogeneous conditions, a similar reaction was carried out in the presence of soluble copper(II) salt. In order to reveal if there was any contribution of Lewis acidity of the metal ion (in contrast to possible redox activity), the oxidation in the presence of $AlCl_3$ was tested. It was found that in a similar reaction of the oxidation of **I** in the presence of $CuCl_2$ (0.1 M ketone, 1.7 M of H_2O_2, $1 \cdot 10^{-2}$ M $CuCl_2$, 24 h at 25 °C), 95% of the starting ketone and about 3% of quinone were found in the reaction mixture, and when $CuCl_2$ was replaced with an equimolar amount of $AlCl_3$, 98% of the starting material were found unchanged. It can be concluded that the low yield in the oxidation of **I** in the presence of HKUST-1 was associated with the intrinsic low catalytic activity of Cu^{2+} ions rather than their low accessibility. Moreover, the low Lewis acidity does not cause such low catalytic activity.

The oxidation of ketones **II-IV** in the presence of HKUST-1 at room temperature led to the formation of mixtures of products at the ketone/H_2O_2 ratio of 1:2 (0.05 M of ketone, 0.1 M of H_2O_2, $5 \cdot 10^{-3}$ M of HKUST-1), as well as at a 17-fold excess of H_2O_2 (0.1 M of **II**, 1.7 M H_2O_2, $1 \cdot 10^{-2}$ M of HKUST-1). The mass spectrum (direct injection of the sample into the ion source) of the reaction mixture sample obtained by the oxidation of **II** (0.1 M of **II**, 1.7 M of H_2O_2, $1 \cdot 10^{-2}$ M of HKUST-1 for 24 h at 25 °C with further processing) is shown in **Figure 3** (a). The mass spectrum obtained corresponds to cyclic lactone **IIa** (the Baeyer-Villiger oxidation product, **Figure 4**) and other substances that could form upon its oxidation by the radical mechanism, which led to a decrease in the carbon chain length [32]. The ^1H NMR spectrum of the reaction mixture after the oxidation of **II** could also be interpreted with the assumption that the resulting mixture contained lactone **IIa** and the products of its deeper oxidation (the products were determined by comparing the positions of the signals with the calculated values; the positions of the signals in the NMR spectrum were calculated using ACD Labs 10.08 software pack program), however the quantitative composition of the reaction mixture could not be determined. The possible oxidation products are shown in **Figure 3** (b).

The GCMS analysis of the reaction mixture obtained in the experiment of the compound **II** oxidation revealed at least three other compounds with longer retention times compared to **II**; molar fractions of **II** and these 3 products had the ratio of 15:23:17:45. The mass spectrum of the second compound in this series corresponded to cyclohexanone **IIe** (**Figure 3**, *b*), which could be formed due to the hydrolysis and the subsequent decarboxylation of **II**. Taking into account the results of several experiments conducted under different conditions, it can be concluded that most of the oxidation products decompose on the column during chromatographic separation (the release of individual portions of water and CO_2 at certain intervals indicates such decomposition).

