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ТОНКИЕ ХИМИЧЕСКИЕ ТЕХНОЛОГИИ

Fine Chemical Technologies

- Theoretical Bases of Chemical Technology
- Chemistry and Technology of Organic Substances
- Chemistry and Technology of Medicinal Compounds and Biologically Active Substances
- Biochemistry and Biotechnology
- Synthesis and Processing of Polymers and Polymeric Composites
- Chemistry and Technology of Inorganic Materials
- Analytical Methods in Chemistry and Chemical Technology
- Mathematical Methods and Information Systems in Chemical Technology

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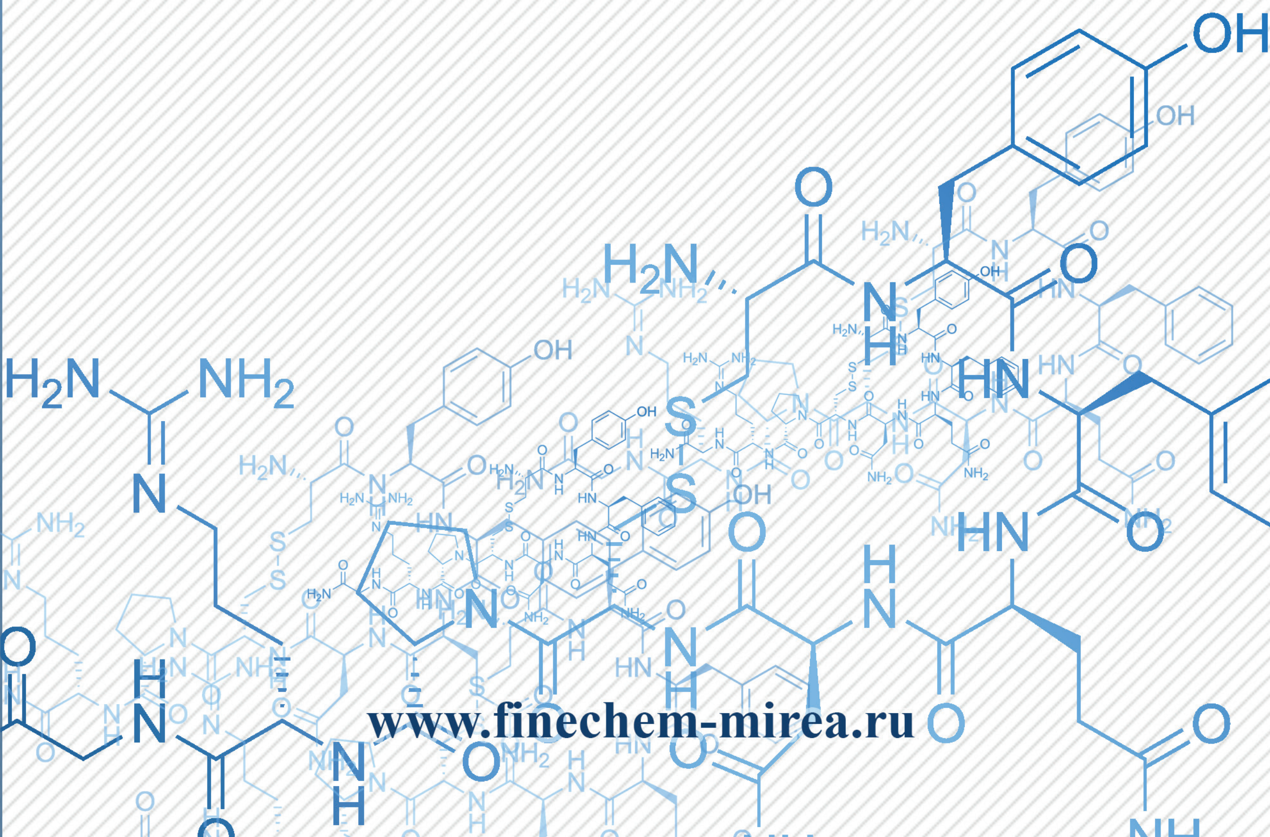

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Phone: +7 (499) 600-80-80 (#31288)
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119571, Москва, пр. Вернадского, 86, оф. Л-119.
Тел.: +7 (499) 600-80-80 (#31288)
E-mail: *seredina@mirea.ru*

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ivanov_i@mirea.ru.

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aiv@ibch.ru.

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aziz@ineos.ac.ru.

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Scopus Author ID 7101971167, ResearcherID AAF-8122-2019
https://orcid.org/0000-0003-4778-5872
blokhin@bsu.by.

Верёвкин Сергей Петрович – д.т.н., профессор Университета г. Росток, Росток, Германия.
Scopus Author ID 7006607848, ResearcherID G-3243-2011,
https://orcid.org/0000-0002-0957-5594,
sergey.verevkin@uni-rostock.de.

Жижин Константин Юрьевич – член-корр. Российской академии наук (РАН), д.х.н., профессор, Институт общей и неорганической химии им. Н.С. Курнакова РАН, Москва, Российская Федерация.
Scopus Author ID 6701495620, ResearcherID C-5681-2013,
http://orcid.org/0000-0002-4475-124X,
kyuzhizhin@igic.ras.ru.

Иванов Игорь Владимирович – д.х.н., профессор, МИРЭА – Российский технологический университет, Москва, Российская Федерация.
Scopus Author ID 34770109800, ResearcherID I-5606-2016,
http://orcid.org/0000-0003-0543-2067,
ivanov_i@mirea.ru.

Кардона Карлос Ариэль – PhD, профессор Национального университета Колумбии, Манизалес, Колумбия.
Scopus Author ID 7004278560,
http://orcid.org/0000-0002-0237-2313,
ccardonaal@unal.edu.co.

Койфман Оскар Иосифович – академик РАН, д.х.н., профессор, президент Ивановского государственного химико-технологического университета, Иваново, Российская Федерация.
Scopus Author ID 6602070468, ResearcherID R-1020-2016,
http://orcid.org/0000-0002-1764-0819,
president@isuct.ru.

Крутько Эльвира Тихоновна – д.т.н., профессор Белорусского государственного технологического университета, Минск, Беларусь.
Scopus Author ID 6602297257,
ela_krutko@mail.ru.

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aiv@ibch.ru.

Музафаров Азиз Мансурович – академик РАН, д.х.н., профессор, Институт элементоорганических соединений им. А.Н. Несмеянова РАН, Москва, Российская Федерация.
Scopus Author ID 7004472780, ResearcherID G-1644-2011,
https://orcid.org/0000-0002-3050-3253,
aziz@ineos.ac.ru.

Ivan A. Novakov – Academician at the RAS,
Dr. Sci. (Chem.), Professor, President of the Volgograd
State Technical University, Volgograd,
Russian Federation.
Scopus Author ID 7003436556, ResearcherID I-4668-2015,
http://orcid.org/0000-0002-0980-6591,
president@vstu.ru.

Alexander N. Ozerin – Corresponding Member of the RAS,
Dr. Sci. (Chem.), Professor, Enikolopov Institute
of Synthetic Polymeric Materials of the RAS,
Moscow, Russian Federation.
Scopus Author ID 7006188944, ResearcherID J-1866-2018,
https://orcid.org/0000-0001-7505-6090,
ozerin@ispm.ru.

Tapani A. Pakkanen – PhD, Professor, Department
of Chemistry, University of Eastern Finland, Joensuu,
Finland.
Scopus Author ID 7102310323,
tapani.pakkanen@uef.fi.

Armando J.L. Pombeiro – Academician at the Academy
of Sciences of Lisbon, PhD, Professor, President of the Center
for Structural Chemistry of the Higher Technical Institute
of the University of Lisbon, Lisbon, Portugal.
Scopus Author ID 7006067269, ResearcherID I-5945-2012,
https://orcid.org/0000-0001-8323-888X,
pombeiro@ist.utl.pt.

Dmitrii V. Pyshnyi – Corresponding Member of the RAS,
Dr. Sci. (Chem.), Professor, Institute of Chemical Biologyand
Fundamental Medicine, Siberian Branch of the RAS,
Novosibirsk, Russian Federation.
Scopus Author ID 7006677629, ResearcherID F-4729-2013,
https://orcid.org/0000-0002-2587-3719,
pyshnyi@niboch.nsc.ru.

Alexander S. Sigov – Academician at the RAS,
Dr. Sci. (Phys. and Math.), Professor, President
of MIREA – Russian Technological University, Moscow,
Russian Federation.
Scopus Author ID 35557510600, ResearcherID L-4103-2017,
sigov@mirea.ru.

Alexander M. Toikka – Dr. Sci. (Chem.), Professor,
Institute of Chemistry, Saint Petersburg State University,
St. Petersburg, Russian Federation.
Scopus Author ID 6603464176, ResearcherI D A-5698-2010,
http://orcid.org/0000-0002-1863-5528,
a.toikka@spbu.ru.

Andrzej W. Trochimczuk – Dr. Sci. (Chem.),
Professor, Faculty of Chemistry, Wrocław University
of Science and Technology, Wrocław, Poland.
Scopus Author ID 7003604847,
andrzej.trochimczuk@pwr.edu.pl.

Aslan Yu. Tsivadze – Academician at the RAS,
Dr. Sci. (Chem.), Professor, A.N. Frumkin Institute
of Physical Chemistry and Electrochemistry of the RAS,
Moscow, Russian Federation.
Scopus Author ID 7004245066, ResearcherID G-7422-2014,
tsiv@phyche.ac.ru.

Новаков Иван Александрович – академик РАН,
д.х.н., профессор, президент Волгоградского
государственного технического университета, Волгоград,
Российская Федерация.
Scopus Author ID 7003436556, ResearcherID I-4668-2015,
http://orcid.org/0000-0002-0980-6591,
president@vstu.ru.

Озерин Александр Никифорович – член-корр. РАН,
д.х.н., профессор, Институт синтетических
полимерных материалов им. Н.С. Ениколопова РАН,
Москва, Российская Федерация.
Scopus Author ID 7006188944, ResearcherID J-1866-2018,
https://orcid.org/0000-0001-7505-6090,
ozerin@ispm.ru.

Пакканен Тапани – PhD, профессор, Департамент
химии, Университет Восточной Финляндии, Йоенсуу,
Финляндия.
Scopus Author ID 7102310323,
tapani.pakkanen@uef.fi.

Помбейро Армандо – академик Академии наук
Лиссабона, PhD, профессор, президент Центра
структурной химии Высшего технического института
Университета Лиссабона, Португалия.
Scopus Author ID 7006067269, ResearcherID I-5945-2012,
https://orcid.org/0000-0001-8323-888X,
pombeiro@ist.utl.pt.

Пышный Дмитрий Владимирович – член-корр.РАН,
д.х.н., профессор, Институт химической биологии
и фундаментальной медицины Сибирского отделения РАН,
Новосибирск, Российская Федерация.
Scopus Author ID 7006677629, ResearcherID F-4729-2013,
https://orcid.org/0000-0002-2587-3719,
pyshnyi@niboch.nsc.ru.

Сигов Александр Сергеевич – академик РАН,
д.ф.-м.н., профессор, президент МИРЭА – Российского
технологического университета, Москва,
Российская Федерация.
Scopus Author ID 35557510600, ResearcherID L-4103-2017,
sigov@mirea.ru.

Тойкка Александр Матвеевич – д.х.н., профессор,
Институт химии, Санкт-Петербургский государственный
университет, Санкт-Петербург, Российская Федерация.
Scopus Author ID 6603464176, Researcher ID A-5698-2010,
http://orcid.org/0000-0002-1863-5528,
a.toikka@spbu.ru.

Трохимчук Анджей – д.х.н., профессор,
Химический факультет Вроцлавского политехнического
университета, Вроцлав, Польша.
Scopus Author ID 7003604847,
andrzej.trochimczuk@pwr.edu.pl.

Цивадзе Аслан Юсупович – академик РАН,
д.х.н., профессор, Институт физической химии
и электрохимии им. А.Н. Фрумкина РАН, Москва,
Российская Федерация.
Scopus Author ID 7004245066, ResearcherID G-7422-2014,
tsiv@phyche.ac.ru.

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REVIEW ARTICLE

Department of Physical Chemistry in M.V. Lomonosov Institute of Fine Chemical Technologies at the RTU MIREA: From the beginning to the present

To the 120th anniversary of the Department

Alexandra V. Grashkina, Vitaly R. Flid✉

MIREA – Russian Technological University (M.B. Lomonosov Institute of Fine Chemical Technologies), Moscow, 119571 Russia
✉*Corresponding author, e-mail: vitaly-flid@yandex.ru*

Abstract

Objectives. *To review the prerequisites for the origin of physical chemistry at the turn of the 19th–20th centuries and to evaluate the contribution of the Department of Physical Chemistry at the M.V. Lomonosov Institute of Fine Chemical Technologies in the development of the main areas of chemical science.*
Results. *The study considers the historical retrospective of the appearance of the Department of Physical Chemistry at the beginning of the 20th century. The main areas of scientific activity over the past 120 years are shown.*
Conclusions. *The Department of Physical Chemistry has made a significant contribution to the formation of physical and chemical knowledge among specialists in wide areas of chemical science and chemical technology. The Department of Physical Chemistry through its pedagogical and scientific activities maintains and expands the areas development, based on the unity of theory and practice, established by its founders. The decisive role of fundamental research in the development of new technologies is also shown.*

Keywords: *physical chemistry, thermodynamics, kinetics, catalysis, molecular theory and nature of chemical bonds, N.D. Zelinsky, S.G. Krapivin, Ya.K. Syrkin*

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ОБЗОРНАЯ СТАТЬЯ

Кафедра физической химии Института тонких химических технологий имени М.В. Ломоносова РТУ МИРЭА: От истоков до наших дней

К 120-летию кафедры

А.В. Грашкина, В.Р. Флид✉

МИРЭА – Российский технологический университет (Институт тонких химических технологий им. М.В. Ломоносова), Москва, 119571 Россия
✉*Автор для переписки, e-mail: vitaly-flid@yandex.ru*

Аннотация

Цели. *Рассмотрение предпосылок возникновения физико-химического направления на рубеже XIX–XX веков. Оценка вклада кафедры физической химии им. Я.К. Сыркина Института тонких химических технологий имени М.В. Ломоносова в развитие основных направлений химической науки.*
Результаты. *Освещена историческая ретроспектива возникновения кафедры физической химии в начале XX века. Приведены основные направления ее функционирования на протяжении 120 лет.*
Выводы. *Кафедра внесла значительный вклад в формирование физико-химического мышления специалистов в различных направлениях химической науки и химических технологий. На протяжении всей своей педагогической и научной деятельности кафедра сохраняет и преумножает вектор развития, базирующийся на единстве теории и практики, заложенный ее основателями. Показана определяющая роль фундаментальных исследований при разработке новых технологий.*

Ключевые слова: *физическая химия, термодинамика, кинетика, катализ, теория строения молекул и природа химической связи, Н.Д. Зелинский, С.Г. Крапивин, Я.К. Сыркин*

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INTRODUCTION

The establishment of the Physical Chemistry Laboratory at the Moscow Higher Women's Courses (MHWC) coincided with the global tectonic shifts in world history. The same global changes are characteristic of the development of science at the turn of the 19th and 20th centuries when new areas of research were established based on the outstanding achievements in physics, chemistry, biology, and other natural sciences.

Physical chemistry is an advanced, continuously, and intensively developing field of chemical sciences, now taught as an independent discipline in the specialized departments of many higher educational institutions in Russia and the world. In 2023, one of the oldest in Russia departments, the Department of Physical Chemistry of the M.V. Lomonosov Institute of Fine Chemical Technologies (IFCT), celebrates its 120th anniversary.

HOW IT ALL STARTED. THE FIRST PHYSICAL CHEMISTRY LABORATORIES

It is interesting that the formation of physical chemistry as a branch of science and as a subject of teaching went on in parallel for several centuries. The first separate course of lectures on this discipline was presented in 1752–1753 to students of the Academic University in St. Petersburg by Mikhail Vasilievich Lomonosov. He was convinced that chemistry and physics would develop more successfully only as a result of "mutual assistance" [1–4].

Although M.V. Lomonosov considered physical chemistry to be the leading direction in the development of chemical science, he did not establish a separate department or a specialized laboratory for systematic research in this field. This was natural. Lomonosov's scientific thinking was far ahead of his time: 18th century chemistry and physics possessed neither theoretical nor experimental data upon which physical chemistry could develop independently [5].

Only 100 years later, in the second half of the 19th century, physical chemistry was established as its own scientific field and academic discipline. The development of this branch of chemistry at that time and the identification of its tasks were primarily associated with the names of Wilhelm Friedrich Ostwald and Jacobus Henricus van't Hoff, who worked in Germany.

In 1871, the world's first department of physical chemistry was established at the University of Leipzig. The head of the new department was the physicist Gustav Heinrich Wiedemann who took up the post in the same year[1] [6]. The cofounder of the department and its second head (from 1887) was Ostwald. In 1885, he gave a separate course on physical chemistry at the University of Leipzig [6–8]. In 1898, the first independent Institute of Physical and Theoretical Chemistry in Europe and the world was opened on the basis of the University of Leipzig, and Ostwald became the first director of the new institution [9].

The second center for the development of physical chemistry was the University of Berlin, where in 1878 a specialized department was founded.[2] Particularly intensive research in physical chemistry began here in 1896, when J.H. van't Hoff started working at the university. In 1901, he was awarded the first Nobel Prize in Chemistry for the development of the theory of solutions [6].

Later, at the beginning of the 20th century, physical chemistry departments and laboratories began to appear in other European countries.

In Russia, the development of physical chemistry was more rapid. The creation of this scientific discipline was directly connected with the name of the great Russian scientist andencyclopedist M.V. Lomonosov, who worked at the Academic University—the predecessor of St. Petersburg State University. However, although the history of physical chemistry in this educational institution began at the very moment of its foundation, it was not until 1914 when a specialized department was established.[3]

In the second half of the 19th century, physical chemistry began to be taught in a number of Russian universities, for example in Kazan and Moscow, but without separate departments and laboratories [2, 10].

The eminent Russian physical chemist, Ivan Alekseevich Kablukov, had been lecturing on physical chemistry at the Chemical Department of the Faculty of Physics and Mathematics at the Moscow University, since 1886. From 1921, I.A. Kablukov was appointed as the head of the new Laboratory of Inorganic and Physical Chemistry. In 1925, the Physical Chemistry Laboratory was separated from the Inorganic Chemistry Laboratory and Professor Evgeny Ivanovich Shpitalsky[4] was appointed its head. In 1929, the independent Department of Physical Chemistry was established simultaneously with the formation of the Faculty of Chemistry of the Moscow State University. This is now considered the official year of birth of the Department of Physical Chemistry of the Moscow State University [11, 12].

One of the oldest independent departments of physical chemistry in Russia is that of the St. Petersburg State Electrotechnical University.

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[1] Universität Leipzig: Geschichte. URL: https://www.chemie.uni-leipzig.de/en/faculty/history. Accessed February 25, 2023.

[2] Humboldt-Universität zu Berlin. Geschichte des Instituts für Chemie. URL: https://www.chemie.hu-berlin.de/en/department-en/geschichte. Accessed February 25, 2023.

[3] From the history of the Institute of Chemistry of St. Petersburg State University. Department of Physical Chemistry. Updated on March 21, 2017. URL: https://chem.spbu.ru/phys/42-sectiondepartment/phischem/1971-istoriya-kafedry.html. Accessed February 25, 2023.

