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INNOVATIVE ORGANOCATALYSIS AS PROMISING TREND IN OXIDATION REACTIONS WITH MOLECULAR OXYGEN



The prospects for innovative organocatalytic aerobic oxidation developed by IPOCC of the NAS of Ukraine have been outlined. The practice of oxidizing the hydrocarbons and 5-hydroxymethylfurfural with molecular oxygen under mild conditions has been improved by using the organic compound, N-hydroxyphthalimide, as key catalyst. For the oxidation of coal and substrates whole molecules are capable of keto-enol tautomerism, the use of dimethyl sulfoxide as a solvent is an innovative method that ensures the action of basic catalysts.

Keywords: organocatalysis, aerobic oxidation, hydrocarbons, coal, 5 hydroxymethylfurfural, N hydroxyphthalimide, and dimethyl sulfoxide.

The oxidation of organic substances is widely used in the industry, for organic synthesis. Traditionally, for a long while (especially, for the production of pharmaceutical substances), for oxidizing organic substrates the so called *stoichiometric* oxidants such as manganese dioxide, chromic acid, potassium dichromate, selenium dioxide, and nitric acid have been used. However, the environmental characteristics of these processes (E-factor and efficiency) are extremely poor, and the wastes are toxic.

The first innovative step towards a significant improvement of these processes was the use of oxygen as oxidizer and transition metals as catalysts [1]. The catalytic oxidation is key process for manufacture of dyes, agrochemicals, fragrances, widely used mineral oxygen-containing compounds such as adipic, terephthalic and isophthalic acids; maleic and phthalic anhydrides; phenol; 1,4-butanediol; industrial alcohols and organic peroxides. These catalysts are notable for their relatively high acti-

vity under mild conditions of reaction [2, 3]. In terms of green chemistry and sustainable development, the molecular oxygen is ideal oxidizer due to its natural origin, accessibility, low price, environment friendly properties, and the highest atomic effectiveness among the oxidizers. However, the use of transition metal compounds for the catalysis of oxidation reactions by molecular oxygen, as a rule, is associated with the following problems:

- ✦ Activation of O₂ is not always successful under mild conditions;
- ✦ Necessity of additives for oxidizing the transition metal in the presence of O₂;
- ✦ High chemo-selectivity of processes is not always reachable;
- ✦ Incompliance with principles of green chemistry.

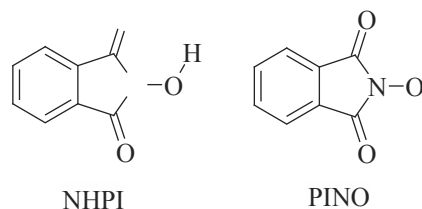
In addition, the sensitivity of metal-organic catalysts to the presence of water that is an oxidation product in many cases complicates the technologies using metal-containing catalysts. High price makes them inefficient, and toxicity of metallic compounds entails additional measures for preventing the environment pollution.

Since the catalytic aerobic oxidation of organic compounds is of paramount importance for the industrial synthesis of oxo-functionalized chemical derivatives in terms of both economic and environmental standpoints, the search of more effective systems for these processes remains an important task, although one could think that these comprehensively studied reactions are not promising for further research. However, this is not the case. Unexpectedly, new prospects open up in the sphere of homogeneous catalysis.

Organic catalysis that is among key directions in modern organic chemistry is an innovative method for these comprehensively studied processes [4]. The L.M. Litvinenko Institute of Physical, Organic and Coal Chemistry of the NAS of Ukraine (IPOCC) has a strong scientific school from the date of its establishment and has accumulated a huge experience in studying the action of organic catalysts in heterolytic reactions [5, 6]. The innovativeness of their application in radical chain oxidation is associated with the fact that it is very difficult to imagine an organic compound that being directly involved in the process where there are many active radicals and oxygen would return unmodified to catalytic cycle and not decay.

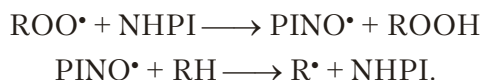
Starting with the mid-1990s, the organic catalysis has been considered a promising strategy for developing methods of organic compound oxidation [7]. The first example of application of organic catalyst to the reactions of organic substrate oxidation by molecular oxygen is N-hydroxyphthalimide (NHPI) that gives phthalimide-N-oxyl radical (PINO) in catalytic cycle.

Unlike almost all metal-containing catalysts that act at the stage of chain initiation by reacting with hydroperoxides (primary oxidation product), oxygen molecule or substrate, the new organic catalyst speeds up the reaction being involved in the chain continuation. This is especially important in the view of the fact that in this case, the selectiveness of process by target product increases, insofar as, usually, the by-products are formed in reactions of chain termination. Their share grows as the initiation rate increases.