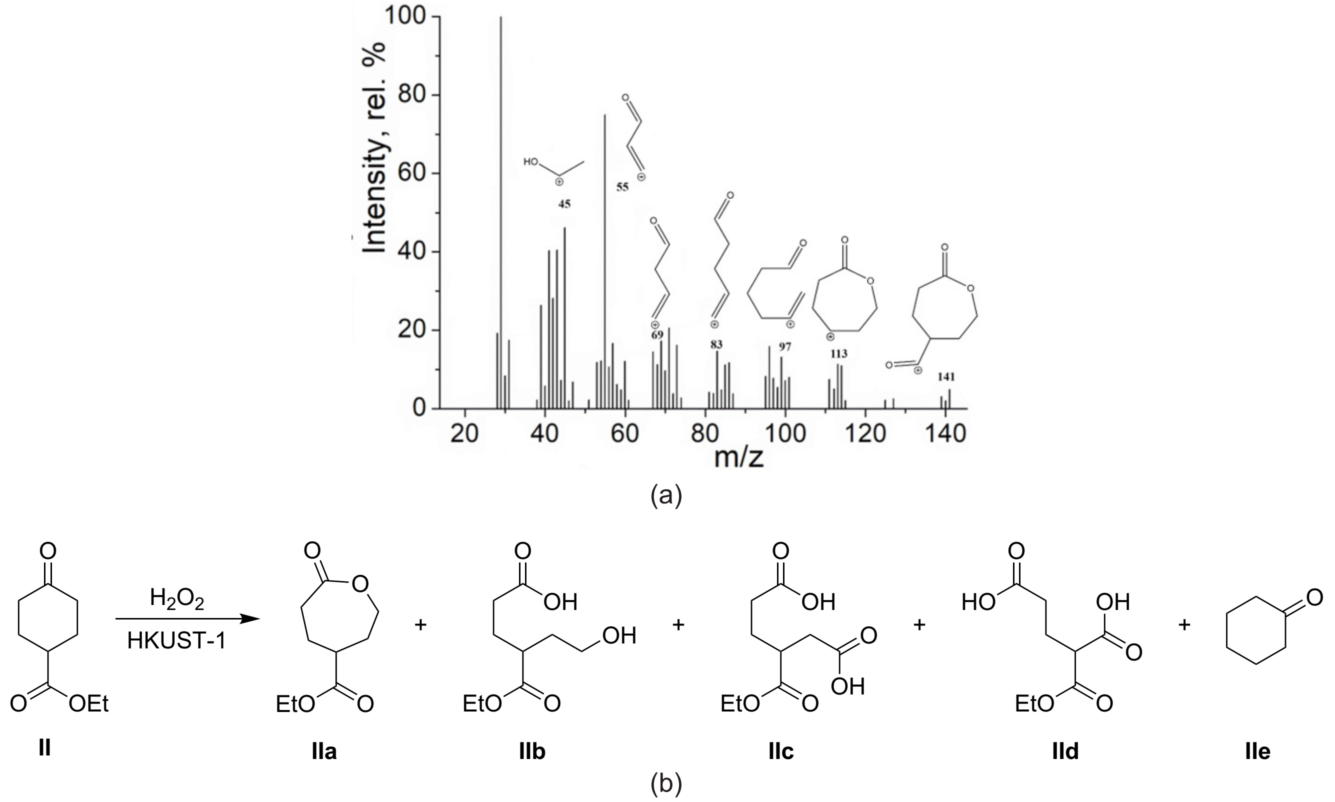


Figure 3. The mass spectrum of the products of the oxidation of **II** by H_2O_2 in the presence of HKUST-1 (**a**) and the scheme showing the oxidation of products **II** (**b**)

At the same time, not all possible products, especially di- and polycarboxylic acids, gave peaks in GCMS due to low volatility, the ability to rearrange and decarboxylation, as well as the tendency to form multicharged ions. Thus, it can be concluded that the oxidation of **II** resulted in the formation of a mixture of products, in which no predominant compounds could be isolated.

In a separate experiment, changes in the composition of the reaction mixture in the process of the oxidation of **II** (0.1 M) with hydrogen peroxide (1.7 M) in the presence of $2 \cdot 10^{-2}$ M of HKUST-1 at 70 °C were monitored. The amount of lactone **IIa** could be estimated by the integral intensity of peak at $\delta = 4.35$ ppm, which corresponded to the CH_2 group near the oxygen atom in the 7-membered lactone cycle, the amount of acid **IId** – by the integral intensity of the signal at $\delta = 3.65$ ppm, which corresponded to the CH group in the malonate fragment. Taking into account that the positions of the signals of the CH_3 and CH_2 groups in the $\text{-}CO_2C_2H_5$ fragment coincided in all oxidation products, the integral intensity of the CH_2 group ($\delta = 4.10$–4.14) could be considered as an indicator of the total content of unreacted **II** and all products of its oxidation, except the products formed upon the hydrolysis of the ester and subsequent reactions. The content of other possible reaction products could not be considered in this calculation since there were no signals in their spectra that did not overlap each other. It can be noted that in the period from 60 to 150 min at 70 °C, the content of lactone **IIa** and acid **IId** remained almost unchanged and was equal to 15 and 20-30%, respectively (**Figure 4**). When the reaction time increased to 180 min, the content of lactone **IIa** and acid **IId** increased to 22 and 50%, respectively (the percentage was calculated relative to the total amount of all compounds in the mixture having the ethyl group). The stable level of concentrations of **IIa** and **IId** in the reaction mixture over a long period of time can be explained by similar values of the rates of the formation of these substances and subsequent oxidation and agreed well with the above conclusion about the formation of several oxidation products.