[4] Pentin Yu.A. About the Department of Physical Chemistry (Chemical Faculty of Moscow State University and its departments (history and current state)). URL: https://www.chem.msu.su/rus/teaching/zorkii/12(pentin).html. Accessed April 14, 2023.

In 1891, Professor Aleksandr Aleksandrovich Krakau founded the Department of Chemistry at the Electrotechnical Institute of Emperor Alexander III. Here, special courses in electrochemistry and physical chemistry were taught in addition to lectures on inorganic and analytical chemistry. In 1906, the Electrochemistry Department was created at the Institute. It was later to become the Electrochemistry Faculty, comprising the Departments of Inorganic Chemistry, Theoretical and Applied Electrochemistry, and a separate Department of Physical Chemistry.[5]

At the same time, physical chemistry was successfully developed at the Empress Catherine II Mining Institute (now St. Petersburg Mining University) This educational institution was founded in 1773 [13] and in 1774 it began offering chemical classes and laboratories for the analysis of mineral raw materials. An independent course in physical chemistry and a separate department appeared at the Institute in 1908. The first professor in the Department of Physical Chemistry (1908–1919) was Peter Petrovich von Weymarn, one of the founders of colloidal chemistry.[6]

AT THE ORIGINS OF THE DEPARTMENT OF PHYSICAL CHEMISTRY IN IFCT. THE APPEARANCE OF THE LABORATORY OF PHYSICAL CHEMISTRY AT THE MHWC

N.D. Zelinsky and S.G. Krapivin

The history of the IFCT dates back to the MHWC established in 1900 by Vladimir Ivanovich Guerrier [14–18], where a few years later the teaching of physical chemistry began in the format of a separate educational cycle. Thus, the Department of Physical Chemistry, now bearing the name of Ya.K. Syrkin, can be considered the oldest in Russia.

In this section, we will focus in more detail on little-known archival materials being published for the first time.

The study of chemistry was provided at the Courses of the Physics and Mathematics Faculty by the 1900 “Regulations on the MHWC”. The leading chemists of the time, Alexander Nikolaevich Reformatsky and later Nikolai Dmitrievich Zelinsky, were invited to establish laboratories and teach classes, introducing students to the basics of general, inorganic, and organic chemistry. It soon became clear, however, that the initial scope of the course was insufficient to cover all the problems of the rapidly developing chemical sciences.

In the 1903–1904 academic year at the initiative of N.D. Zelinsky, the future academician, the study of a new discipline—physical chemistry—was included in the curriculum of the IV course at the Mathematical and Natural Departments of the Faculty of Physics and Mathematics of Moscow State University (Fig. 1). Sergey Gavrilovich Krapivin, a private Associate Professor at Moscow State University, was invited to teach this subject (Fig. 2).

Although at that time the MHWC provided students with an education of almost university level, the Courses did not have university status or the appropriate organizational structure [16–18]. The teaching of scientific subjects was carried out in laboratories, the directors of which usually gave lectures, conducted practical classes, and provided comprehensive support for the educational process, i.e., the laboratory performed functions similar to those of a university department.

Thus, just as the Lomonosov IFCT became the successor of MHWC [14, 15], so did the Ya.K. Syrkin Department of Physical Chemistry, which became the successor of the Laboratory of Physical Chemistry and Quantitative Analysis, the first head of which was S.G. Krapivin. The outstanding scientist N.D. Zelinsky (1861–1953) was the initiator and ideological inspirer of the

Fig. 1. N.D. Zelinsky[7]
(photo from the beginning of 1900s).

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[5] V.I. Ulyanov (Lenin) St. Petersburg State Electrotechnical University LETI. History of the Department of Physical Chemistry. URL: https://etu.ru/ru/fakultety/ifio/sostav-instituta/kafedra-fizicheskoy-himii/istoriya-kafedry. Accessed April 14, 2023.

[6] St. Petersburg Mining University. History of the Department of Physical Chemistry. URL: https://spmi.ru/istoriya-kafedry-fizicheskoy-khimii. Accessed April 14, 2023.

[7] N.D. Zelinsky. URL: https://permneft-portal.ru/upload/medialibrary/a58/a58de474fe619089f4e9ec3450405840.jpg. Accessed April 14, 2023.

Fig. 2. S.G. Krapivin[8]
(photo of 1925).

creation of such a laboratory. He was already world-renowned in those years. In 1901, N.D. Zelinsky established a laboratory of organic chemistry at the Department of Chemistry, which he headed until 1911. However, his interests also extended to other rapidly developing areas of science and technology, far beyond the boundaries of traditional organic synthesis. In fact, N.D. Zelinsky was one of the founders of organic catalysis, petrochemistry, and adsorption. He foresaw and was well aware of the timeliness of the organization of the physicochemical direction in the MHWC and the training of specialists in this direction (Figs. 3–5).

S.G. Krapivin (1868–1927) was an outstanding individual. In 1889, he graduated with honors from Novorossiysk University in Odessa. While still a student, he began scientific research in the field of physical chemistry under the guidance of N.D. Zelinsky, who at that time was a private lecturer at the University of Novorossiysk [19] (Fig. 6).

In order to deepen his theoretical knowledge and improve his practical skills, in 1890–1892 Sergey Gavrilovich went to Germany to study in the laboratories of Nernst, Ostwald, and van't Hoff. Upon his return to Russia, Krapivin passed his Master's examination which allowed him to teach at the university. In 1896, he moved to Moscow at the invitation of N.D. Zelinsky where he worked as a laboratory assistant and private lecturer in the organic chemistry laboratory of Moscow University [20].

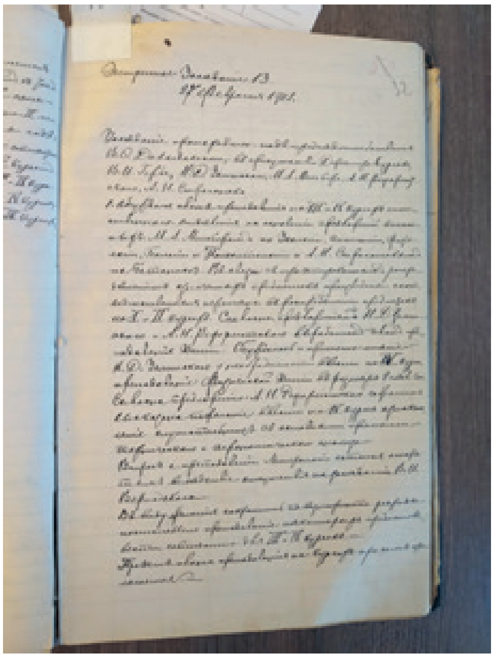

Fig. 3. A page of the protocol of the February 27, 1902 emergency meeting of teachers of the Physico-Chemical Institute of the MHWC with a proposal by N.D. Zelinsky to introduce the teaching of physical chemistry in the 4th year of the Natural Department. Central Archive of Moscow. F. 363. In. 1. N. 6.

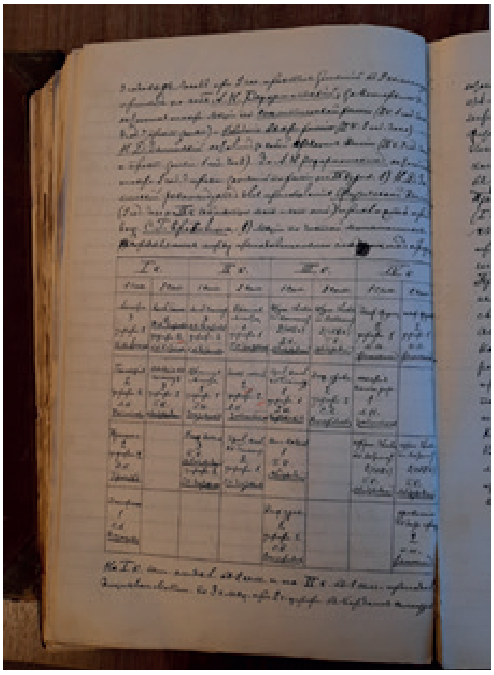

Fig. 4. A page of the protocol of the meeting 15.04.1903 at which N.D. Zelinsky proposes to invite S.G. Krapivin as a teacher of physical chemistry. Central Archive of Moscow. F. 363. In. 1. N. 8.

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[8] S.G. Krapivin. URL: http://encyclopedia.tversu.ru/index.php?title=Krapivin,_sergey_gavrilovich. Accessed April 14, 2023

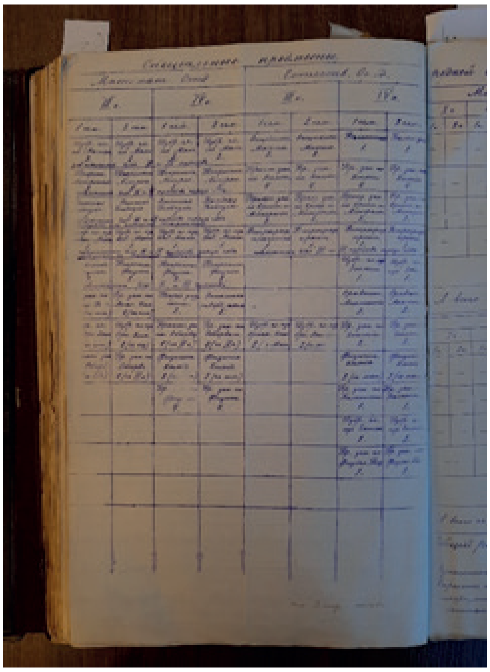


Fig. 5. Draft of a new teaching plan at the Mathematical and Natural Departments of the MHWC (Explanatory note to the draft change in the teaching plan, meeting of the Faculty of Physics and Mathematics on 08.09.1903). The decision to open in the 4th year and introduce the teaching of physical chemistry from the 1903–1904 academic year among the special subjects in both departments (on 3 sheets). Central Archive of Moscow. F. 363. In. 1. N. 8.

In 1903, S.G. Krapivin began to teach at the MHWC. At the same time, he was given the opportunity to set up his own laboratory. The pedagogical and scientific activity of S.G. Krapivin was very fruitful during his management of the Laboratory of Physical Chemistry and Quantitative Analysis of the MHWC. This was despite the heavy administrative burden associated with the purchase of the necessary equipment and reagents, recruitment, and participation in the work of the Chemical Commission of the Faculty. In the space of 15 years, he published a number of basic and applied works, textbooks, and translations of foreign works (Figs. 7 and 8).

S.G. Krapivin's scientific interests during this period were connected with the study of the effect of neutral salts present in solutions on the rate of chemical reactions, and determining electric conductivity of salt solutions in methanol. He also continued his research in organic chemistry which he had commenced at the Moscow State University. He applied the condensation reaction in the presence of aluminum chloride to unsaturated hydrocarbons, obtaining a number α,β of unsaturated ketones (Darzens–Krapivin reaction). The scientific achievements of S.G. Krapivin also include the development of a method for the determination of ammonia in waste water [20–22].

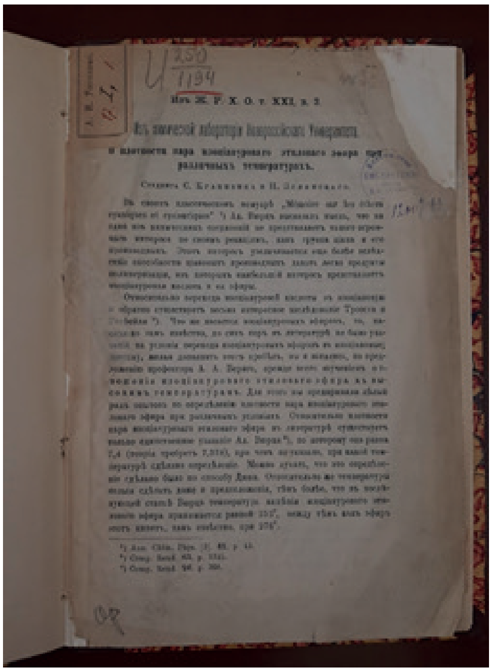
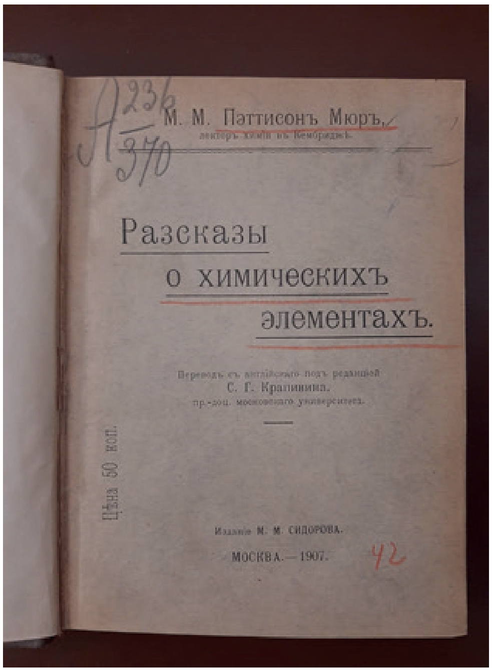


Fig. 6. Article written by the student S.G. Krapivin and N.D. Zelinsky "About the vapor density of isocyanuric ethyl ether at various temperatures," 1888.



А 236/370

М. М. Пэттисонъ Мюръ,
лекторъ химiи въ Кембриджѣ.

Разсказы
о химическихъ
элементахъ.

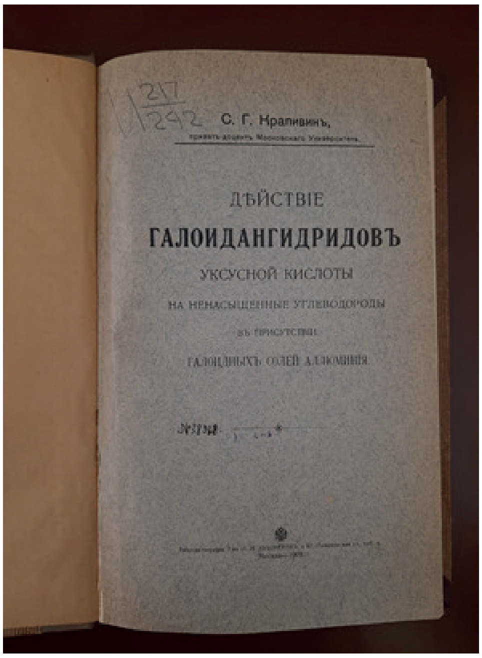
Переводъ съ англiйскаго подъ редакцiей
С. Г. Крапивина.
пр.-доц. московскаго университета.

Цѣна 50 коп.

Изданiе М. М. СИДОРОВА.
МОСКВА.—1907.

42

Fig. 7. Pattison Mur M.M. Stories of the Chemical Elements (1907), translation edited by Krapivin S.G. (with a foreword by the editor S.G. Krapivin).



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С. Г. Крапивинъ,

ДѢЙСТВІЕ
ГАЛОИДАНГИДРИДОВЪ
УКСУСНОЙ КИСЛОТЫ
НА НЕНАСЫЩЕННЫЕ УГЛЕВОДОРОДЫ
ВЪ ПРИСУТСТВІИ
ГАЛОИДНЫХЪ СОЛЕЙ АЛЛЮМИНІЯ

Fig. 8. Krapivin S.G. The action of acetic acid halides on unsaturated hydrocarbons in the presence of aluminum halide salts, Moscow, 1909 (page 1).

We need also to emphasize the pedagogical talent of S.G. Krapivin. He paid great attention to the methodology of teaching chemistry and clearly understood the importance of experimental work by students directly in the laboratory. He wrote, "…Experience has shown that the theoretical foundations, without which practical skills cannot be correctly assimilated, are particularly well absorbed by the students if, during the work itself, theoretical explanations of certain misunderstandings are given," [23]. Therefore, laboratory workshops were an integral part of the study of physical chemistry and quantitative analysis already during the period of his activity at the MHWC. Subsequently, the presentation of courses and lectures for chemistry teachers at higher and secondary educational institutions in various cities in Russia (Tver, Orenburg, Samara, Penza, Smolensk, etc.) made him a well-known methodologist and advocate of science [20–22].

In 1918, after the reorganization of the MHWC into the 2nd Moscow State University, S.G. Krapivin was appointed to the post of Dean of the Chemical and Pharmaceutical Department of the Faculty of Physics and Mathematics [20]. Last but not least, thanks to the efforts of Sergey Gavrilovich, the teaching of physical chemistry was maintained at an independent department, despite the drastic changes in the MHWC. Until 1924, S.G. Krapivin successfully combined administrative and scientific work, continuing to head the laboratory which he had set up.

A knight of science and a true teacher, S.G. Krapivin created, developed and preserved the Department during perhaps the most difficult periods of its existence: during the student riots of the early 20th century, the First World War, the February and October Revolutions, and the Civil War. The colossal expenditure of physical and mental energy could not fail to affect his health, and Sergey Gavrilovich died prematurely before the age of 60.

The development of physical chemistry at IFCT was continued by other national physical chemists [14], but the traditions of teaching this discipline, combining the deep basic training of students with the development of various practical skills, laid down by those who stood at the origins of the department, have always been carefully preserved.

A BRIEF OVERVIEW OF THE DEPARTMENT'S ACTIVITIES FROM 1925–2023

Much more is known about this period of the Department's life, so we will only briefly consider the main stages of its development.

From 1925 to 1931, the Department was headed by Professor Ya. I. Mikhailenko, a specialist in atomic and molecular spectroscopy [14]. During these years, departments of atomic and molecular theory were added to the traditional sections of the physical chemistry course: chemical thermodynamics, solution theory, and chemical kinetics.

From 1931 to 1974, the department was headed by Yakov Kivovich Syrkin, the greatest scientist, outstanding organizer of science and teacher, later to become Academician of the USSR Academy of Sciences (1964), laureate of the Stalin Prize [14, 24]. He was one of the founders of the most important areas of physical chemistry: the theory of molecular structure and the doctrine of chemical kinetics. His fundamental work on the nature of chemical bonding, thermodynamics and the kinetics of chemical reactions in solutions largely determined the development of many subsequent studies in theoretical chemistry. The contributions of Ya.K. Syrkin to the development of modern methods of quantum chemical calculations of electronic structures of molecules, application of new physical methods for a deeper study of chemical bonding are enormous. He was one of the first to develop the idea of using transition metal complexes in homogeneous catalysis. Under his leadership (together with I.I. Moiseev, later an Academician of the Russian Academy of Sciences (1929–2021)), the palladium allyl complex, a key intermediate or precursor in many catalytic processes, was first synthesized and characterized (1959). Between 1960–1962, the first series of classical experiments on the homogeneous catalytic oxidation of ethylene and propylene in the presence of palladium complexes was carried out (together with I.I. Moiseev and M.N. Vargaftik). Syrkin's fundamental research in thermodynamics and quantum chemistry is still relevant to the development of coordination chemistry, electrochemistry, molecular biology, and biochemistry [14, 25–29].

At that time (1957), a laboratory for the study of chemical bonding and molecular structure was created, thus greatly increasing the possibilities for research. Full-time researchers appeared, scientific groups were formed and a certain scientific direction was developed. Opportunities for postgraduate study expanded, and students were widely involved in scientific work [27].

Syrkin brilliantly combined his great scientific work with pedagogical activity. His lectures were constantly updated to take account of the latest advances in science. The physical chemistry course which he created was very different from the standard course in the discipline. It was based on the department: "The structure of matter and the nature of chemical bonding". Then the departments of "Chemical kinetics" and "Chemical thermodynamic" were substantially revised [28, 29]. This course structure is currently being maintained.