The data obtained with the help of Google Scholar (as of 2015.07.18) show that, within 1991–1995, only 4 papers and 1 patent concerning the use of NHPI as catalyst in liquid phase oxidation were published. Since that time, the number of publications was growing rapidly and, in 2014, it reached 200 per year. Starting with 1995, (Ishii, Y. [7, 8]) 972 articles and 153 patents have been issued. The majority of researches have been carried out in Japan, where catalysis was discovered and in China, more than 300 in each country. They are followed the United States, Italy, the Netherlands, and France (more than 100). Romania, Russia, Poland, and Ukraine have numbered over 30 publications and patents, while other countries have only individual works. It should be noted that many researches have been made by international teams.

The IPOCC researches have addressed several key problems related to the strategy of innovation technologies with the use of organic catalysis. One of the most important question concerning NHPI was whether this substance acts as catalyst or as initiator. It was widely discussed in publications (Hermans [9]). The IPOCC studies have showed that the answer depends on both the substrate (RH) and co-catalysts. For the oxidation of unsaturated compounds, including those that do not have activated C-H-bonds, N-hydroxyphthalimide acts as typical initiator [10, 11], whereas for the oxidation on C-H-bonds of alkyl arenes (or alkanes), it is a catalyst [12] accelerating the chain growth by reactions



However, it has been unexpectedly established that NHPI plays one more role in the oxidation of unsaturated compounds. The studies of the structure of macromolecules created during polymerization

of methyl methacrylate have showed that in addition to the initiation, NHPI regulates the structure of growing macro-chain, i.e. under conditions of methyl methacrylate polymerization reaction, complexes are formed between NHPI (or its derivatives) and growing active nucleus of macro-radical that creates conditions for building syndiotactic macromolecules containing more than 80% syndiotactic diads [13]. The syndiotactic polymers are notable for higher strength, density, and melting temperature.

Among new applications of N-hydroxyphthalimide, there is its use for obtaining oxygen-containing compounds by oxidation of substrates made of biomass. A gradual exhaustion of fossil minerals as well as an increase in the cost of their extraction stimulate innovative R&Ds aimed at using renewable resources of biomass for producing chemical substances. To this end, the optimal component of inedible biomass is cellulose. The essence of innovation is the design of catalytic processes for selective transformation of cellulose into platform compounds under mild conditions with further production of valuable chemical substances on their basis. Taking into account the above mentioned fact, the oxidation of 5-hydroxymethylfurfural (HMF), a basic platform compound in the cellulose transformation, into 2,5 furandicarboxylic acid (FDCA), a multifunctional structural element and promising alternative option to terephthalic acid, a base of petroleum origin, is of profound importance. This is one of the most attractive reactions for designing effective chemical processes based on renewable resources.

The IPOCC has been carrying out researches in two directions: the process of obtaining HMF and reactions of its oxidation by molecular oxygen. In order to improve the existing not very effective methods for obtaining 5 hydroxymethylfurfural, the transformations of monosaccharides and disaccharides as models of renewable vegetable raw material have been studied. Conditions for material increase in its yield have been identified.

For the first time, a set of catalysts of N hydroxyphthalimide type has been studied in 5 hydroxymethylfurfural oxidation reactions. The role of

various systems based on these catalysts in the mentioned reactions has been researched as well. These systems have been showed to be effective for catalytic oxidation of HMF by molecular oxygen. 2,5 diformilfuran, a promising oxygen-containing monomer has been established to be the basic product of 5 hydroxymethylfurfural aerobic oxidation catalyzed by N hydroxyphthalimide [14]. As a result, an effective method for obtaining 2,5 diformilfuran using N hydroxyphthalimide-Cu(NO₃)₂ catalytic system has been designed [15]. 5 hydroxymethylfurfural is oxidized by molecular oxygen under very mild conditions: at a temperature 50 °C and at an oxygen pressure of 1 atmosphere, i.e. as compared with the existing methods, the researchers have managed to decrease temperature and pressure, to reduce harmful wastes and costs, and to increase yield of 2,5-diformilfuran.

The use of widespread organic solvent, dimethyl sulfoxide (DMSO), in aerobic oxidation processes is an innovative approach. The effect of DMSO is so strong that it can be considered a catalyst. An especially strong manifestation is reported for the co-catalytic reactions with basic compounds, in particular, the amines [16], and for the oxidation of compounds with C–H-bond neighboring to carbonyl group or ready to keto-enol tautomerism (for example, in anthrone). In other solvents, the amines do not show catalytic effect. In some cases, they act as inhibitors.

A catalytic system based on DMSO has been created. Under mild conditions, it enables obtaining such an important monomer as *d,l* camphoric acid through oxidation by molecular oxygen [17]. Previously, this acid was obtained through oxidation of camphor by strong nitric acid with large emission of harmful gases and aggressive environment corroding the equipment.