The formation of lactone **IIa** was a consequence of the Baeyer-Villiger oxidation of the ketone, which took place at the acidic sites of the catalyst [4, 5]. Further oxidation occurred, most likely, by the radical mechanism, and led to a shortening of the hydrocarbon chain [12, 33]. At the same time, it should be noted that the formation of carboxylic acids (such as **IIc** and **IId**) could take place without the formation of lactone **IIa** and the product of its hydrolysis **IIb** as intermediates.

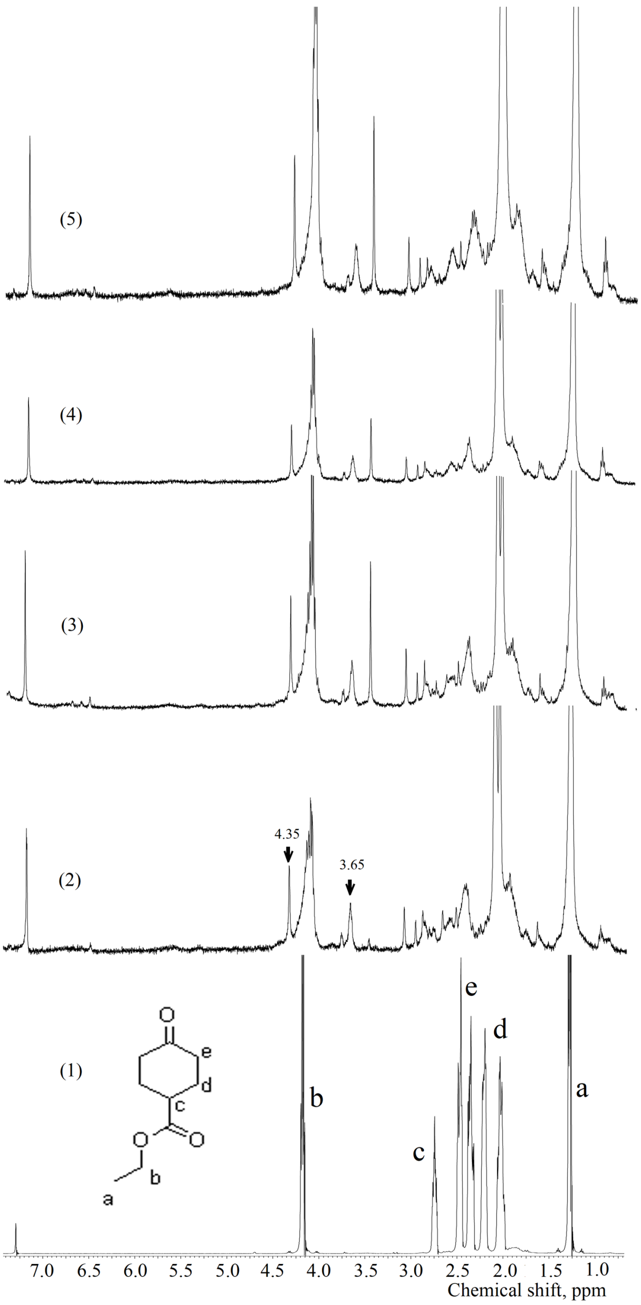


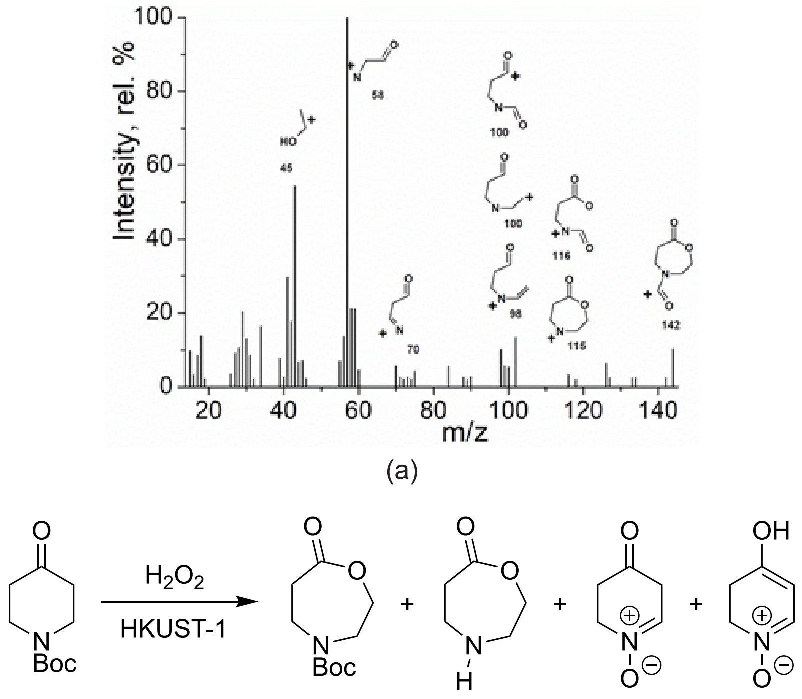
Figure 4. The change of ^{1}H NMR spectra of the reaction mixture in the process of oxidation of **II** (0.1 M) with hydrogen peroxide (1.7 M) in the presence of $2\cdot10^{-2}$ M of HKUST-1 at 70 °C along with the spectrum of the starting compound: (**1**) starting **II**, (**2**) in 60 min, (**3**) in 90 min, (**4**) in 120 min, and (**5**) in 150 min

The reaction of **III** with H_2O_2 in the presence of HKUST-1 under the same conditions as in the case of **II** (0.1 M of ketone, 1.7 M of H_2O_2, $1\cdot10^{-2}$ M of HKUST-1, 24 h at 25 °C) led to the formation of a mixture of products. The DI-mass spectrum of this mixture contained several peaks. Some of them could be assigned to 4-piperidinone and lactone formed upon oxidation of **III** and elimination of the *tert*-butoxycarbonyl group (**Figure 5**, *b*). The NMR spectrum of the reaction mixture contained signals that could be attributed to the starting material, lactone, and products of the subsequent oxidation with cleavage of the cycle, similar to the oxidation of **II**. It was not possible to reliably identify all the signals in the NMR spectrum, but several characteristic features of the spectrum