After the death of Syrkin, the duties of head of department from 1974 to 1976 were performed by Madeleine Grigorievna Shirmazan, his student and closest collaborator. She was an excellent methodologist and teacher and later the scientific secretary of the IFCT [28, 29].

From 1976 to 1983, the department was headed by Academician Vitaly Iosifovich Goldansky, an outstanding physical chemist, [14, 28, 29]. He had an unusually wide range of scientific interests. He predicted the phenomenon of two-proton radioactivity, laid the foundations for the chemical applications of Mesbauer spectroscopy, the physical chemistry of the positron and positronium, and established a temperature criterion for the region of tunnel junctions. He made great contributions to developing the theory of low-temperature polymerization of formaldehyde, conformational transitions in protein globules and other areas. During this period, the Department's scientific contacts both at home and abroad were significantly strengthened and expanded.

From 1983 to 1988, the Department was headed by Prof. Georgii Adrianovich Grigoriev, a specialist in non-equilibrium thermodynamics. During this period, the department moved to a new building on Vernadskii Prospekt. G.A. Grigoriev's organizational and economic skills enabled the department to get through this difficult period practically without affecting the scientific and educational process, and to acquire new modern equipment [14, 29].

In 1988, Professor Aleksandr Anatolievich Ovchinnikov, Corresponding Member of the USSR Academy of Sciences, became Head of the Department. He developed a theory of the structure of large molecules with a system of conjugated bonds which made it possible to predict their physicochemical properties. A.A. Ovchinnikov made a significant contribution to the physical chemistry of organic semiconductors and the theory of redox reactions in polar media [14].

From 1991 to 2004, the department was headed by Professor Andrei Pavlovich Belov, a student of I.I. Moiseev. His research interests included the chemistry and structure of allyl complexes of transition metals, the mechanisms of homogeneous catalytic oxidation reactions of unsaturated compounds, and the chemistry of furan compounds [14]. Despite the difficult economic conditions of the time, the Department managed to maintain much of its scientific and educational potential. At the initiative of A.P. Belov and with his active participation, a Chemistry Department was established for bachelor degree students studying at chemical faculties with a natural science profile. In 1998, the first graduation ceremony for undergraduate students took place. In 2000, the first Master's theses in the Physical Chemistry Master's program were assessed. For the first time, the department had its own graduates! Most of them were postgraduate students and employees of departments or institutes of the Russian Academy of Sciences. Within a short period of time, the department carried out important methodological work, organized new original lecture courses and laboratory workshops.

Since 2005, the department has been headed by Professor Vitaly Rafailovich Flid who continues to develop the traditions of the outstanding IFCT scientific school in the field of physical chemistry and catalysis. Over the past few years, the department has built up a skilled team of like-minded educators and researchers. Under the leadership of Doctors of Sciences, R.S. Shamsiev, O.N. Shishilov, S.M. Pestov, N.A. Yashtulov, and V.R. Flid, traditional scientific directions and groups have been maintained and new ones formed: homogeneous metal complex catalysis and intermediates chemistry; synthesis, structure and practical application of allylic complexes of transition metals; quantum chemistry as applied to metal complex and heterogeneous catalytic systems; optical sensors and EPR-spectroscopy; heterogeneous catalysis; catalytic chemistry of complex carboxyclic compounds; physics and chemistry of liquid crystals; synthesis and surface properties of photonic crystals; physical chemistry of fuel cells and nano-electro-catalysis; physicochemical bases of qualified biomass processng; new frame polymers and membranes for gas separation; and new materials for implants in cardiovascular surgery. Work is continuing on the frontiers of photochemistry, green chemistry and ecology, as well as the use of chemical converters of solar energy, and hydrogen energy. Research is carried out in small research groups (2–3 staff or teachers, 1–2 postgraduates, and 2–3 students).

The teaching staff of the Department consists of 22 scientists (6 Professors, Doctors of Sciences, 11 Associate Professors, Candidates of Sciences, 3 Senior Lecturers, and 2 Assistants). The scientific staff varies from 5 to 20 people, depending on the current work on grants, contracts, and scientific and technical programs. Each year 8–12 people study in the Postgraduate School and 1 staff member on the Doctoral Program. Bachelor’s and Master’s students are involved in all scientific work. A Scientific School on Catalysis has been established and registered with the Department. The department was one of the initiators of the creation of the “Center for Catalytic and Mass Transfer Processes,” equipped with state-of-the-art facilities. The Center carries out scientific and technological work within the framework of major projects of national economic importance.

CONCLUSIONS

With its considerable human, methodological, and technological potential, the Department of Physical Chemistry at the M.V. Lomonosov IFCT of RTU MIREA is able to resolve some of the most complex theoretical and practical problems. A complex combination of experimental, theoretical, and methodological approaches is successfully implemented through the interaction of different scientific groups, all united by the ambition to resolve matters of common interest. This was what the founding fathers of the Department of Physical Chemistry—N.D. Zelinsky, S.G. Krapivin, and Ya.K. Syrkin—predicted and aspired to in their selfless dedication to science.

Authors’ contributions

A.V. Grashkina – analysis of literary sources and Internet resources, investigation of archival materials, writing the text of the review;

V.R. Flid – conceptualization of the review, scientific editing of materials, critical revision with the addition of valuable intellectual content.

The authors declare no conflicts of interest.

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About the authors:

Alexandra V. Grashkina, Master Student, Department of Physical Chemistry, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (86, Vernadskogo pr., Moscow, 119571, Russia). E-mail: grass_975@mail.ru. https://orcid.org/0009-0000-4957-4118

Vitaly R. Flid, Dr.Sci. (Chem.), Professor, Head of the Department of Physical Chemistry, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (86, Vernadskogo pr., Moscow, 119571, Russia). E-mail: vitaly-flid@yandex.ru. Scopus Author ID 6602997346, ResearcherID H-1781-2017, RSCI SPIN-code 8790-3380, https://orcid.org/0000-0001-6559-5648

Об авторах:

Грашкина Александра Витальевна, магистр кафедры физической химии им. Я.К. Сыркина Института тонких химических технологий им. М.В. Ломоносова, ФГБОУ ВО «МИРЭА – Российский технологический университет» (119571, Россия, Москва, пр-т Вернадского, д. 86). E-mail: grass_975@mail.ru. https://orcid.org/0009-0000-4957-4118

Флид Виталий Рафаилович, д.х.н., профессор, заведующий кафедрой физической химии им. Я.К. Сыркина Института тонких химических технологий им. М.В. Ломоносова, ФГБОУ ВО «МИРЭА – Российский технологический университет» (119571, Россия, Москва, пр-т Вернадского, д. 86). E-mail: vitaly-flid@yandex.ru. Scopus Author ID 6602997346, ResearcherID H-1781-2017, SPIN-код РИНЦ 8790-3380, https://orcid.org/0000-0001-6559-5648

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REVIEW ARTICLE

Regarding certain stages of the development of quantum chemistry in Russia: Experience from the Ya.K. Syrkin Department of Physical Chemistry of the M.V. Lomonosov Institute of Fine Chemical Technologies

Konstantin V. Bozhenko✉

Federal Research Center of Problems of Chemical Physics and Medicinal Chemistry, Russian Academy of Sciences, Chernogolovka, Moscow Oblast, 142432 Russia
✉*Corresponding author, e-mail: bogenko@icp.ac.ru*

Abstract

Objectives. *To analyze the history of the development of quantum chemistry and software for quantum chemical calculations in Russia at the Ya.K. Syrkin Department of Physical Chemistry of the M.V. Lomonosov Institute of Fine Chemical Technologies of RTU MIREA.*
Results. *This work presents a historical overview of the development of quantum chemistry at the Ya.K. Syrkin Department of Physical Chemistry from Academician Ya.K. Syrkin to Professor V.R. Flid. It provides a summary of the work with the participation of the author in 1980s–1990s. Quantum-chemical models used to describe some of the intercalation reactions in a bond are considered in comparison with the well-known Woodward–Hoffman and Fukui approaches. The work outlines fundamentals of studies on the design of bifunctional compounds.*
Conclusions. *The physical significance of the exchange interaction constant is given a visual meaning: it establishes the change in spin density on the metals forming complexes of the type in question when passing from isolated cations in the composition of the complexes. The work provides recommendations to synthetic chemists regarding the selection of components in the synthesis of magnetic sublattices of bifunctional materials. It also examines the high level of scientific research carried out at the Ya.K. Syrkin Department of Physical Chemistry and its relevance to the world science level.*

Keywords: *quantum chemical calculations, molecular orbitals, bond embedding reactions, bifunctional materials*

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ОБЗОРНАЯ СТАТЬЯ

О некоторых этапах развития квантовой химии в России и на кафедре физической химии им. Я.К. Сыркина ИТХТ им. М.В. Ломоносова

К.В. Боженко✉

Федеральный исследовательский центр проблем химической физики и медицинской химии Российской академии наук, Черноголовка, Московская область, 142432 Россия
✉*Автор для переписки, e-mail: bogenko@icp.ac.ru*

Аннотация

Цели. *Проанализировать историю развития квантовой химии и программного обеспечения для квантово-химических расчетов в России и на кафедре физической химии им. Я.К. Сыркина Института тонких химических технологий (ИТХТ) им. М.В. Ломоносова РТУ МИРЭА.*
Результаты. *Представлен исторический очерк развития квантовой химии в ИТХТ на кафедре физической химии им. Я.К. Сыркина от самого академика Я.К. Сыркина до профессора В.Р. Флида. Обобщены данные работ с участием автора, проводимые им на кафедре физической химии им. Я.К. Сыркина в 80-е и в начале 90-х годов XX века. Рассмотрены квантово-химические модели для описания некоторых реакций внедрения в связь в сопоставлении с известными подходами Вудворда–Гоффмана и Фукуи. Изложены основы работ по дизайну бифункциональных соединений.*
Выводы. *Получено наглядное значение физического смысла константы обменного взаимодействия – она определяет изменение спиновой плотности на металлах, образующих комплексы рассмотренного типа, при переходе от изолированных катионов к ним же в составе комплексов. Даны рекомендации химикам-синтетикам по подбору компонент при проведении синтеза магнитных подрешеток бифункциональных материалов. Продемонстрирован высокий уровень научных исследований, выполняемых в ИТХТ на кафедре физической химии им. Я.К. Сыркина и их соответствие мировому уровню науки.*

Ключевые слова: *квантово-химические расчеты, молекулярные орбитали, реакции внедрения в связь, бифункциональные материалы*

Для цитирования: Боженко К.В. О некоторых этапах развития квантовой химии в России и на кафедре физической химии им. Я.К. Сыркина ИТХТ им. М.В. Ломоносова. *Тонкие химические технологии*. 2023;18(4):298–314. https://doi.org/10.32362/2410-6593-2023-18-4-298-314

INTRODUCTION

The development of quantum chemistry in Russia as an independent branch of quantum mechanics from its beginnings to the present day is inseparable from the Ya.K. Syrkin Department of Physical Chemistry of the M.V. Lomonosov Institute of Fine Chemical Technologies (IFCT) of MIREA – Russian Technological University (RTU MIREA). Many researchers rightly believe that the founders of quantum chemistry in the USSR to be Academician Yakov Kivovich Syrkin and Professor Mirra Efimovna Dyatkina. Syrkin and Dyatkina actively promoted and developed the molecular orbital (MO) method at the dawn of quantum chemistry [1], forming the basis of all its modern computational methods [2–7]. This was undoubtedly a gift of scientific foresight, since at that time Roothaan [8] had not yet proposed the MO—linear combination of atomic orbitals (AO) (MO–LCAO) method. This was the practical implementation of the Hartree–Fock method and enabled the resolution of the Schrödinger equation for various multielectronic systems. In contrast to the Heitler–London method [9], which was popular at the time, each electron in the molecule was assumed to move in an averaged field of the remaining electrons and nuclei, i.e., the traditional concept of directed chemical bonds disappeared. It is not surprising, therefore, that at first many researchers were very hostile to this method which Syrkin and Dyatkina called the method of molecular orbits. It was not until many years later when localized orbitals were included in quantum chemical programs. This eliminated the disadvantage of the MO method and it now occupies a leading position in the vast majority of calculations. It is impossible to describe in detail the difficulties experienced by Syrkin and Dyatkina in such a short story, but representatives of the older generation of chemists and physicists are well aware of them. Personally, I regard this struggle for the triumph of truth as a scientific achievement. Since the nature of this review relates to the field of memory, I would say that I studied under the students of our outstanding teachers. These were the loyal followers of Syrkin and Dyatkina: my teachers Oleg Petrovich Charkin and Nina Mikhailovna Klimenko. I would like to cite one encounter with Syrkin, which will forever remain in my memory. In the spring of 1972, Charkin called Syrkin with a request to oversee my entrance exam to the graduate school of the Academy of Sciences of the Soviet Union (USSR). Syrkin asked for as much clarification of the date of the exam as possible. I picked the date at random: 4 October. Six months later, on 5 October, I took the exam with him in the old building of the N.S. Kurnakov Institute of General and Inorganic Chemistry of the USSR Academy of Sciences. This showed not only the care of a great scientist for me, then a very young man, but also a great clarity in matters of work. As a result, I was enrolled in the postgraduate course of the Institute of New Chemical Problems of the USSR, at the Academy of Sciences in the Laboratory of Quantum Chemistry of Professor O.P. Charkin. After graduating in 1976, I was appointed to the Department of Physical Chemistry of IFCT, which today bears the name of Academician Ya.K. Syrkin. The work of the founders of quantum chemistry in Russia is now being successfully continued by the Head of the Department, Professor V.R. Flid. I worked here in the group of N.M. Klimenko for fourteen years until 1990. I have to say a few words about the educational process in the department during those years. Although I was not a full-time teacher, but a research associate, the Rector ordered me to deliver a course directly related to quantum chemistry: the theory of symmetry groups in quantum chemistry. At that time, a textbook written by N.M. Klimenko and G.N. Kartsev, “The Theory of Symmetry Groups for Quantum Chemical Calculations,” had been published at IFCT. It proved useful in introducing students to the following important concepts: symmetry elements and operations; abstract group theory; point symmetry groups; group representation theory; the relationship of symmetry group theory to quantum mechanics; and linear combinations of functions reduced by symmetry. Later, at the Moscow Institute of Physics and Technology (2001–2003) and the Lomonosov Moscow State University (2011–2021), I saw that these prestigious universities did not have such a course separately. Students had to study, either on their own or in other courses, such concepts as spectroscopy and many others without which it is difficult to imagine fields of physics and chemistry where the properties of individual quantum systems are studied. This was the fundamental approach to the study of quantum chemistry laid down by Syrkin and Dyatkina.

Next, I would like to share my memories of the results of my work at the Department and later at the institutes of the Russian Academy of Sciences (RAS). Almost all of my work (about 270) is done using MO methods. At various times, the Department was headed by such remarkable scientists as Academician V.I. Goldansky and Corresponding Member of the Russian Academy of Sciences A.A. Ovchinnikov and I have fond memories of each of them. Before going into specific scientific results, I would like to mention an important organizational aspect that was discussed at the turn of 1970s–1980s. At that time, scientific collectives were engaged on resolving the fundamental question of whether to write quantum chemical programs themselves or to use foreign software. We actually needed to do this hard work ourselves, in order to keep up with the countries where such programs are written. However, it takes large teams of programmers to write such powerful programs available in countries that developed General Atomic and Molecular Electronic Structure System (GAMESS)[1], GAUSSIAN[2], MOLPRO[3] and other software. This was not the case in the USSR, and the way to acquire such programs within the international division of labor proved to be more effective. This was preferable not only for Soviet scientists, but also for representatives of other developed countries where such programs were not being created. My teacher, Professor O.P. Charkin, played an important role in providing Soviet scientists with modern software systems. This greatly contributed to the development of quantum chemistry in USSR. Charkin also educated a number of well-known quantum chemists, including Professor A.I. Boldyrev and V.G. Zakzhevsky, co-author of the GAUSSIAN program. He is an example of academic prowess and great diligence with regard to his students.

Before moving on to specific scientific results, I would like to note the generally accepted view that quantum chemistry resolves the following main tasks:

− prediction of the possibility of the existence of different molecular systems in the form of a stable combination of atoms;

− prediction of the geometric and electronic structure of such systems;

− prediction of the most probable ways of chemical reactions;

− implementation of computer design of connections with specified properties.

Together with advances in computer technology, the last two tasks, inaccessible at the beginning of the development of quantum chemistry, have become the most urgent. Therefore, in the remainder of this review, the solution to these tasks will be considered with reference to a number of examples.

CERTAIN WORKS OF THE DEPARTMENT AND INSTITUTES OF THE RUSSIAN ACADEMY OF SCIENCES

In the mid-1970s, calculations of the potential energy surfaces (PES) of chemical reactions were just beginning in USSR. Using the model of valence states previously proposed and developed by Professor Charkin to describe the regularities of energies of sequential bond cleavage in iso-bonded variable-valence series, we proposed a model for finding optimal ways of reagent convergence in reactions of type (1) [10–12]:

$$MX_{k-2} + X_2 \rightarrow MX_k. \qquad (1)$$

We were interested not only in the thermodynamic stability of the products of such reactions, but also in the presence of activation barriers along the optimal paths of convergence of the reagents. The model, which enables us to find such paths, is described in sufficient detail in [12]. Here we will only consider its formulation and briefly outline its advantages over other well-known models. The main provisions of the qualitative model for describing the approximate mechanism of reactions of introduction into communication are as follows.

1. If the convergence of the MX_{k-2} and X_2 reagents along the shortest geometrically path is associated with the intersection of terms[4] and the jump-like promotion of the M atom, and effective donor–acceptor interaction is impossible, then the barriers are large at high promotion energies E_v(M), and small if E_v(M) are small. If effective donor–acceptor interaction is allowed without any costs for E_v(M), then there may be no barriers at all.

2. If the shortest path is forbidden, then of all other possible reaction paths, the minimum activation barrier will correspond to those angles of attack and mutual orientations of the reagents where there are the most favorable opportunities for effective donor–acceptor interaction of the reagents throughout the reaction path without significant expenditure of energy E_v(M) for spasmodic promotion.

Thus, it can be assumed that small or zero activation barriers should correspond to the shortest pathways of $M(^1D) + X_2 \rightarrow MX_2$ or $M(^1D) + Y \rightarrow MY$ type reactions, where M are atoms of type O, C, S, Si, and their heavier analogues in the state ^1D, and $XM(^1\Delta) + X_2 \rightarrow MX_3$, where MX are molecules of the type NH and PH in the state $^1\Delta$, X = H, halogen, alkyl, etc., Y is an atom or valence unsaturated molecule with a closed shell of the type $Be(^1S_0)$, $BH(X^1\Sigma)$, $CH_2(^1A_1)$, $CO(X^1\Sigma)$, $NH(^1A_1)$, $HNO(^1A_1)$, etc. Indeed, *ab initio* calculations of the shortest paths of reactions $O(^1D) + H_2 \rightarrow H_2O(^1A_1)$ [13], $C(^1D) + H_2 \rightarrow CH_2(^1A_1)$[14], $Be(^1S) + O(^1D) \rightarrow BeO(^1\Sigma)$ [15],

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[1] https://www.msg.chem.iastate.edu/gamess/. Accessed May 10, 2023.

[2] https://gaussian.com/. Accessed May 10, 2023.

[3] https://www.molpro.net/. Accessed May 10, 2023.