An innovative method for oxidizing coal by molecular oxygen in high-base environments has been designed at the IPOCC [18, 19]. It applies for oxidizing various types of coal, except for the anthracites. The study of kinetics of oxidation of different types of coal by molecular oxygen in the presence of alkali has showed that under given conditions, the

low metamorphic types of coal are oxidized most effectively, as a result of presence of groups with high C–H *pH* in the coal structure [20]. DMSO as organic solvent plays an important role in this process. The reaction runs under mild conditions (at an oxygen pressure less than 1 atmosphere, at a temperature of 60–80 °C). In this case, oxidation leads to the formation of humic acids as basic products of reaction. The highest initial oxidation rate has been reported for gaseous humate (*Gh*) that was used for the study. The coal (after removal of humic acids) was repeatedly oxidized by oxygen in DMSO and in alkaline environment during 150 minutes. The humic acids were extracted from oxidized coal, and the number of COOH groups was determined. 0.80 g humic acids were obtained from 1 g coal; the analysis of their content was as follows (%): C – 74.30; H – 5.67; S – 1.53; N – traces.

CONCLUSIONS

The innovative application of organic catalysts (or solvents) for speeding up the reactions of obtaining oxygen-containing products through oxidation by molecular oxygen has good prospects in both industry and in chemical synthesis practice.

1. In the case of oxidation through C–H bonds (aerobic oxidation of alkanes, alkyl arenes, oxygen-containing compounds of various structure), the use of hydroxyl-containing catalysts enables reactions under mild conditions, with higher conversion and selectivity as compared with the conventional methods. This innovative approach is very promising for obtaining many important oxygen-containing compounds. For instance, cumene is oxidized by molecular oxygen in order to obtain cumene hydroperoxide (world production reaches 6.7×10^6 t/annually), acetone (5×10^6 t/annually), phenol (8.3×10^6 t/annually), α -methylstyrol, and acetophenone. This list can be extended with transformation of cyclohexane into adipic acid (6×10^6 t/annually) the production of which has been launched at several plants in Ukraine. Direct oxidation by molecular oxygen would be very useful for the chemical industry, in particular, in the view of the fact that this process is much more en-

vironment friendly that the conventional techniques for production of adipic acid, which is associated with emission of harmful nitrogen oxides, as a result of oxidation by nitric acid. Oxidation of hydrocarbons, such as toluene, *n*-xylene, and propylene, by molecular oxygen is a very important industrial process enabling to obtain benzoic (3×10^6 t/annually) and terephthalic acids (11.4×10^6 t/annually), dimethyl terephthalate (4.1×10^6 t/annually), and propylene oxide (4×10^6 t/annually) from petroleum raw materials [21];

2. The catalytic systems based on dimethyl sulfoxide are promising if the substrate to be oxidized is a compound having C–H-bond activated by carbonyl group or C–H-ready for keto-enol tautomerism [22, 23] and the reaction is targeted towards obtaining bicarboxylic (or polycarboxylic) acids or quinones. Dimethyl sulfoxide ensures effective action of base catalysts in oxidation by molecular oxygen.

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ІННОВАЦІЙНИЙ ОРГАНOKАТАЛІЗ —
ПЕРСПЕКТИВНИЙ НАПРЯМОК У РЕАКЦІЯХ
РІДИННОФАЗНОГО OKИСНЕННЯ
МОЛЕКУЛЯРНИМ KИСНЕМ

Показано перспективність інноваційного органокаталізу в аеробному окисненні та отриманні в Інституті фізико-органічної хімії і вуглехімії ім. Л.М. Литвиненка НАН України досягнення в цій області. Важливим нововведенням у практику окиснення молекулярним киснем вуглеводнів і 5 гідроксиметилфурфурулу в м'яких умовах стало використання органічної сполуки N гідроксифталіміду як ключового каталізатора. У випадку окиснення вугілля і субстратів, у молекулах яких є групи, здатні до кето-енольної таутомерії, інноваційним є використання диметилсульфоксиду як розчинника, що забезпечує дію основних каталізаторів.

Ключові слова: органокаталіз, аеробне окиснення, вуглеводні, вугілля, 5оксиметилфурфурулу, диметилсульфоксид.

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ИННОВАЦИОННЫЙ ОРГАНOKАТАЛІЗ —
ПЕРСПЕКТИВНОЕ НАПРАВЛЕНИЕ
В РЕАКЦИЯХ ЖИДКОФАЗНОГО OKИСЛЕНИЯ
МОЛЕКУЛЯРНЫМ KИСЛОРОДОМ

Показаны перспективность инновационного органокатализа в аэробном окиснении и полученные в Институте физико-органической химии и углехимии им. Л.М. Литвиненко НАН Украины достижения в этой области. Важным нововведением в практику окисления молекулярным кислородом углеводородов и 5-гидроксиметилфурфурула в благоприятных условиях стало использование в качестве катализатора органического соединения N-гидроксифталимида. В случае окисления угля и субстратов, в молекулах которых имеются группы, способные к кето-енольной таутомерии, инновационным является использование диметилсульфоксида в качестве растворителя, обеспечивающего действие основных катализаторов.

Ключевые слова: органокатализ, аэробное окисление, углеводороды, уголь, 5-оксиметилфурфурулу, диметилсульфоксид.

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