could be noted. Thus, the spectrum of the mixture of the reaction products contained at least four signals of the *tert*-butyl group in the range of δ = 1.44–1.53 ppm instead of one signal of such a group in the starting ketone at δ = 1.45 ppm and the similar group in lactone at δ = 1.53 ppm (calculated value; signal of *tert*-butanol formed upon the hydrolytic cleavage of the Boc group was observed at δ = 1.28 ppm). The increase in the number of signals was an indicator of the formation of at least four compounds containing the unchanged fragment -N–C(=O)–O*t*Bu, upon the oxidation of **III**. A signal at δ = 4.6 ppm could be attributed to the CH_2 group near the O atom in a 7-membered lactone cycle. In addition, there were new signals at δ = 8.01, 7.25 and 5.14 ppm in the spectrum of the reaction mixture, which could be attributed to nitrone **IIIc** and its tautomer **IIId**.

The reaction of **IV** with H_2O_2 in the presence of HKUST-1 under the same conditions led to the formation of a mixture. The DI-mass spectrum of this mixture corresponded to the lactone formed upon the Bayer-Villiger oxidation of **IV** (**Figure 6**). However, the formation of the compounds with a lower molecular weight could not be excluded.

Higher conversions of **II**–**IV** in reactions with H_2O_2 compared to the conversion of **I** may be explained by a higher reactivity of the aliphatic ketones, which is possibly due to steric effects (the presence of a bulk benzene ring near the carbonyl group in aromatic ketones) or differences in the electronic structure of such ketones. A similar dependence of the conversion on the nature of the ketone was observed in the process of oxidation of ketones by H_2O_2 in the presence of tungsten-containing heteropolyacids [34].