[4] The intersection of terms here refers to the intersection of potential curves corresponding to different spin multiplicities of the reaction system.

and others show the smooth binding nature of their potential curves. According to our ab initio model, calculations of the shortest reaction paths $BH(X_1\sum) + H_2 \rightarrow BH_3$ [10], $CH_2(^1A_1)+H_2\rightarrow CH_4$[16],$CH_2(^1A_1)+CH_2(^1A_1)\rightarrow H_2CCH_2$[17], $CH_2(^1A_1) + CO(X^1\sum) \rightarrow CH_2CO$ [18], etc., show the presence of potential barriers with a height of several tens of kcal. The qualitative conclusions of the model should be retained during the transition from symmetric molecules X_2 to asymmetric molecules XX". Indeed, the *ab initio* calculation of the $CO_2 + H_2O \rightarrow OC(OH)_2$ reaction [19] shows the presence of a high barrier (~53 kcal).

For a better understanding of the essence of our model, we will consider the reaction $CH_2(^1A_1) + H_2 \rightarrow CH_4$. Initially, the hydrogen molecule is positioned in such a way that the axis of the unshared electron pair of the carbon atom ^{12}(C) is parallel to the axis of the hydrogen molecule. As the reagents approach, when they pass the area with a high barrier, the hydrogen molecule unfolds until its axis is perpendicular to the plane of the $CH_2(^1A_1)$ molecule. It then connects to it without a barrier to form the CH_4 molecule. In the process of convergence of the reagents, a counter smooth flow of electron density occurs from the unsheltered electron pair of the carbon atom ^{12}(C) to the vacant $\sigma_u^0(H_2)$ orbital of the hydrogen molecule; then back from the filled orbital $\sigma_g^2(H_2)$ to the vacant $p\pi^0(C)$ orbital of the carbon atom. This confirms the validity of our model, according to which a smooth flow of electron density does not lead to the formation of high barriers.

Let us briefly consider how our model compares with other well-known models. Our model introduces a quantitative characteristic of the barrier height estimation: the promotion energy of the atom M E_v(M) which can be estimated from atomic spectra. According to the model, the barrier should be large at high promotion energies E_v(M), and small at low E_v(M). Furthermore, the Woodward–Hoffman rules [20], for example, do not provide recommendations for finding accessible reaction paths when the shortest path is prohibited. Using the approach of Fukui [21] and Pearson [22], it is possible in principle to obtain recommendations for finding ways of reacting with minimal barriers. However, they completely ignore the mechanism of electron density redistribution during the reaction and do not investigate the mechanism of intramolecular interactions, which cause the formation of barriers. The most important advantage of our model is the ability to compare the heights of barriers of the same type of reactions by the value of E_v(M) of isolated atoms, without calculating their PES. This can be done even more precisely by the magnitude of the energies of singlet-triplet or doublet-quartet excitations of MX_n molecules containing the central M atom.

A little later, in collaboration with Professor O.N. Temkin's group, we studied widespread nucleophilic addition reactions on asymmetric alkynes [23, 24]. The issues were considered in relation to two real problems, which arise in such responses, in addition to the problems of multiple bond activation and regioselectivity of addition in the case of asymmetric alkynes. This is particularly important for directional synthesis. There are nucleophilic addition reactions, which violate the Markovnikov rule. In order to clarify the reasons for non-compliance with the Markovnikov rule, we performed calculations in a number of cases of the reactions of nucleophilic (Nu) addition of hydride ion (H^-), fluoride ion (F^-), lithium hydride molecule (LiH) and Li^+/H^-ion pair to acetylene and methylacetylene molecules.

The study investigated the influence of the Nu type on the course of addition reactions, the validity of the well-known Klopman–Fukui approach and the Hudson "non-intersection" rule, the influence of the substituent, the electrophile and the polarity of the solvent on the reactivity of alkyne. Based on calculations, we interpreted experimental data on the absence of addition reactions with a hard nucleophile F^- in polar media without electrophilic assistance and the ease of reactions with soft nucleophiles H^-, BH_4^-, AlH_4^-, etc. in such media. The study also established the reasons for non-compliance with the Markovnikov rule in reactions with H. The role of the electrophile in controlling the regioselectivity of such reactions was shown.

Other things need to be noted about our work together with the group of Professor E.A. Polenov. Among other works, the angular dependence of the constants of the isotropic hyperfine interaction with the nuclei of atoms in the π-radical β-position was investigated [25]. Based on the assumption that it is possible to isolate two-orbital two-center basis fragments with conformation independent mixing coefficients from a once filled boundary MO, an analytical form of this angular function was obtained.

Using the MO–LCAO method, a method was proposed to theoretically establish the angular dependence of spin populations of AO β-atoms in π-radicals. It was shown that the type of this dependence is determined by the local symmetry of the radical center and the substituent. By isolating conformationally independent blocks in the MO combining AO β-atoms into π-systems, the paper presents an effective technique, which establishes a simple way to consistently describe the angular dependence of the constants of the isotropic hyperfine interaction with β-atoms, taking into account the local symmetry of the substituent. It was also found that for conformational rotation, rather subtle effects of the spin density (SD) distribution can be correctly described by semiempirical methods.

Finally, I would like to focus on the latest stage in the development of quantum chemistry: the computer design of compounds with specific properties. A few years ago, on the initiative of Academician S.M. Aldoshin, we started studying bifunctional compounds with both photochromic and magnetic properties. Bifunctional materials are extremely important in the development of new displays, information and energy storage and conversion devices, sensors, etc. [26].

They consist of anionic layers of a magnetic sublattice between which are photochromic cations, such as spiropyrans. At the same time, the development of new hybrid crystalline materials, in which magnetic and photochromic sublattices are combined and interact with each other, requires the solution of a number of experimental problems. At the present time, hybrids of photochromic diarylethene and ferromagnetic layered compounds $\mathrm{Co^{II}}$, $\mathrm{Cu^{II}}$ are known. However, open and closed forms of diarylethene form hybrids with different magnetic properties. When the hybrid compound is irradiated, photochrome isomerization does not occur, and the properties of the magnetic sublattice do not change. Unlike diarylethenes, representatives of another class of photochromes—spiropyrane cations—act as photo switches of magnetic properties of a number of hybrids based on bimetallic oxalate $\mathrm{Cr^{III}}$ and $\mathrm{Mn^{II}}$, dithiooxalate $\mathrm{Fe^{III}}$ and $\mathrm{Fe^{II}}$, thiophosphate $\mathrm{Mn^{II}}$.

The first photomagnetic hybrid was obtained by S. Benard in 2001, the second, in the laboratory of Academician S.M. Aldoshin in 2007. Research is currently underway there to obtain crystals of photochromic hybrid materials with an oxalate sublattice from other metal pairs (Cr and Ni, Fe and Mn, Cr and Co, and others). It is obtained on the basis of a cationic spiropyran containing a quaternary $\mathrm{N^+}$ atom in a pyridine cycle placed in a side aliphatic chain. Its magnetic sublattice consists of complexes formed by oxalate as an intermetal bridge and a pair of $\mathrm{Cr^{III}}$ and $\mathrm{Mn^{II}}$, $[\mathrm{Cr^{III}Mn^{II}(Ox)_3}]^-$. This bifunctional compound is a ferromagnet with a Curie temperature of 5.1 K. The value of μ_{eff} at high temperatures (300 K) ~7 μ_B[5] agrees well with the calculated 7.07 μ_B ($g = 2$) for two paramagnetic ions $\mathrm{Mn^{II}}$ and $\mathrm{Cr^{III}}$ [26]. Thus, these studies are pioneering. Figure 1 shows a fragment of such a connection.

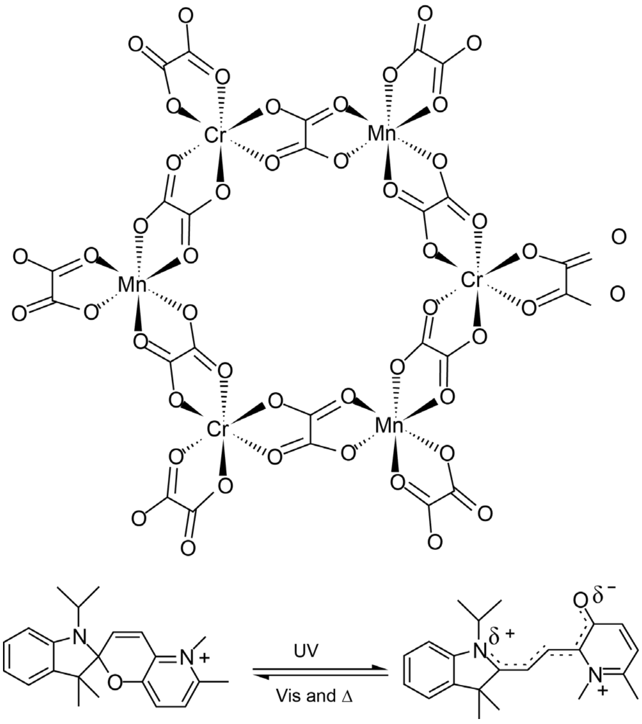

Fig. 1. Fragment of a bifunctional compound is at the top. The opening and closing of the photochromic element under the action of radiation is shown below [26].

The aim of our study was to search for such a region in the Periodic table where metal pairs can provide maximum ferromagnetic exchange interaction, in order to facilitate the selection of appropriate components for synthetic chemists during such synthesis. A further aim was to search for such ligands, which, in combination with these metal pairs, lead to maximum ferromagnetic exchange interaction. However, the main objective was to find a complex that correctly simulated the exchange interactions in a magnetic sublattice. We started this search by calculating complexes containing oxalate as a ligand and a pair of $\mathrm{Cr^{III}}$–$\mathrm{Ni^{II}}$ metals [27].

Calculations of all complexes were performed using the GAUSSIAN-03 program[6] in the B3LYP/LANL2DZ[7] approximation with full optimization of the geometric structure of each complex in the ground energy state with maximum spin multiplicity. In order to find the optimal complex in terms of structure and size, we calculated several different complexes, of which the complexes shown in Fig. 2.

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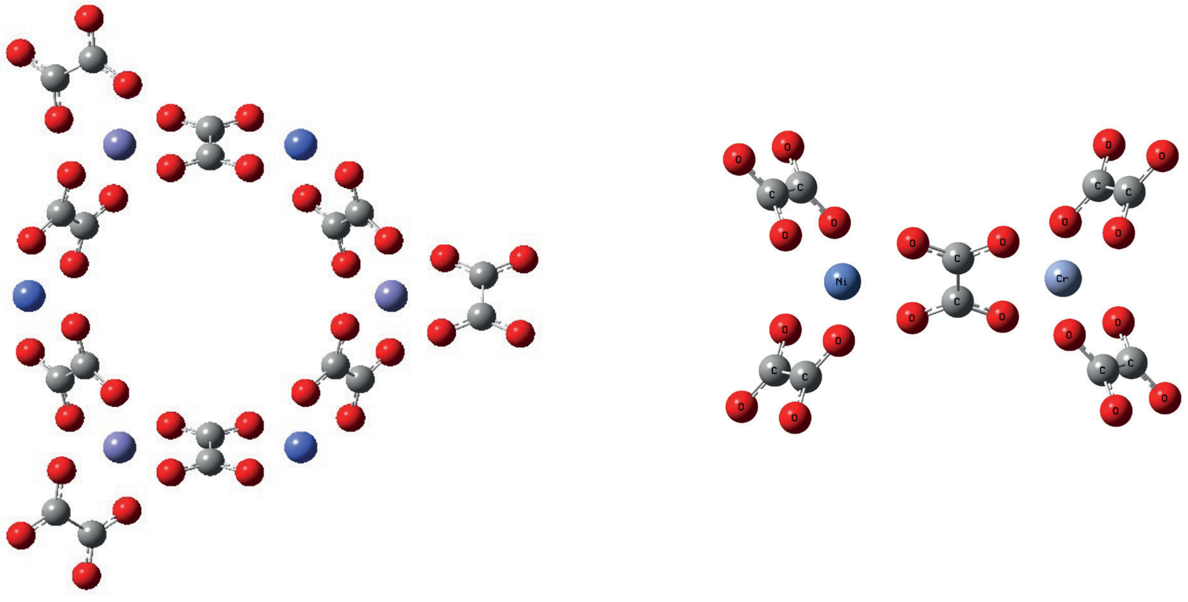
[5] μ_B – Bohr magneton.

[6] License to Use Agreement: Gaussian. Inc. 340 Quinnipiac Street. Building 40. Wallingford. CT 06492.

[7] B3LYP/LANL2DZ is the 3-parametric Becke–Lie–Yang–Parr density functional with a Los Alamos National Laboratory 2 double-ζ (LANL2DZ) basic set.



(a) (b)

Fig. 2. Complex: (a) in the form of a ring, (b) formed by one pair of di- and trivalent transition metal atoms and five anions of oxalate intermetal bridges.

The most effective complex was a pair of metals and five oxalate anions. In less machine time gave almost the same geometric and electronic structure as a much larger complex in the form of a ring. It was chosen by us to calculate complexes with other metal pairs. At the same time, it was shown that optimizing the geometry of such complexes of only nine key structural parameters leads to almost the same results as full geometry optimization. This enables us to preserve the symmetry that these complexes possess in a solid, while at the same time reducing the number of optimized parameters (without such an approach, their number approaches one hundred).

Obviously, this approach makes it possible for a large number of such complexes for different pairs of metals to be calculated with a minimum of human and machine time, necessary to find the most effective ones in terms of ferromagnetic properties. The simplification we propose is optimal for the choice of the structure of the anions of bimetallic complexes and allows us to model the magnetic sublattice quite correctly.

We then carried out calculations to find optimal ligands (intermetallic bridges) which would provide maximum ferromagnetic exchange interaction. To this end, we calculated the exchange interaction constant (*J*) and the SD in such anions for the four most popular ligands L (L is oxalate, oxamide, hydroxamate, or dithiooxamide) and various pairs of tri- and divalent 3d metals [28].

Thus, we calculated anion complexes containing oxalate, oxamide, dithiooxamide anions and hydroxamic acid anion as the intermetallic bridge for various pairs of di- and trivalent transition metal atoms. The types of ligands are shown in Fig. 3 and examples of calculated complex anions are shown in Fig. 4.

All calculations are performed in the above-mentioned approximation with full optimization of the geometry with the maximum spin multiplicity value for each anion. These are complexes of the type $[M_1^{III}M_2^{II}(L)5]$. M_1 and M_2 are transition metal atoms, and $(L)_5$ means five anions of one of the

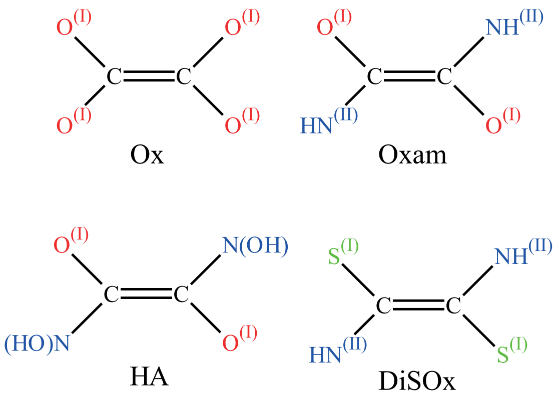
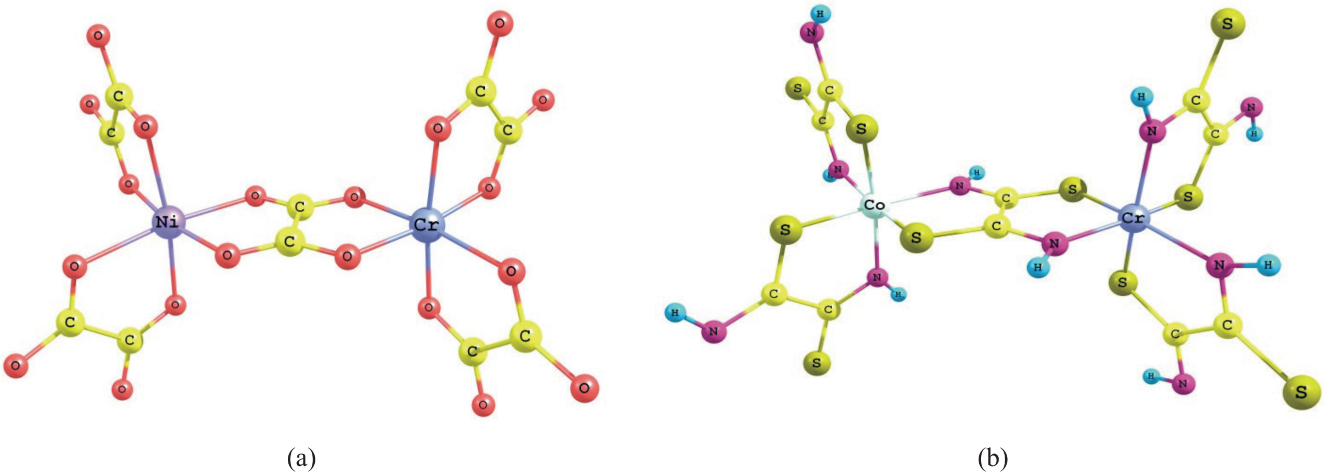


Fig. 3. Types of ligands included in the calculated bimetallic complexes.



(a) (b)

Fig. 4. Anion of a bimetallic complex: (a) with oxalate, (b) with dithiooxamide.

above ligands. Then, using the ORCA program[8], we calculated the values of the exchange interaction constant J. These calculations, as shown by comparison with the literature data, give not only the correct sign of the constant J, but also almost exact quantitative values. In this respect, this program is optimal, since it allows us to obtain the values of the exchange interaction constants with an accuracy of several inverse centimeters. On the other hand, it is only possible to obtain the correct sign of these constants using the GAUSSIAN-03 program. The values of the exchange interaction constants J are estimated in the B3LYP/TZV[9] approximation, in which the broken symmetry (BS) method is implemented [29]. It consists of calculating the total energy of the high-spin (HS) state; subsequent localization of orbitals; and calculation with them of the low spin state with BS. This allows the energy of the low-spin state to be calculated more accurately using a single-determinant Density Functional Theory approach. In the ORCA program, expressions obtained from the analysis of the spin-Hamiltonian of the form $\mathbf{H} = -2J\cdot\mathbf{S}_A\cdot\mathbf{S}_B$ (Heisenberg–Dirac–Van Vleck model) are used to calculate the constants J:

$$J(1) = -(E[\mathrm{HS}]-E[\mathrm{BS}]) / S^2_{\max}) \text{ [31–33]},$$
$$J(2) = -(E[\mathrm{HS}] - E[\mathrm{BS}]) / (S_{\max}(S_{\max} + 1)) \text{ [34]},$$
$$J(3) = -(E[\mathrm{HS}] - E[\mathrm{BS}]) / (<S_2>_{\mathrm{HS}} - <S_2>_{\mathrm{BS}})) \text{ [35]}.$$

With their help, almost identical values of the constant J are obtained, differing by 1–2 cm^{-1}. The values of the exchange interaction constant obtained by the formula $J(3) = -(E[\mathrm{HS}] - E[\mathrm{BS}])/(<S^2>_{\mathrm{HS}} - <S^2>_{\mathrm{BS}}))$ are considered the most theoretically justified, and therefore were taken as its values. The high precision values obtained for the exchange interaction constants allow us to judge not only the nature of the exchange interaction (ferromagnetic or antiferromagnetic), but also where it is strongest. This, in turn, enables us to conclude that it is advisable to use this pair of metals with this ligand (intermetal bridge) for the synthesis of a magnetic sublattice.

Table 1 shows the calculated values for these constants, as well as the charge states of the complexes, the eigenvalues of the operator S^2 for the maximum value of the HS $<S^2>_{\mathrm{HS}}$ and BS states. Table 1 also shows the mononuclear complexes formed by trivalent chromium, divalent nickel and trivalent iron, which have negative values of the exchange interaction constants for all four types of ligands, corresponding to the antiferromagnetic exchange interaction in them. For complexes formed by a pair of trivalent chromium and divalent nickel, the maximum value of J occurs for complexes with dithiooxamide as a ligand (~14 cm^{-1}). For complexes formed by a pair of trivalent chromium and divalent cobalt, the maximum value of J also occurs for complexes with dithiooxamide as a ligand (~9 cm^{-1}). Moreover, for both pairs of metals, the exchange interaction is ferromagnetic in nature. Thus, the combinations of $\mathrm{Cr^{III}}$–$\mathrm{Ni^{II}}$ and $\mathrm{Cr^{III}}$–$\mathrm{Co^{II}}$ with dithiooxamide lead to the most pronounced ferromagnetic properties in the complexes studied by us.

Then, an expanded search was carried out for the components of the magnetic sublattice which provide the maximum ferromagnetic exchange interaction in it [38], based on the assumption that

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[8] Neese F. ORCA – An *ab initio*, DFT, and Semiempirical Program Package 2.8-01. Bonn: Universität Bonn; 2010. http://wild.life.nctu.edu.tw/~jsyu/OrcaManual_2_9.pdf. Accessed August 10, 2023.

[9] B3LYP/TVZ is the 3-parametric Becke–Lie–Yang–Parr density functional with a triple zeta valence (TZV) basis set.

Table 1. Charge states of complexes (Charge), maximum value of spin (S_{max}), eigenvalues of the operator S^2 for the maximum value of high-spin ($<S^2>_{HS}$) and broken-symmetry ($<S^2>_{BS}$) states, exchange interaction constants calculated by us (J_1, J_2, J_3) and found experimentally (J_{exp}), (cm^{-1})

$[L_2M_1^{III}LM_2^{II}L2]^{n-}$	Charge	S_{max}	$<S^2>_{HS}$	$<S^2>_{BS}$	J_1	J_2	J_3	J_{exp}
$Ox_2Cr^{III}(Ox)Cr^{III}Ox_2$	−4	3	12.0411	3.0405	−4.01	−3.01	−4.01	−3.1[34]
$Ha_2Cr^{III}(Ha)Cr^{III}Ha_2$	−4	3	12.0888	3.0852	−3.40	−2.55	−3.40	–
$DiSOx_2Cr^{III}(DiSOx)Cr^{III}\ DiSOx_2$	−4	3	12.1188	3.1226	−10.16	−7.62	−10.17	–
$Oxam_2Cr^{III}(Oxam)Cr^{III}Oxam_2$	−4	3	12.0483	3.0479	−8.98	−6.73	−8.98	–
$Ox_2Cr^{III}(Ox)Ni^{II}Ox_2$	−5	5/2	8.7765	2.7752	7.99	5.7	8.32	3.5 [35]
$DiSOx_2Cr^{III}(DiSOx)Ni^{II}\ DiSOx_2$	−5	5/2	8.8201	2.8149	13.85	9.90	14.42	–
$Oxam_2Cr^{III}(Oxam)Ni^{II}Oxam_2$	−5	5/2	8.7771	2.7762	1.33	0.95	1.39	–
$HA_2Cr^{III}(HA)Ni^{II}HA_2$	−5	5/2	8.7783	2.7768	5.32	3.80	5.54	–
$Ox_2Ni^{II}(Ox)Ni^{II}Ox_2$	−6	2	6.0056	2.0028	−14.66	−9.77	−14.65	−22.8 [36]
$Ha_2Ni^{II}(Ha)Ni^{II}Ha_2$	−6	2	6.0092	2.0080	−8.06	−5.37	−8.05	–
$DiSOx_2Ni^{II}(DiSOx)Ni^{II}\ DiSOx_2$	−6	2	6.0084	2.0029	−24.64	−16.4	−24.6	–
$Oxam_2Ni^{II}(Oxam)Ni^{II}Oxam_2$	−6	2	6.0081	2.0079	−1.1	−0.73	−1.1	–
$Ox_2Fe^{III}(Ox)Fe^{III}Ox_2$	−4	5	30.0135	5.0067	−4.05	−3.37	−4.04	−3.4 [37]
$Ha_2Fe^{III}(Ha)Fe^{III}Ha_2$	−4	5	30.0208	5.0163	−1.66	−1.38	−1.66	–
$DiSOx_2Fe^{III}(DiSOx)Fe^{III}\ DiSOx_2$	−4	5	30.0268	5.0136	−6.35	−5.29	−6.35	–
$Oxam_2Fe^{III}(Oxam)Fe^{III}Oxam_2$	−4	5	30.0144	5.0058	−5.51	−4.59	−5.51	–
$DiSOx_2Cr^{III}(DiSOx)Co^{II}DiSOx_2$	−5	3	12.0726	3.0668	8.93	6.70	8.92	–
$Oxam_2Cr^{III}(Oxam)Co^{II}Oxam_2(I)$	−5	3	12.0328	3.0301	7.01	5.26	7.01	–
$Oxam_2Cr^{III}(Oxam)Co^{II}Oxam_2(II)$	−5	3	12.0290	3.0284	0.82	0.62	0.82	–
$HA_2Cr^{III}(HA)Co^{II}HA_2$	−5	3	12.0295	3.0278	3.13	2.35	3.13	–
$Ox_2Cr^{III}(Ox)Co^{II}Ox_2$	−5	3	12.0284	3.0269	5.09	3.82	5.09	1.8 [35]

the exchange interaction constant J between metals forming such complexes increases during the transition from 3d to 4d transition metals.

This assumption is based on an example with a complex containing a pair of metals Mo^{III}–Mo^{III}, for which the value of $J < 0$ is greater in absolute magnitude than in a complex containing a pair of Cr^{III}–Cr^{III} [39]. This can be explained by the greater diffusivity of the 4d Mo shell, compared to the 3d Cr shell. It is natural to assume that even at $J > 0$, the values of J would increase for atoms of other metals during the transition from 3d to 4d metals, and possibly to 5d metals. This is especially interesting in relation to complexes I, optimal for modeling a magnetic lattice, as mentioned earlier. In this regard, we performed calculations of complexes I for metal pairs, including M_1 = Cr, Mo; M_2 = Ni, Co, Tc, Ru, Rh, Pd, with dithiooxamide and oxalate [38].

We will briefly describe the methodology of our calculations in this and subsequent papers. The geometric structure of the complex anions I was calculated using the GAUSSIAN-03 program in the B3LYP/LANL2DZ approximation with optimization of the geometric parameters of the complex for the maximum value of the spin multiplicity corresponding to its ground state. Then, with the geometry obtained in the B3LYP/TZV approximation, the constant J and the SD in these complex anions were calculated according to the ORCA program.

Complexes with Pd are designed for its HS state. It is believed [40] that Pd is usually in a low spin state and is diamagnetic. It was interesting to model its magnetic properties for an HS state by analogy with the spin states of other metals of this series. Our calculation of the [DiSOx$_2$ Cr^{III}DiSOxPd^{II}DiSOx$_2$]$^{5-}$complex for the low-spin Pd state in the same approximation as for the HS state showed that its total energy is less advantageous by 6.53 kcal/mol compared to the total energy of the same HS complex.

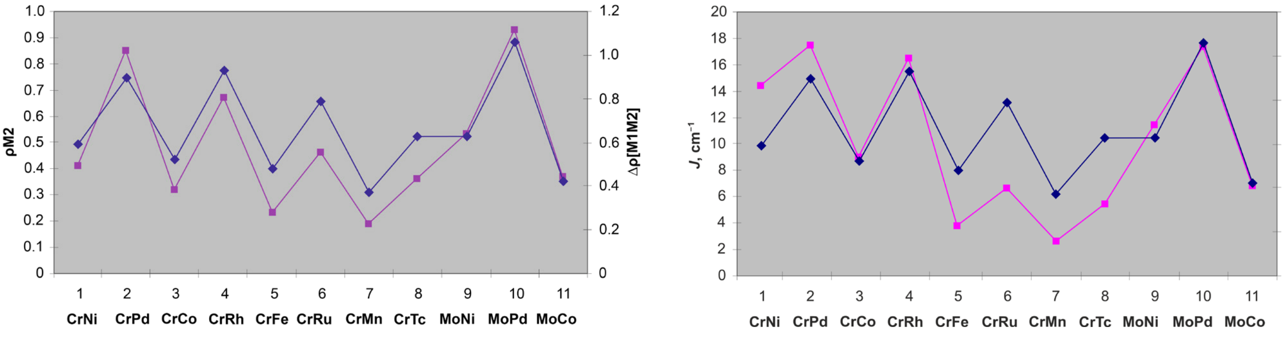
Table 2. Values of the exchange interaction constant J (cm^{-1}), energies of the complex in the high-spin (S_{max}) state (E_{HS}) and broken-symmetry state (E_{BS}) (a.u.), calculated using the ORCA program in the approximation B3LYP/TZV, Ox is oxalate, DiSOx is dithiooxamide [38]

$[L_2M1^{III}LM2^{II}L_2]^{5-}$	E_{HS}	E_{HS}	S_{max}	J
		L = DiSOx		
$\mathrm{Cr^{III}{-}Ni^{II}}$	−7469.309739	−7469.309344	5/2	14.42
$\mathrm{Cr^{III}{-}Pd^{II}}$	−10901.226790	−10901.226312	5/2	17.46
$\mathrm{Cr^{III}{-}Co^{II}}$	−7343.774151	−7343.773785	3	8.92
$\mathrm{Cr^{III}{-}Rh^{II}}$	−10649.077525	−10649.076847	3	16.52
$\mathrm{Cr^{III}{-}Fe^{II}}$	−7224.704428	−7224.704222	7/2	3.78
$\mathrm{Cr^{III}{-}Ru^{II}}$	−10404.686713	−10404.686350	7/2	6.64
$\mathrm{Cr^{III}{-}Mn^{II}}$	−7112.017316	−7112.017139	4	2.59
$\mathrm{Cr^{III}{-}Tc^{II}}$	−10167.887799	−10167.887428	4	5.43
$\mathrm{Mo^{III}{-}Ni^{II}}$	−10402.537096	−10402.536783	5/2	11.42
$\mathrm{Mo^{III}{-}Pd^{II}}$	−13834.344788	−13834.344315	5/2	17.29
$\mathrm{Mo^{III}{-}Co^{II}}$	−10276.884624	−10276.884348	3	6.75
		L = Ox		
$\mathrm{Cr^{III}{-}Ni^{II}}$	−4438.630797	−4438.630570	5/2	8.31
$\mathrm{Cr^{III}{-}Pd^{II}}$	−7870.426056	−7870.425737	5/2	11.68
$\mathrm{Cr^{III}{-}Co^{II}}$	−4313.084500	−4313.084500	3	5.09
$\mathrm{Cr^{III}{-}Rh^{II}}$	−7618.362167	−7618.361861	3	7.47
$\mathrm{Cr^{III}{-}Fe^{II}}$	−4194.030180	−4194.030027	7/2	2.80
$\mathrm{Cr^{III}{-}Ru^{II}}$	−7373.977893	−7373.977694	7/2	3.64
$\mathrm{Cr^{III}{-}Mn^{II}}$	−4081.347112	−4081.346974	4	2.01
$\mathrm{Cr^{III}{-}Tc^{II}}$	−7137.188425	−7137.188211	4	3.13
$\mathrm{Mo^{III}{-}Ni^{II}}$	−7371.736998	−7371.736806	5/2	7.04
$\mathrm{Mo^{III}{-}Pd^{II}}$	−10803.531705	−10803.531433	5/2	9.97
$\mathrm{Mo^{III}{-}Co^{II}}$	−7246.190992	−7246.190797	3	4.76

It follows from Table 2, obtained in [38], that in complexes with dithiooxamide and oxalate anion, the maximum values of the constant *J* occur in a complex containing a pair of metals $Cr^{III}–Pd^{II}$. Moreover, for complexes with dithiooxamide and oxalate anions as ligands, the values of the constant *J* decrease in the series $J(Cr^{III}–Pd^{II}) > J(Cr^{III}–Rh^{II}) > J(Cr^{III}–Ru^{II}) > J(Cr^{III}–Tc^{II})$. Thus, for 4d metals, during the sequential transition from Tc^{II} to Pd^{II} with the same trivalent 3d metal atom, the ferromagnetic properties of complexes I, and hence the properties of the magnetic sublattice formed by these complexes, are enhanced. Table 2 shows $J(Cr^{III}–Pd^{II}) \approx J(Mo^{III}–Pd^{II})$ in complexes with dithiooxamide, which indicates a slight change in the constant *J* when replacing a trivalent 3d metal atom with a trivalent 4d metal atom. Approximately the same ratio holds with the oxalate ligand. It was also shown in [38] that the replacement of a divalent 3d metal atom with a divalent 4d metal atom leads to an increase in *J*. Thus, together with the established regularity about an increase in the constant *J* during the transition from Tc^{II} to Pd^{II}, we confirmed and clarified the assumption about an increase in the constant *J* during the transition from 3d metal atoms to 4d metal atoms.

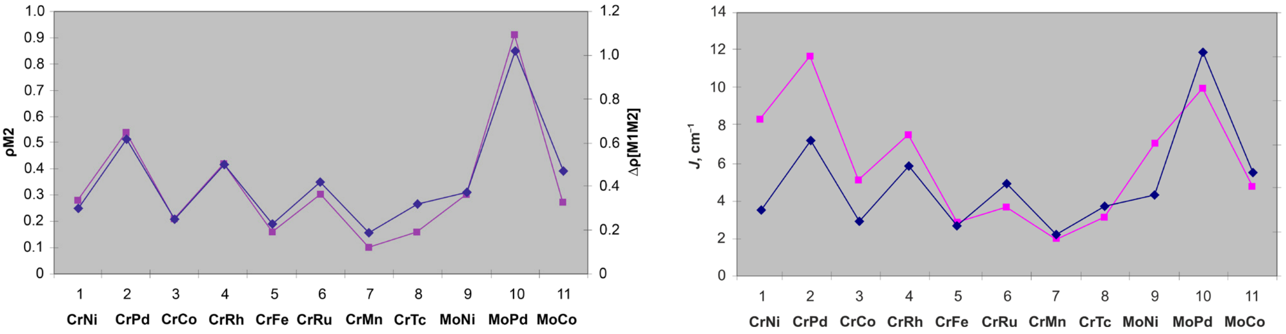
Based on these results, it was concluded in [38] that in the magnetic sublattice of bifunctional materials, an increase in the ferromagnetic exchange interaction should be expected during the transition from divalent 3d metal atoms to divalent 4d metal atoms.

The SD distribution on metal atoms in the complexes under consideration was analyzed in comparison with their isolated $M1^{3+}$ and $M2^{2+}$ cations. We also examined changes in SD depending on the M1 and M2 metals and L ligands included in the complex. Concepts such as ρM1 and ρM2 (the sum of SDs on the atoms of the coordination sphere of tri- and divalent metals, respectively) and Δρ[M1M2] (the total change in SD on the M1 and M2 atoms compared with isolated $M1^{3+}$ and $M2^{2+}$ cations) were also introduced. A clear correlation was shown between ρM2 and Δρ[M1M2], as well as between the constant *J* and Δρ[M1M2] for both ligands. This correlation is shown in Figs. 5 and 6.



(a) (b)

Fig. 5. Correlations in I complexes with dithioxamide L = DiSOx [38]: (a) ρM2 (red line) and Δρ[M1M2] (blue line), (b) constants *J* (red line) and Δρ[M1M2] (blue line).



(a) (b)

Fig. 6. Correlations in I complexes with oxalate L = Ox [38]: (a) ρM2 (red line) and Δρ[M1M2] (blue line), (b) constants *J* (red line) and Δρ[M1M2] (blue line).

It was concluded that a ligand could be regarded as a SD conductor when it flows from one atom of one metal to another during complex formation. The greater this overflow, the greater the constant of exchange interaction between them, and the more pronounced the magnetic properties. This circumstance clarifies the physical meaning of the constant of exchange interaction.

Our recent study continues the search for metal pairs providing maximum ferromagnetic exchange interaction in complexes modeling the magnetic sublattice of bifunctional materials [41]. The aim of this work was to further expand the range of transition metals, which provide the maximum value of *J*. In order to do this, we performed calculations of type I complexes and metal pairs containing M1 = Mo; M2 = Mn, Fe, Tc, Ru, Rh and Pd with a dithiooxamide ligand. This is most effective in providing the maximum value of *J*, as shown above. We have now considered not Cr, but Mo as a trivalent metal. The calculations were performed in the same approximation as in previous works. The settlement procedure also remained the same: the hexametric structure of complex anions I was calculated using the GAUSSIAN-03 program. This was done in the B3LYP/LANL2DZ approximation with optimization of the geometric parameters of the complex for the maximum value of the spin multiplicity corresponding to their basic energy state. Then, with the geometry obtained in the B3LYP/TZV approximation, the constant *J* and the SD in these complex anions were calculated using the ORCA program.

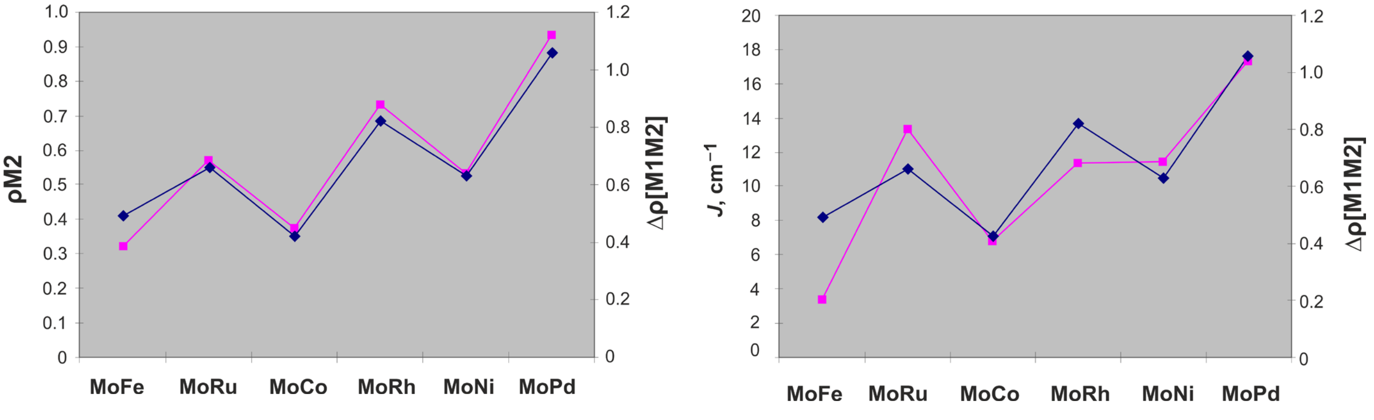
The values of the exchange interaction constant *J* (cm^{-1}) calculated in [41], the energy of complexes in the HS state (E_{HS}) and the BS state (E_{BS}) (a.u.), the HS state (S_{max}) are given in Table 3.