The catalytic oxidation of ketones by H_2O_2 can occur by the Baeyer-Villiger mechanism or by the radical mechanism (**Figure 7**). However, a clear dependence on the nature of the catalyst cannot be found. Generally, it can be noted that the use of mild Lewis acids like Sn-, Ge-containing silicates, MoO_3, or complexes of Pt(II) resulted in the Baeyer-Villiger oxidation. The same effect was also found in the case of strong Lewis acids like $AlCl_3$. All catalysts shown on **Figure 7**, which favored radical oxidation, contained redox-active



(a)

III **IIIa** **IIIb** **IIIc** **IIId**

(b)

Figure 5. The mass spectrum of the products of oxidation of **III** by H_2O_2 in the presence of HKUST-1 (a) and the scheme showing products of oxidation of **III** (b)

sites. However, a potentially redox-active catalyst Co(III) salen was found to catalyze the Baeyer-Villiger oxidation (probably, as its redox potential falls out of the suitable range for generation of radicals from H_2O_2) [15]. Notably, the Baeyer-Villiger oxidation can be followed by the radical oxidation [35] in the presence of the same catalyst. The PCPs, studied herein, seem to be able to catalyze the Baeyer-Villiger oxidation, but there are evidences of radical oxidation pathway in the presence of such catalysts.

Generally, soft Lewis acids are considered as the most efficient catalysts for the Bayer-Villiger oxidation [5, 36]. There are examples of the Baeyer-Villiger ketone oxidation catalyzed by coordination compounds of Cu(II) [23, 37, 38] and

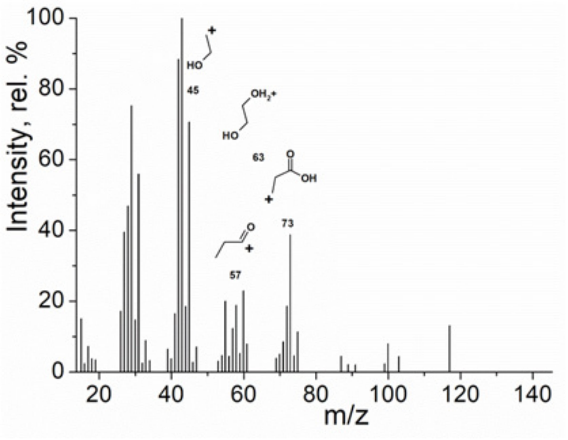


Figure 6. The mass spectrum of the products of oxidation of **IV** by H_2O_2 in the presence of HKUST-1

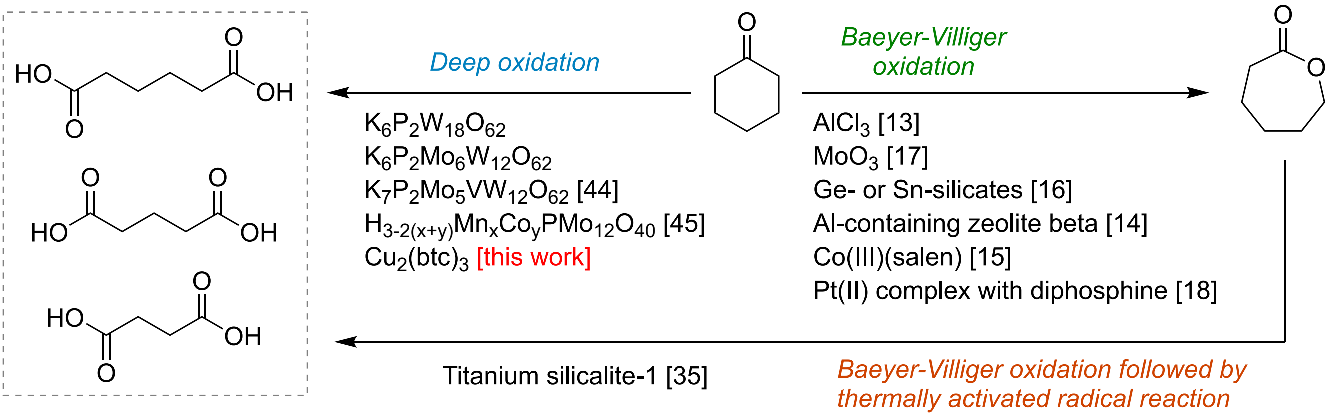


Figure 7. The catalytic oxidation of ketones by H_2O_2 in the presence of different catalysts