Table 3 shows that the maximum values of *J* take place in complex with MoIII–PdII. In addition, the value of *J* increases during the transition from Fe^{II} to Pd^{II}, i.e., when moving along the period from left to right, similar to the complexes considered in the previous work. Thus, for 4d metals, the ferromagnetic properties of complexes I increase during transition from FeII to PdII without changing the trivalent atom of the 4d metal. At the same time, the values of *J* also increase when moving along the subgroup from top to bottom. It can be said that the values of the exchange interaction constant increase as one moves from left to right and from top to bottom on the Periodic table. Thus, we managed to determine the area of the Periodic table with the maximum values of the constant *J*. This conclusion may be useful to synthetic chemists in selecting components for the synthesis of a magnetic sublattice of bifunctional materials.

Analysis of the Mulliken SD distribution on metal atoms in complexes compared to isolated cations by a trivalent and a divalent cation showed the presence of correlations similar to those obtained in the previous work. There is a correlation between ρM2 and Δρ[M1M2], as well as the correspondence of Δρ[M1M2] to the value of *J* (Fig. 7).

Table 3. Calculated values of the exchange interaction constant *J* (cm^{-1}), the energy of complexes in the HS state (E_{HS}) and the BS state (E_{BS}) (a.u.), and the HS state (S_{max}) [41]

$[L_2M1^{III}LM2^{II}L_2]^{5-}$	E_{HS}	E_{BS}	S_{max}	*J*
$Mo^{III}–Fe^{II}$	−10157.92816	−10157.92798	7/2	3.27
$Mo^{III}–Ru^{II}$	−13337.79223	−13337.79150	7/2	13.34
$Mo^{III}–Co^{II}$	−10276.88462	−10402.53678	3	6.75
$Mo^{III}–Rh^{II}$	−13582.18732	−13582.18685	3	11.32
$Mo^{III}–Ni^{II}$	−10402.53710	−10402.53678	5/2	11.42
$Mo^{III}–Pd^{II}$	−13834.34479	−13834.34432	5/2	17.29



(a) (b)

Fig. 7. Correlation on M1 and M2 atoms in I complexes compared with SD on isolated cations—trivalent M1 and divalent M2 [41]: (a) ρM2 (red line) with total change in SD Δρ[M1M2] (blue line), (b) constant *J* (red line) with total change SD Δρ[M1M2] (blue line).

It can be concluded that here, too, the ligand plays the role of a SD conductor when redistributed from one metal atom to another as a result of complex formation. The greater the redistribution, the greater the exchange constant between the atoms. This fact illustrates another aspect of the physical significance of the exchange constant interaction.

CONCLUSIONS

In this way, our research has given a visual meaning to the physical significance of the exchange interaction constant: it determines the SD change on metals forming complexes of the type under consideration during the transition from isolated cations to them as part of complexes. Recommendations can be given to synthetic chemists for the selection of components in the synthesis of magnetic sublattices of bifunctional materials.

Throughout the development of quantum chemistry, from its emergence as an independent branch of physical chemistry and quantum mechanics to the present day, research by Russian scientists has been in line with the most important areas of science. In terms of their level, they were no inferior to foreign studies and continue to be popular. This is evidenced by publications in leading scientific journals and regular invitations to participate in major international forums.

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About the author:

Konstantin V. Bozhenko, Dr. Sci. (Chem.), Professor, Leading Researcher, Federal Research Center of Problems of Chemical Physics and Medical Chemistry, Russian Academy of Sciences (1, Akademika Semenova pr., Chernogolovka, Moscow oblast, 142432, Russia). E-mail: bogenko@icp.ac.ru. Scopus Author ID 57211719875, ResearcherID D-5219-2019, RSCI SPIN-code 3355-4370, http://orcid.org/0000-0002-5786-5297

Об авторе:

Боженко Константин Викторович, д.х.н., профессор, ведущий научный сотрудник, ФГБУН Федеральный исследовательский центр проблем химической физики и медицинской химии Российской академии наук (142432, Россия, Московская обл., г. Черноголовка, пр. академика Семёнова, д. 1). E-mail: bogenko@icp.ac.ru. Scopus Author ID 57211719875, ResearcherID D-5219-2019, SPIN-код РИНЦ 3355-4370, http://orcid.org/0000-0002-5786-5297

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RESEARCH ARTICLE

Structure of 2-nitro-2’-hydroxy-5’-methylazobenzene: Theoretical and spectroscopic study

Anastasiya A. Fedorova, Olga V. Lefedova, Sergey A. Shlykov✉

Ivanovo State University of Chemistry and Technology, Ivanovo, 153000 Russia
✉*Corresponding author, e-mail: lnw94@yandex.ru*

Abstract

Objectives. *2-Hydroxy-nitroazobenzenes comprise reagents for the synthesis of heteroaromatic compounds, in the molecules of which the benzene and azole cycles are annulated. These reagents are widely used in the production of chemical products for various industries. In particular, 2-2’-hydroxy-5’-methylphenylbenzotriazole is used as an effective photo stabilizer for polystyrene and polyethylene. A promising method for its preparation is the liquid-phase catalytic hydrogenation of 2-nitro-2'-hydroxy-5'-methylazobenzene (2NAB). The aim of the present study was to establish the structure of 2NAB in solutions of different composition.*

Methods. *Theoretical calculations were carried out within the framework of the density functional theory at a temperature of 298.15 K for the gas phase at B3LYP/6-311++G(d, p) and M06-2X/6-311++G(d, p) levels; for hexane, 2-propanol, toluene at B3LYP/6-311++G(d, p) level using the conductor-like polarizable continuum model. An experimental study to determine the probable isomeric structure of 2NAB in various solvents, including sodium hydroxide (NaOH) and acetic acid (CH_3COOH) additives, was carried out using infrared (IR) and ultraviolet (UV) spectroscopy.*

Results. *The most probable structure of 2NAB isomers for the gas phase and a number of solvents was determined. Experimental and theoretical IR and UV spectra were obtained. The thermodynamic characteristics of the reaction of intramolecular proton transfer from –OH to –N=N– group in the gas phase were calculated.*

Conclusions. *A comparison of the experimental and calculated results supports the conclusion that the cis-isomer should be considered most probable for the gas phase. For the studied solutions, a trans-isomer of 2NAB with hydrogen bonds formed between the hydroxyl group hydrogen and the β-nitrogen atom of the azo group of dye molecule should be considered as the most likely structure. In the studied individual and binary solvents, prototropic equilibrium is shifted towards the azo form of the dye, while intramolecular proton transfer is possible only in aqueous diethylamine and dimethylformamide solutions with additions of NaOH.*

Keywords: *2-nitro-2'-hydroxy-5'-methylazobenzene, intramolecular proton transfer, hydrogen bond, IR spectroscopy, UV spectroscopy, quantum chemical calculations*

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НАУЧНАЯ СТАТЬЯ

Структура молекулы 2-нитро-2’-гидрокси-5’-метилазобензола: Теоретическое и спектральное исследование

А.А. Федорова, О.В. Лефедова, С.А. Шлыков✉

Ивановский государственный химико-технологический университет, Иваново, 153000 Россия
✉*Автор для переписки, e-mail: shlykov@isuct.ru*

Аннотация

Цели. *2-Гидроксинитроазобензолы – реагенты синтеза гетероароматических соединений, в молекулах которых аннелированы бензольный и азольный циклы, широко использующиеся при производстве химических продуктов для различных областей промышленности. В частности, 2-2’-гидрокси-5’-метилфенилбензотриазол используется в качестве эффективного фотостабилизатора полистирола и полиэтилена. Перспективным методом его получения является жидкофазная каталитическая гидрогенизация 2-нитро-2’-гидрокси-5’-метилазобензола (2НАБ). Целью нашей работы стало установление структуры 2НАБ в растворах различного состава.*

Методы. *Теоретические расчеты проводились в рамках теории функционала плотности при температуре 298.15 K для газовой фазы на уровнях B3LYP/6-311++G(d, p) и M06-2X/6-311++G(d, p), для гексана, 2-пропанола, толуола на уровне B3LYP/6-311++G(d, p) с использованием континуальной модели сольватации. Экспериментальное изучение предполагаемого изомерного строения 2НАБ в различных растворителях, в том числе с добавками гидроксида натрия (NaOH) и уксусной кислоты (CH_3COOH), проведено с помощью инфракрасной (ИК) и ультрафиолетовой (УФ) спектроскопии.*

Результаты. *Определена наиболее вероятная структура изомеров 2НАБ для газовой фазы и ряда растворителей. Получены экспериментальные и теоретические ИК-, УФ-спектры исследуемых веществ. Рассчитаны термодинамические характеристики реакции внутримолекулярного переноса протона от –ОН к –N=N– группе в газовой фазе.*

Выводы. *Сравнение экспериментальных и расчетных результатов позволило сделать заключение, что наиболее вероятным для газовой фазы следует считать цис-изомер, а для изученных растворов транс-изомер 2НАБ с водородными связями, образующимися между водородом гидроксигруппы и β-атомом азота азогруппы. В изученных индивидуальных и бинарных растворителях прототропное равновесие смещено в сторону азоформы красителя, а внутримолекулярный перенос протона возможен только в водных растворах диэтиламина и диметилформамила с добавками NaOH.*

Ключевые слова: *2-нитро-2'-гидрокси-5'-метилазобензол, внутримолекулярный перенос протона, водородная связь, ИК-спектроскопия, УФ-спектроскопия, квантово-химические расчеты*

***Для цитирования**:* Федорова А.А., Лефедова О.В., Шлыков С.А. Структура молекулы 2-нитро-2'-гидрокси-5'-метилазобензола: Теоретическое и спектральное исследование. *Тонкие химические технологии.* 2023;18(4):315–327. https://doi.org/10.32362/2410-6593-2023-18-4-315-327

INTRODUCTION

Nowadays, substituted nitrobenzenes are among the most widely-used multi-purpose compounds. Among this class of substances, 2-hydroxynitroazobenzenes occupy a special position, since forming the initial products for the synthesis of heteroaromatic compounds, in whose molecules the benzene and azole rings are annulated. Substituted 2*H*-benzotriazoles are used as effective absorbers of ultraviolet (UV) light, light stabilizers of polymers, and analytical reagents for a number of cations. As such, they are used as additives to increase the light resistance of dyes, pigments, and enamels, for obtaining complex compounds with metals, and in other areas [1–8].

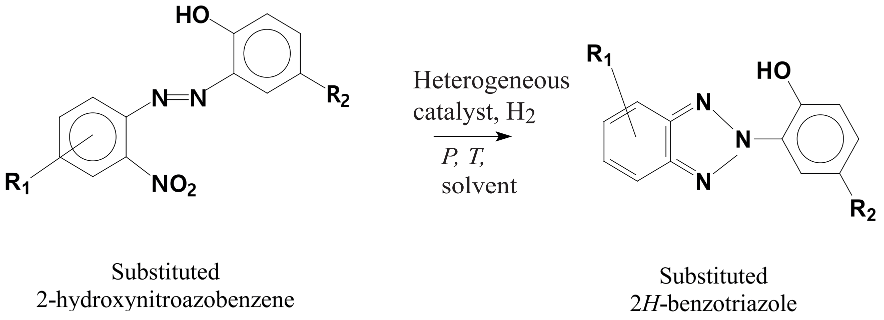
The main method for the preparation of substituted benzotriazoles remains the chemical reduction of the corresponding 2-hydroxynitroazobenzenes with zinc or hydrazine hydrate in an alkaline water–alcohol medium, or with dithionite in aqueous alkaline solutions [9, 10].

For the preparation of 2*H*-benzotriazoles, a promising method is liquid-phase hydrogenation of the corresponding 2-hydroxynitroazobenzenes. The latter contain nitro and azo groups that actively interact with hydrogen under hydrogenation conditions to form a triazole cycle (Scheme 1).

The selectivity of reductive cyclization under hydrogenation conditions is largely determined by the structure of the starting compound [11, 12]. In this regard, there is a need to have the most complete possible information about the electronic and spatial structure of 2-hydroxynitroazobenzenes, which subsequently determine the whole variety of chemical transformations.

In the present work, 2-nitro-2'-hydroxy-5'-methylazobenzene (2NAB) was chosen as the object of study. Comprising the starting compound for the synthesis of an effective photostabilizer of polystyrene and polyethylene, 2-(2'-hydroxy-5'-methylphenyl)benzotriazole (BT, Tinuvin®), it does not have any identified carcinogenic properties. Therefore, BT-stabilized films, in addition to other applications, can be used for food packaging.

It is known that azo dyes can exist in various tautomeric forms. For the 2NAB molecule, due



Scheme 1. Method for the preparation of substituted *2H*-besotriazoles.

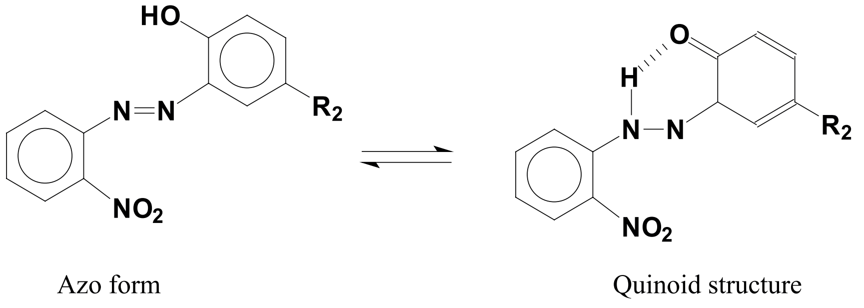
to the presence of a proton-donor hydroxyl group and its close spatial arrangement to the azo group, the possibility of intramolecular proton transfer (that is, prototropic equilibrium) can be assumed (Scheme 2).

Therefore, when considering the structure of 2NAB, it is necessary to take into account the possibility of the formation and presence of quinoid structures in the reaction mixture, as well as to calculate the thermodynamic characteristics of a possible process of intramolecular proton transfer.

MATERIALS AND METHODS

The calculations based on density functional theory for a gas phase at a temperature of 298.15 K were carried out using the Gaussian03 software package (*Gaussian Inc.*, USA) [13]. The Becke–Lee–Yang–Parr (B3LYP) density functional was primarily used. The 6-311++G(d, p)[1] basis set, having proven itself well in calculations of complex organic compounds, was selected. A number of calculations were carried out using the M06-2X[2] functional (high-nonlocality functional with double the amount of nonlocal exchange (2X)) and the conductor-like polarizable continuum model (cpcm). The ChemCraft[3] software (Russia) was used to visualize the calculation results and prepare initial approximations for subsequent geometry optimization.

In order to search for probable conformers for the 2NAB molecule, we scanned the C–C–N=N rotation angle of the nitrobenzene ring with respect to the –C–N= bond in the 2NAB molecule with a step of 10° at the B3LYP/6-311++G(d, p) level. Examples of scan results are shown in Fig. 1. Next, the rotation angles of the functional groups relative to the benzene rings were scanned at steps of 10° for the established configurations of conformers with different mutual positions of the $–NO_2$ and –OH groups (*cis*- and *trans*-). No new conformers were found.



Scheme 2. Eautomerism for the 2-nitro-2’-hydroxy-5’-methylazobenzene molecule.

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[1] 6-311++G(d, p) is a triple valence-split basis with diffuse functions on heavy atoms and hydrogen atoms and with the addition of d-type polarization functions for each atom from Li to Ca and p-type polarization functions for each light atom (H, He).

[2] The M06-2X functional, a hybrid meta-functional including 54% of the Hartree–Fock exchange, is one of the most accurate empirical functionals for working on mismatched electron density.

[3] Zhurko G.A. Chemcraft – graphical program for visualization of quantum chemistry computations. Ivanovo, Russia, 2005. Version 1.8, build 654. https://www.chemcraftprog.com. Accessed August 08, 2023.

Further, the structures corresponding to configurations with the lowest energies were completely optimized, the bond vibration frequencies were calculated, and infrared (IR) and UV spectra were modeled. In order to calculate the energy of an intramolecular hydrogen bond (IMHB), the structures of isomers that do not form hydrogen bonds due to the rotation of the –OH group by 180° relative to the –N=N– bond were optimized. The geometry of quinoid forms was determined for all obtained 2NAB conformers to evaluate the energy barriers and thermodynamic characteristics of proton transfer from the –OH group to the α or β nitrogen atoms of the azo group. The structure of transition states was established using quadratic synchronous transit (QST2 and QST3) methods and confirmed using the internal reaction coordinate procedure. The found structures of transition states were verified by establishing the first imaginary vibrational frequency corresponding to the transition of the hydrogen atom from the hydroxy group to the azo group.

The experimental IR spectrum of 2NAB molecules was obtained on potassium bromide (KBr) tablets using an Avatar 360 ESP spectrophotometer (*Nicolet Instrument Corporation*, USA). The spectrum was recorded using the built-in program and automatic recording of peaks in a frequency range of 400–4000 cm^{-1}. The preparation of the control sample and analysis sequence followed the standard procedure.

UV spectral studies were carried out with the use of a Leki SS2110 UV spectrophotometer (*Mediora OÜ*, Finland) in the wavelength range of 220–450 nm. Hexane, which does not exhibit specific solvation, was used in the preparation of a 2NAB solution, along with solvents used in liquid-phase hydrogenation reactions. The measurements were carried out with respect to the pure solvent at an absorbing layer thickness of 1 cm using quartz cuvettes. The wavelengths corresponding to the absorption maxima were obtained mathematically processing the obtained spectral curves using the accompanying software. The preparation of control solutions and the sequence of analysis followed the standard procedure.

RESULTS AND DISCUSSION

Geometry and thermodynamic calculations

Scanning of the rotation angles of the functional groups relative to the benzene rings in the 2NAB molecules showed that the 2NAB molecule can be in a state of *cis-trans* isomerism with a high probability of having an IMHB between the α or β nitrogen atom of the azo group and the hydrogen atom of the hydroxy group, which are in the *ortho* position relative to each other.

The results of quantum chemical calculations for possible spatial structures of 2NAB isomers with and without hydrogen bonds for transition states corresponding to the transfer of a proton from the hydroxy group to the α or β nitrogen atom of the azo group are given together with the quinoid structures in Tables 1–3 and in Figs. 1 and 2.

The calculations show a significant difference in ground state energies for different isomers: up to a value of 15.33 kJ/mol in calculations using B3LYP and 12.3 kJ/mol in calculations using M06-2X.

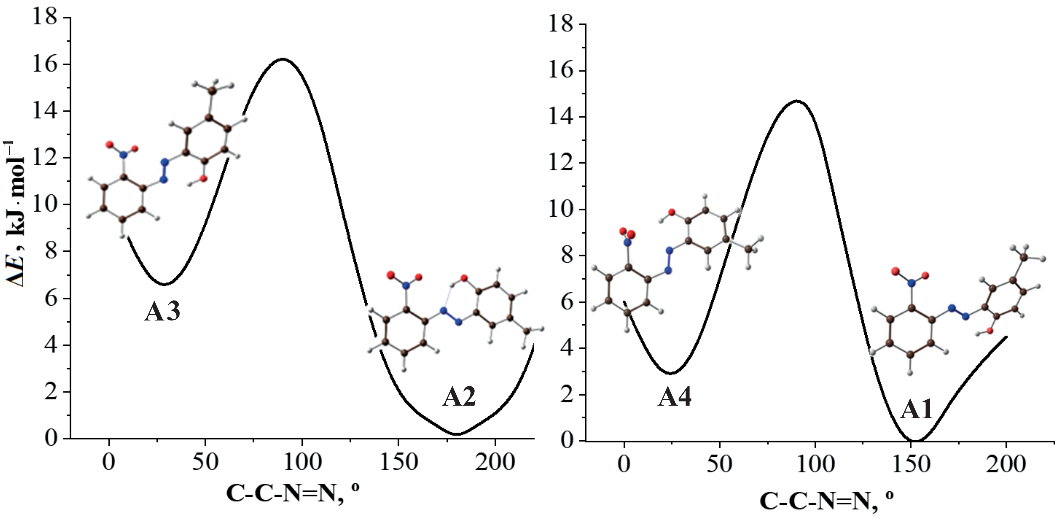


Fig. 1. Potential energy surface profiles obtained by scanning the rotation angle –C–C–N=N– of the nitrobenzene ring about the –C–N= bond in the 2-nitro-2'-hydroxy-5'-methylazobenzene (2NAB) molecule with a step of 10° at B3LYP/6-311++G(d, p) level. Relative energies of conformers are given in Table 1.