Fe(III) by oxygen [39]. $Cu(OTf)_2$ was found to be an efficient catalyst for the Baeyer-Villiger oxidation of cyclic ketones by *m*CPBA [17]. Several Fe- and Cu-containing systems were found to be efficient catalysts of the Baeyer-Villiger oxidation in the O_2/benzaldehyde system, such as Fe–Sn–O catalysts for the oxidation of cyclohexanone to ε-caprolactone [40], iron(III)-containing mesoporous silica (MCM-41) [41], a Cu-SiO_2 catalyst with highly dispersed copper species and various metal valences for the oxidation of cyclohexanone to ε-caprolactone [42], a bifunctional hybrid catalyst originated from copper tetrasulfophthalocyanine (CuPcTs) and hydrotalcite [43]

Conclusions

The oxidation of cyclohexanone analogs with hydrogen peroxide in the presence of a porous coordination polymer HKUST-1 led to the formation of a mixture of products containing the corresponding lactones (formed by the Baeyer-Villiger process) and other compounds formed by a deeper oxidation of the organic compounds with cleavage of the ring and reduction of the hydrocarbon chain length. Unlike aliphatic ketones, α-tetralone underwent almost no conversion in the reaction with H_2O_2 in the presence of HKUST-1, and the oxidation of the same ketone in the presence of $Fe_2(OH)_3$(btc) led to the formation of a number of products with low yields. Among them, 1,4-naphthoquinone was dominant (in contrast to cyclic lactone – the expected Baeyer-Villiger oxidation product). The oxidation of ketones in the presence of the PCPs studied occurred mainly by the radical mechanism, which can be explained by insufficient Lewis acidity of Cu^{2+} and Fe^{3+} ions in the environment of oxygen atoms.

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Information about the authors:
Emir N. Abdullayev, Engineer of the Department of Porous Compounds and Materials, L. V. Pisarzhevsky Institute of Physical Chemistry of the National Academy of Sciences of Ukraine.
Andrii M. Mishura, Leading Engineer of the Department of Free Radicals, L. V. Pisarzhevsky Institute of Physical Chemistry of the National Academy of Sciences of Ukraine.
Ievgenii A. Iermolenko, Ph.D. Student of Institute of Organic Chemistry of the National Academy of Sciences of Ukraine; Chemist, Enamine Ltd.
Anton S. Lytvynenko, Ph.D. in Chemistry, Research Fellow of the Department of Porous Compounds and Materials, L. V. Pisarzhevsky Institute of Physical Chemistry of the National Academy of Sciences of Ukraine; https://orcid.org/0000-0001-5528-9989.
Maksim O. Kolosov, Ph.D. in Chemistry, Deputy Dean for Research, School of Chemistry, V. N. Karazin Kharkiv National University; https://orcid.org/0000-0002-6714-0513.
Olena G. Shvets, Ph.D. in Chemistry, Junior Researcher, School of Chemistry, V. N. Karazin Kharkiv National University; https://orcid.org/0000-0003-4791-2114.
Kostyantyn S. Gavrilenko, Ph.D. in Chemistry, Senior Researcher, Faculty of Chemistry, Taras Shevchenko National University of Kyiv; Manager, Enamine Ltd.; https://orcid.org/0000-0001-7487-6660.
Sergiy V. Kolotilov (*corresponding author*), Corresponding Member of the National Academy of Sciences of Ukraine, Dr.Sci. in Chemistry, Deputy Director for Research, L. V. Pisarzhevsky Institute of Physical Chemistry of the National Academy of Sciences of Ukraine; https://orcid.org/0000-0002-4780-4378; e-mail for correspondence: s.v.kolotilov@gmail.com.