Table 1. Calculated relative energies ΔE of possible structures of 2NAB, barriers E_a, enthalpies ΔH^o_{298}, Gibbs free energies ΔG^o_{298} (kJ/mol) of intramolecular proton transfer from –OH to –N=N– group, and imaginary frequencies ν_i (cm^{-1}) for transition states (TS).

Isomer/state[a]		**IMHB**[a]	**B3LYP/6-311++G (d, p)**					**M06-2X/6-311++G (d, p)**				
			ΔE^{b}	E_a	ΔH^o_{298}	ΔG^o_{298}	ν_i	ΔE^{c}	E_a	ΔH^o_{298}	ΔG^o_{298}	ν_i
Trans	**A1**	α	16.2	71.7	42.2	44.05	1596	12.3	93.4	69.6	71.0	1443
	A`1	–	39.3					32.7				
	TS1	α	87.9					105.7				
	B1	α	58.8					82.3				
Cis	**A2**	β	3.5	15.8	−3.94	−2.54	1515	0.00	25.4	9.95	10.0	1421
	A`2	–	51.1					46.6				
	TS2	β	19.3					25.4				
	B2	β	0.00					10.2				
Trans	**A3**	β	10.5	15.2	6.60	7.49	1454	8.6	4.6	19.3	20.2	1335
	A`3	–	54.9					48.0				
	TS3	β	25.8					13.3				
	B3	β	17.2					28.0				
Cis	**A4**	α	18.8	79.3	48.2	50.6	1600	11.0	101	76.3	74.8	1478
	A`4	–	47.5					40.9				
	TS4	α	98.1					111.8				
	B4	α	67.6					87.2				

Note: [a]IMHB – intramolecular hydrogen bond; **A** – azo form with IMHB; **A`** – azo form without IMHB; **TS** – transition state for the reaction of intramolecular proton transfer; **B** – quinoid structures formed in the reaction of intramolecular proton transfer; numbers **1**, **2**, **3**, **4** correspond to the isomers with different position of –OH and $–NO_2$ groups regarding to –N=N– bond or without H-bond with different N atoms (α or β) in the azo group.

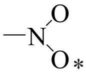
[b]ΔE – energies of the structures relative to that of **B2**.

[c]ΔE – energies of the structures relative to that of **A2**.

Table 2. Characteristics of the hydrogen bond for different conformers of 2NAB for the gas phase

Isomer/state	**IMHB (atom –N=N–)**	E_{IMHB}**, kJ/mol**			**Bond length, Å**		
		B3LYP	**M06-2X**	**[14]**	**B3LYP**	**M06-2X**	**[14]**
Trans	α	23.2	20.4	16.74–62.76	2.14	2.16	1.50–2.20
Cis	β	47.6	46.6		1.81	1.87	
Trans	β	44.4	39.3		1.77	1.82	
Cis	α	28.7	29.9		2.21	2.22	

Table 3. Frequencies in the IR spectrum of 2NAB

Group	*ν*, cm^{-1}				
	B3LYP/6-311++G (d, p)				Experiment
	A2	A\`2	A3	A\`3	
–OH	3361	3758	3322	3756	3410
 *	1580	1586	1594	1591	1618
–N=N–	1540	1555	1543	1554	1525
>CH–NO_2	1374	1385	1394	1394	1348
>CH–OH	1158	1143	1158	1148	1147

* The stretching vibrations of the N–O bond in the NO_2 group are given.

This indicates a high probability of the existence of the **A2** *cis* isomer in the gas phase, as well as a low probability of the presence of the **A3** structure. However, in solvents used in the processes of liquid-phase catalytic hydrogenation of nitro compounds, it is possible to expect a redistribution proportion of **A2** and **A3** conformations in the reaction mixture due to the presence of solvation interactions and a certain structuring of the medium.

It can be concluded from the data in Table 1 that the presence of IMHB with the β nitrogen atom of the azo group, in comparison with that of the α atom, lowers the energy of the ground state to a greater extent both for the *cis* and *trans* isomers. In both cases, the formation of an IMHB contributes to the stabilization of the molecule and the growth of its coplanarity. Calculation of the ΔG^{o}_{298} reaction for the formation of a quinoid structure using the B3LYP and M06-2X functionals showed somewhat different results. The calculation with the B3LYP functional indicates the possibility of quinone formation in the gas phase only in the case of the **A2** isomer; this is because the process of proton transfer with the formation of **B2** is characterized by a low energy barrier. The calculation with the M06-2X functional showed that quinones are not formed regardless of the conformer structure.

A comparison of the IMHB energies for the *cis* and *trans* isomers with the β and α nitrogen atoms of the azo group, calculated from the difference in the energies of the ground state of the corresponding isomers with and without hydrogen bonds (Table 2), shows that they differ by more than 1.5 times. According to the classification [14], the resulting hydrogen bond should be classified as moderately strong with a significant contribution from the electrostatic component. It can be assumed that the IMHB between the hydroxy group proton and the β nitrogen atom of the azo group will also be preserved in the presence of a solvent [11].

Spectra

To select the structure of the 2NAB isomer, whose presence is most likely for the liquid phase, the experimental IR or UV spectra can be used in protic and aprotic solvents (Tables 3, 5, and Fig. 3). Table 3 shows the vibrational frequencies for 2NAB corresponding to the structures of **A2** and **A3** isomers with and without hydrogen bonds.

In our opinion, the comparison of the experimental and theoretical values of vibration frequencies given in Table 3 does not suggest that the **A2** isomer is preferable. It should be emphasized that, in the experimental IR spectrum of 2NAB, there are no characteristic frequencies in the regions of 1570 and 1690 cm^{-1} that correspond to the >C=O, >C=N, and >N–NH– bond vibration frequencies characteristic of the quinoid structure. Consequently, the prototropic equilibrium is shifted towards the 2NAB azo form [11].

Figure 3 shows the UV absorption spectra of 2NAB in hexane (Fig. 3c) in comparison with the calculated spectra of various 2NAB isomers in the gas phase (Figs. 3a and 3b). In the case of the **A3** isomer, the positions of the peaks can be seen to correspond exactly. Calculations within the framework of the M06-2X functional do not reproduce the general form of the experimental spectrum, that is, the position and intensity of electron transitions.

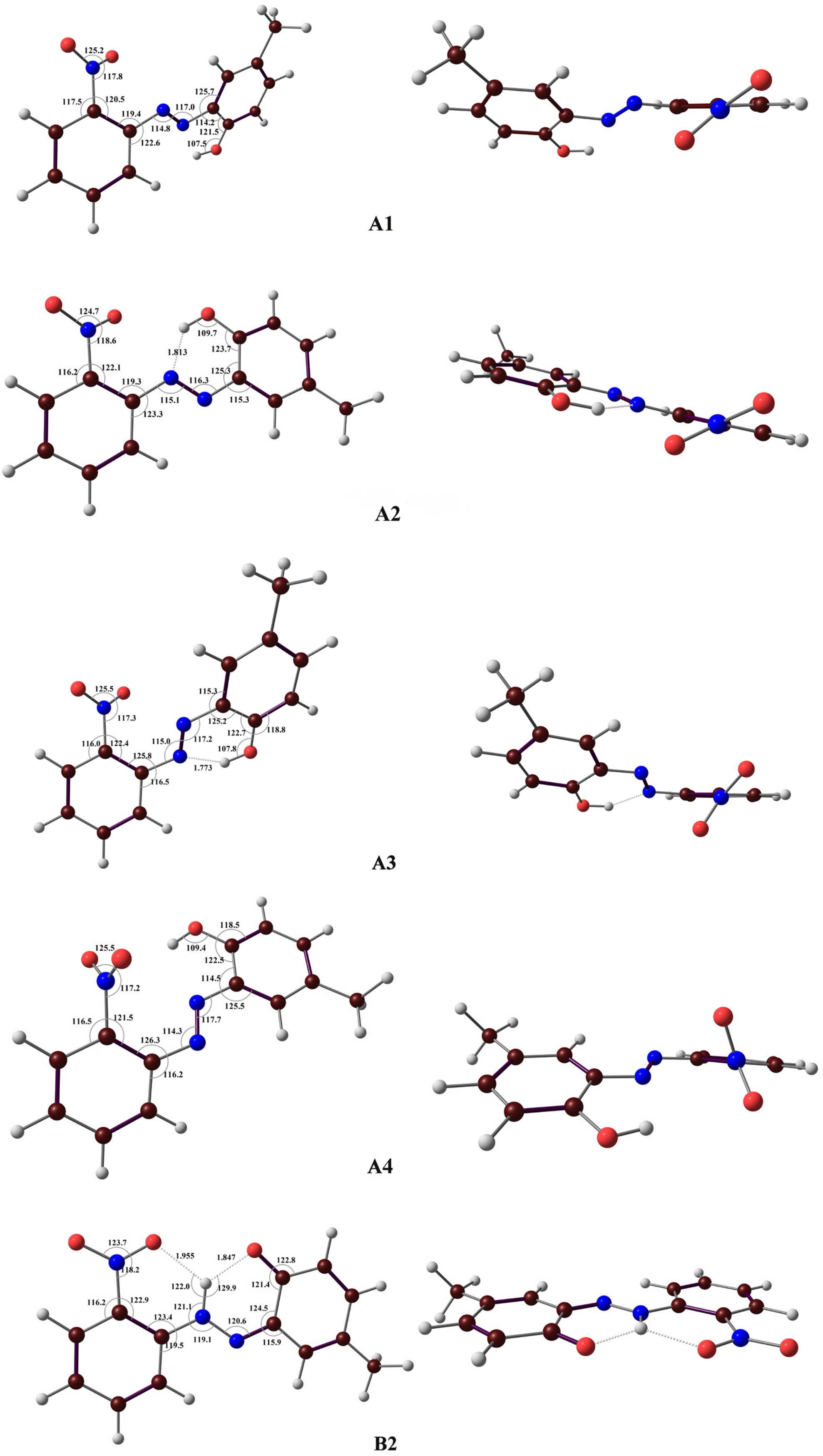
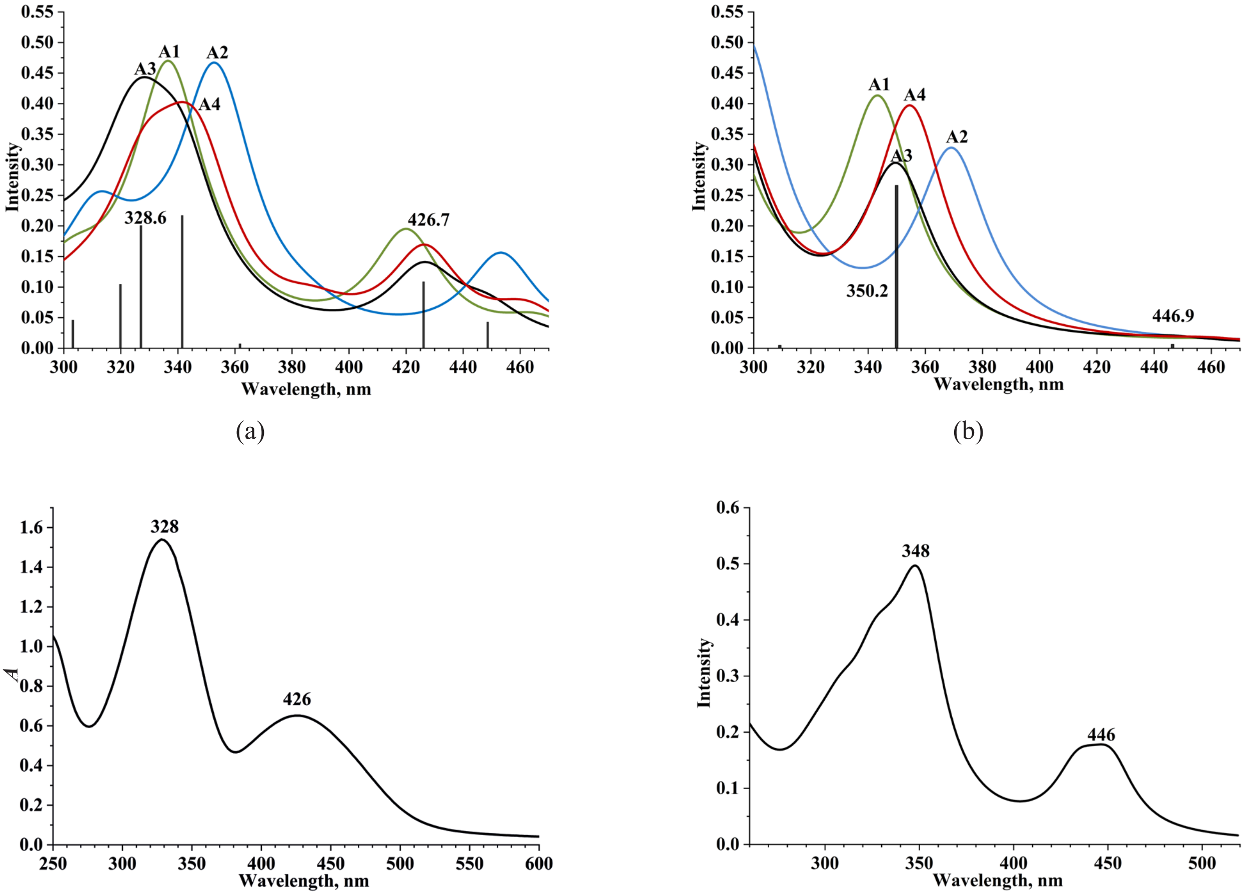


Fig. 2. Optimized structures of 2NAB conformers (B3LYP/6-311++G(d, p)) for the gas.



(a)

(b)

(c)

(d)

Fig. 3. UV absorption spectra of 2NAB: (a) B3LYP/6-311++G(d, p) calculations in the gas phase for the **A1**–**A3** isomers, the intensity and position of electron transitions are shown for isomer **A3**; (b) M06-2X/6-311++G(d, p) calculations for the **A1**–**A3** isomers in the gas phase; the intensity and position of electron transitions are shown for isomer **A3**; (c) experimental spectrum of 2NAB in hexane, where *A* is the optical density; (d) B3LYP/6-311++G(d, p) theoretical calculations for **A3** isomer in hexane in the CPCM model. For each theoretical spectrum (a, b, d), an approximation by a Lorentzian with a 30-nm halfwidth of the peak was performed.

To identify the 2NAB structure in solution, we carried out a complete reoptimization of **A2** and **A3** isomers geometry in the corresponding solvents within the CPCM framework and calculated the UV spectra. The results are presented in Table 4 and in Fig. 3d. It follows from the presented data that, just as in the gas phase, the closest wavelengths of the absorption maxima correspond to the **A3** isomer. For both isomers, a significant shift of the absorption maxima to the longwave region of the spectrum is observed.

The authors of a number of papers [11, 15] have noted that the transition of a proton from the hydroxy group to the azo group and the formation of the quinoid structure should make the UV absorption spectrum of 2NAB single-banded. In our experimental UV absorption spectra of 2NAB in hexane, toluene, 2-propanol, in its aqueous solutions, including those in the presence of base and acid additives, this is not observed (Tables 4 and 5). The position of the absorption maxima does not change even if sodium hydroxide in an aqueous solution of 2-propanol is present in an amount corresponding to the complete ionization of the molecule, i.e., at a ratio of 2NAB : NaOH = 1 : 1.42 or 2NAB : NaOH = 1 : 1.14. The authors of [11, 15] also state that hydroxy-substituted aromatic hydrocarbons can act as donors of a free electron pair with respect to alcohols in the formation of an IMHB as a result of specific solvation, and as acceptors with respect to dimethylformamide (DMF). However, the peak of the absorption maximum in the longwave region in both DMF and diethylamine (DEA), which are characterized by a high acceptor

Table 4. Wavelengths of absorption maxima λ_1 and λ_2 in the UV spectra of 2NAB in solution and molar extinction coefficients ε_1 and ε_2 in solvents

Sovent	$\lg\varepsilon_1^d$, L/(mol·cm)	λ_1, nm			$\lg\varepsilon_2^d$, L/(mol·cm)	λ_2, nm		
		Exp^d	B3LYP/6-311++G(d)				B3LYP/6-311++G(d)	
			A2	A3			A2	A3
n-Hexane	2.59	326	353	342	2.22	426	458	444
Toluene	3.85	326	357	349	3.67	424	461	448
2-Propanol	3.62	328	361	354	3.25	416	467	450

^{d}Experimental values.

capacity with respect to the proton, is also absent. This can be regarded as the fact that, in these solvents, IMHB in the 2NAB molecule is retained; moreover, there is no proton transfer from the hydroxy to the azo group.

The specific solvation of hydroxy-substituted aromatic hydrocarbons at the hydroxy group may characteristically not occur if strong IMHBs are formed, whose energy is higher than 20 kJ/mol [9, 11, 14–17]. The fact that the nitro group is not specifically solvated helps to reduce the universal component of solvation. The change in the thermochemical characteristics of solvation in organic solvents is associated mainly with the aromatic system and the delocalization of π-electrons.

Our experimental data (Table 5) indicate that, by only replacing individual solvents and water–2-propanol solvents by aqueous solutions or solutions in DMF and DEA with NaOH additives, a strong bathochromic shift occurs in the UV spectrum: the band at λ_2 = 414 nm disappears, and a new band appears in the region of 500 nm. According to [11, 15], the presence of an absorption band in the region of 480–550 nm indicates a shift in equilibrium from the azo form of the dye to its quinoid structure.

The authors of [11, 15, 18, 19] also note that substituted nitroazobenzenes are predominantly in the state of *trans* isomerism, especially when going to solvents with a high dielectric constant [18, 19]. The azo form in the UV absorption spectra is characterized by the appearance of a maximum at a wavelength of 320–350 nm, which is associated with π–π* transitions. The presence of an absorption maximum in the region of 420–440 nm indicates an increase in the common conjugation chain along with a higher electron density on the azo group due to its transfer from the phenyl ring [11, 15]. This absorption maximum is due to *n*–π* transitions, in which wavelength regions we noted the appearance of the corresponding maxima.

As noted in [11, 15], the weakening of the IMHB under the influence of a solvent will contribute to a convergence of the energy levels of nitrogen atoms of the azo group. This can also cause an increase in the contribution of orbital control [20] at the stage of associative addition of hydrogen to the azo group under hydrogenation conditions. This increases the contribution of the direction of 2NAB hydrogenation reaction through the formation of 2-nitro-2'-hydroxy-5'-methylhydrazobenzene (2NHB), as well as contributing to a decrease in the yield of products containing a triazole ring. Kinetic studies have proven that the concentration of NHB increases when the reaction is carried out in solvents with pronounced electron-donor properties [19]. At the same time, the ionization of the hydroxy group leads to the destruction of IMHB in the 2NAB molecule, thus increasing its coplanarity. This determines the possibility of simultaneous hydrogenation of both nitro and azo groups. It was experimentally confirmed [21, 22] that the transformation of 2NAB under hydrogenation conditions proceeds according to a parallel-sequential scheme. One of the parallel directions leads to the formation of products containing the triazole ring, while the second direction leads to the formation of the nitro-hydrazo derivative. The latter undergoes intramolecular rearrangement in the presence of sodium hydroxide to form a triazole ring.

When considering the possibility of cyclization of intermediate products formed upon 2NAB hydrogenation, the coplanarity of the considered 2NAB isomers should also be taken into account. From this point of view, cyclization of **A3** and

Table 5. Wavelengths of absorption maxima λ_1 and λ_2 in the UV spectra of 2NAB and molar extinction coefficients ε_1 and ε_2 for individual, binary, and mixed solvents

Sovent		λ_1, nm	$\lg\varepsilon_1$, L/(mol·cm)	λ_2, nm	$\lg\varepsilon_2$, L/(mol·cm)
Dimethylformamide (DMF)		333	3.94	413	3.86
Diethylamine (DEA)		333	3.83	413	3.81
Water–2-propanol	**x_2**	**λ_1**	**$\lg\varepsilon_1$**	**λ_2**	**$\lg\varepsilon_2$**
	0.26	328	1.30	410	0.93
	0.48	328	4.40	412	4.05
	0.68	328	3.62	414	3.25
	0.78	328	4.32	414	3.99
Water–2-propanol–NaOH $x_2 = 0.68$	**2NAB : NaOH**	**λ_1**	**$\lg\varepsilon_1$**	**λ_2**	**$\lg\varepsilon_2$**
	1 : 0.04	328	3.75	416	3.39
	1 : 0.29	328	3.85	414	3.49
	1 : 0.86	328	3.92	414	3.58
	1 : 1.42	328	3.75	414	3.39
	2NAB : CH_3COOH	**λ_1**	**$\lg\varepsilon_1$**	**λ_2**	**$\lg\varepsilon_2$**
	1 : 1.14	330	2.66	414	2.27
Water–NaOH	**C_{NaOH}, mol/L**	**λ_1**	**$\lg\varepsilon_1$**	**λ_2**	**$\lg\varepsilon_2$**
	0.01	330	2.22	496	2.23
	0.10	330	2.11	496	3.31
	1.00	330	3.30	496	3.30
DMF–NaOH	0.01	340	3.98	506	4.06
DEA–NaOH	0.01	345	3.83	516	3.99

A4 isomers can be considered as the most probable structure. Based on the results presented above, preference should be given to structure **A3** due to its higher coplanarity and the absence of a steric hindrance upon the formation of the triazole ring. The calculation of the potential barrier for the nitro group rotation around the C–N bond showed that it does not exceed 13.2 kJ/mol. This will tend to promote the formation of a cycle upon the redistribution of bonds in the associative 2NAB–hydrogen complexes formed under the conditions of 2-hydroxynitroazobenzene hydrogenation. It is also likely that the cyclization will proceed according to a synchronous mechanism of the "*head to head*" type due to the 2NAB molecule being characterized by the separation of charges that can move due to a high degree of conjugation [12, 20].

CONCLUSIONS

The experimental results and theoretical calculations of the 2NAB structures, which are in good agreement with each other, do not contradict our assumptions about possible tautomeric states of 2NAB molecules in solutions. On the basis of the totality of the obtained data, we can conclude that a *trans* isomer structure with a hydrogen bond formed between the hydrogen of the hydroxy group and the β-nitrogen atom azo groups of the dye is most probable for solutions in water, DMF, hexane, and toluene, as well as in water–2-propanol solvents with additions of NaOH and CH_3COOH. Intramolecular proton transfer is possible only in aqueous, DEA, and DMF solutions having additions of NaOH. The formation of quinoid structures is not characteristic of the other studied solvents or the gas phase.

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Authors’ contributions

A.A. Fedorova – conducting calculations, analyzing and systematizing the material, reviewing publications on the topic of the article, writing the text of the article;

O.V. Lefedova – carrying out the synthesis and analysis of compounds, IR spectroscopy, writing the text of the article;

S.A. Shlykov – analysis of the results, writing the text of the article, technical and scientific editing.

The authors declare no conflicts of interest.

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About the authors:

Anastasiya A. Fedorova, Cand. Sci. (Chem.), Associate Professor, Department of Physical and Colloidal Chemistry, Ivanovo State University of Chemistry and Technology (7, pr. Sheremetevsky, Ivanovo, 153000, Russia). E-mail: fedorova@isuct.ru. Scopus Author ID 57206167763, ResearcherID AAE-9416-2019, RSCI SPIN-code 7937-6964, http://orcid.org/0000-0002-2878-0454

Olga V. Lefedova, Dr. Sci. (Chem.), Professor, Department of Physical and Colloidal Chemistry, Ivanovo State University of Chemistry and Technology (7, pr. Sheremetevsky, Ivanovo, 153000, Russia). E-mail: physchem.606@yandex.ru. Scopus Author ID 6603866365, ResearcherID S-7806-2016, RSCI SPIN-code 5785-8474, http://orcid.org/0000-0001-8385-2732

Sergey A. Shlykov, Dr. Sci. (Chem.), Professor, Head of the Department of Physical and Colloidal Chemistry, Ivanovo State University of Chemistry and Technology (7, pr. Sheremetevsky, Ivanovo, 153000, Russia). E-mail: shlykov@isuct.ru. Scopus Author ID 7004449118, Researcher ID W-2154-2017, RSCI SPIN-code 9556-4775, http://orcid.org/0000-0003-4433-3395

Об авторах:

Федорова Анастасия Александровна, к.х.н., доцент кафедры Физической и коллоидной химии ФГБОУ ВО «Ивановский государственный химико-технологический университет» (153000, Россия, Иваново, Шереметевский пр., д. 7). E-mail: fedorova@isuct.ru. Scopus Author ID 57206167763, ResearcherID AAE-9416-2019, SPIN-код РИНЦ 7937-6964, http://orcid.org/0000-0002-2878-0454

Лефедова Ольга Валентиновна, д.х.н., профессор кафедры Физической и коллоидной химии ФГБОУ ВО «Ивановский государственный химико-технологический университет» (153000, Россия, Иваново, Шереметевский пр., д. 7). E-mail: physchem.606@yandex.ru. Scopus Author ID 6603866365, ResearcherID S-7806-2016, SPIN-код РИНЦ 5785-8474, http://orcid.org/0000-0001-8385-2732

Шлыков Сергей Александрович, д.х.н., заведующий кафедрой Физической и коллоидной химии ФГБОУ ВО «Ивановский государственный химико-технологический университет» (153000, Россия, Иваново, Шереметевский пр., д. 7). E-mail: shlykov@isuct.ru. Scopus Author ID 7004449118, ResearcherID W-2154-2017, SPIN-код РИНЦ 9556-4775, http://orcid.org/0000-0003-4433-3395

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RESEARCH ARTICLE

Analysis of phase trajectories for studying the operational evolution of catalytic systems

Alexander F. Schmidt✉, Anna A. Kurokhtina, Elizaveta V. Larina, Nadezhda A. Lagoda

Irkutsk State University, Irkutsk, 664003 Russia
✉Corresponding author, e-mail: aschmidt@chem.isu.ru

Abstract

Objectives. *To establish details of catalytic systems operation using the kinetic method with no needs for the differentiation of primary experimental kinetic data.*
Methods. *Analysis of the time patterns of differential selectivity and relative reactivity of substrates in parallel or competing reactions was used.*
Results. *For various coupling reactions of aryl halides and nucleophiles, the possibility to obtain the data about the evolution of the catalytic systems and patterns of the changes of catalytically active species under dynamic transformations of several active and inactive catalyst forms was demonstrated.*
Conclusions. *The analysis of the evolution of differential selectivity and relative reactivity under competing or parallel reactions is the useful tool for discrimination between probable hypotheses of complex catalytic process operation.*

Keywords: *kinetics, catalysis, palladium, differential selectivity, reaction mechanism*

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НАУЧНАЯ СТАТЬЯ

Анализ фазовых траекторий реакций в исследованиях эволюции функционирования каталитических систем

А.Ф. Шмидт✉, А.А. Курохтина, Е.В. Ларина, Н.А. Лагода

Иркутский государственный университет, химический факультет, Иркутск, 664033 Россия
✉Автор для переписки, e-mail: aschmidt@chem.isu.ru

Аннотация

Цели. *Определение деталей механизмов функционирования каталитических систем с помощью кинетического метода, не требующего дифференцирования первичных экспериментальных кинетических данных.*
Методы. *Анализ закономерностей изменения дифференциальной селективности и относительной реакционной способности субстратов в параллельных и конкурирующих реакциях во времени.*
Результаты. *На примерах различных реакций сочетания арилгалогенидов с нуклеофилами показана возможность получения данных об эволюции каталитических систем и закономерностях изменений природы каталитически активных соединений в условиях динамических превращений нескольких активных и неактивных форм катализатора.*
Выводы. *Эволюционный анализ величин дифференциальной селективности и относительной реакционной способности в ходе конкурирующих или параллельных реакций является эффективным инструментом дискриминации гипотез механизмов сложных каталитических процессов.*

Ключевые слова: *кинетика, катализ, палладий, дифференциальная селективность, механизм реакции*

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INTRODUCTION

In the 1960s, as a result of the intensive development of the chemistry of coordination compounds of transition metals, the scientific direction of liquid-phase catalysis of metal complexes was formed. This term was introduced by Academician I.I. Moiseev, one of the founders of this field of research, who made a huge contribution to its formation and development [1].

Today's chemical industry cannot be imagined without the use of catalysts based on transition metals [2, 3]. An obvious condition for the successful development of synthetic catalytic methods is the establishment of the regularities of catalyst transformations occurring over the course of the used processes. Since "no hypothesis of the mechanism can be considered as proven if it does not correspond to the observed kinetics of the process" [4], kinetic methods can be effectively used for studying the mechanisms of catalytic reactions.

A characteristic feature of reactions involving transition metal complexes is the so-called multirouteness, the concepts of which were developed in the works of I.I. Moiseev, O.N. Temkin, L.G. Brook *et al*. [5–8]. Multirouteness refers to the simultaneous occurrence of several processes coupled to each other with the participation of a catalyst. Kinetic studies with an analysis of the regularities determined in the so-called conjugation nodes of multipath reactions are an extremely effective tool for discriminating between probable hypotheses of the mechanisms of complex catalytic processes [5–8].

Among the kinetic methods for studying the mechanisms of catalytic reactions, approaches based on estimating the differential selectivity (DS) of a catalyst for a certain product as a parameter that does not depend on the concentration of active species can be singled out. This concentration is typically nonstationary and changes significantly during a catalytic reaction due to the course of formation-deactivation (poisoning) processes. However, when combined with the need to differentiate kinetic data to calculate the DS value as the ratio of product accumulation rates to the total rate of all processes involving a catalyst, the complexity of kinetic studies in general leads to the fact that DS is extremely rarely used in studies of reaction mechanisms. To overcome the described difficulties, a method was developed for estimating the DS value using the so-called phase trajectories, which require exclusively integral kinetic data [9, 10]. Subsequently, this approach, proposed for the first time to distinguish cases of catalysis of the Mizoroki–Heck and Suzuki–Miyaura cross-coupling reactions by dissolved palladium molecular complexes in solution or compounds in a heterogeneous phase [9], was developed for solving a wide range of problems related to the determination of the structure and composition of catalytically active compounds and mechanisms (stages) of their transformation inside and outside the main catalytic cycle in various catalytic processes [9–18].

In the present work, we attempted to demonstrate the possibilities of developing this approach for analyzing the genesis of a catalytic system in time using the example of a number of aryl halide coupling reactions catalyzed by Suzuki–Miyaura and Mizoroki–Heck palladium compounds, as well as in the direct arylation of heteroaromatic compounds.

PHASE TRAJECTORIES AS A TOOL FOR A COMPARATIVE INVESTIGATION OF RESPONSE OF THE REACTION TO CHANGING CONDITIONS

The originally proposed version of the analysis of phase trajectories in studies of the mechanisms of catalytic reactions assumed that the reaction was carried out under conditions of the so-called artificial multirouteness [5], i.e., when using several (at least two) similar competing substrates [9]. In this case, the concentrations of competing substrates or products formed from them (total concentrations of product groups) are plotted on the axes of phase trajectories. In this case, the slope of the phase trajectory at any of its points is the ratio of the rates of consumption of competing substrates or accumulation of the corresponding products, which unambiguously characterizes the DS value [10].

By comparing the phase trajectories of series of experiments carried out under varying process conditions, it is possible to obtain an unambiguous answer to the question of the effect or absence of the effect of variable parameters on the DS value. The principal advantage of the approach with the analysis of the DS of the reaction using phase trajectories consists in the possibility of its application under the conditions of a real catalytic process without involving the results of model (with the exclusion of one or several components of the reaction systems) and stoichiometric (at low substrate/catalyst ratios) experiments.

ANALYSIS OF THE EVOLUTION OF THE DS OF CATALYTIC REACTIONS

The above-described approach involves comparing phase trajectories in a series of experiments with different initial conditions. However, the analysis of an individual phase trajectory obtained in the course of one experiment can also be used in studies of the mechanisms of catalytic reactions, in particular, to study the transformation dynamics of the active catalyst during the reaction.

In the general case of the transformation of a pair of substrates competing for a common intermediate (Fig. 1a), the shape of the phase trajectory, which describes the change in the ratio of the rates of competing reactions with time, is different from linear. This is due to a change in the ratio of the concentrations of competing substrates during the reaction due to their different reactivity [10]. At the same time, if the phase trajectory is constructed from the concentrations of the products of not competitive, but parallel reactions (Fig. 1b), whose rate is determined solely by the reactivity and concentration of the common intermediate of the parallel reaction, the ratio of the accumulation rates of such products, provided that the nature of the common intermediate remains unchanged, should be constant during the reaction and, therefore, the phase trajectory must be strictly linear.

Situations of parallel reactions of catalytic cycle intermediates arise in reactions involving the formation of isomeric products (regioisomers, stereoisomers, enantiomers, etc.). Thus, the

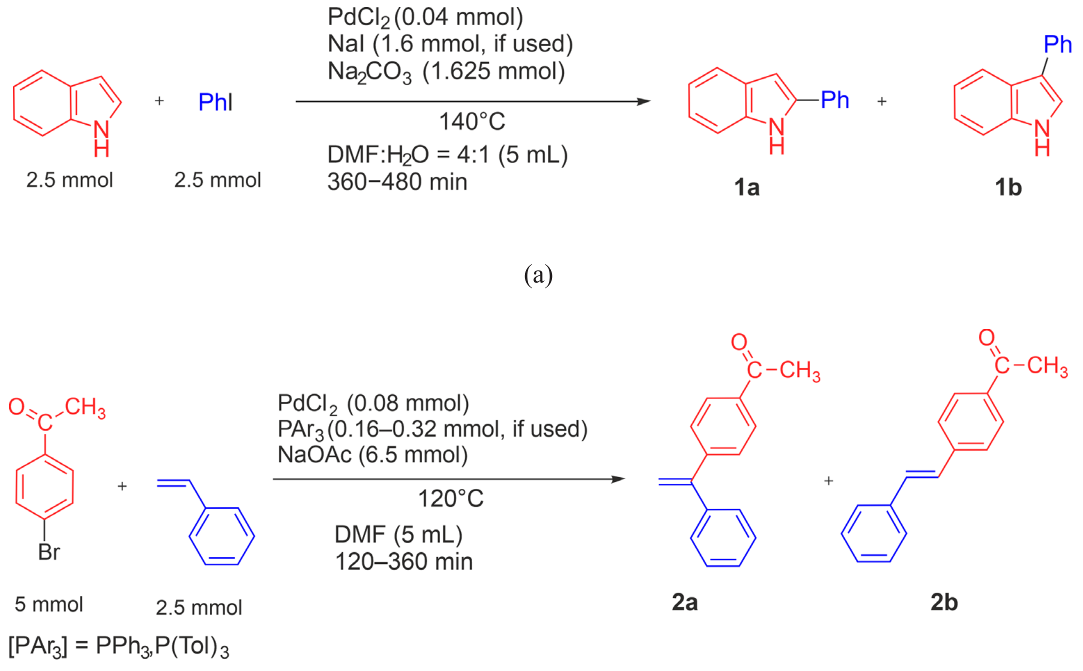
(a) (b)

Fig. 1. General scheme of the reaction with the formation of two products P1 and P2 as a result of:
(a) competitive reaction of two substrates S1 and S2 with common intermediate (X_{com});
(b) two parallel reactions of the common intermediate (X_{com}) (monomolecular, or due to the interaction with the one substrate S).

experimentally observed deviations of phase trajectories from linearity are direct evidence of changes in the nature of the common intermediate in the course of the reaction.

For example, for the reaction of direct arylation of indole with an aryl halide (Fig. 2a), the phase trajectories in the coordinates of the concentrations of C2- and C3-regioisomeric products of indole arylation deviated from linearity (Fig. 3a, curve 1), indicating a change in the composition of catalytically active complexes during the reaction. The change in the catalytic system was also found to be caused by the ratio of the concentrations of base anions capable of being coordinated to palladium and endogenous halide ions [19] that accumulate as a result of the conversion of the initial aryl halide, which changes during the process. This hypothesis was confirmed by the "straightening" of phase trajectories with an increase in the addition of iodide salt, which simulates the effect of endogenous halide ions (Fig. 3a, curve 2) [13].

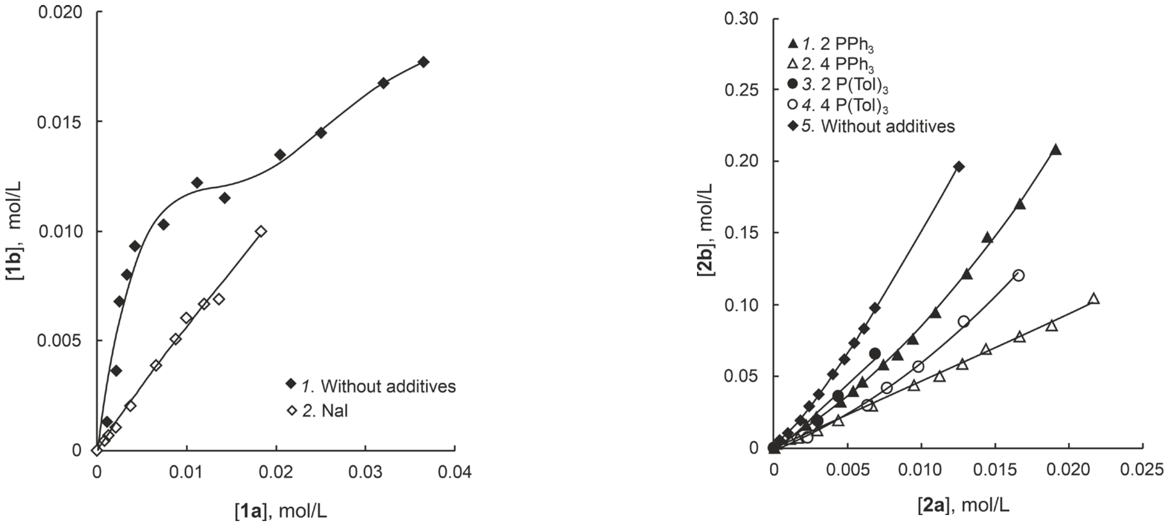
In the Mizoroki–Heck reaction, a comparison of the phase trajectories in the coordinates of concentrations of α- and β-regioisomeric products of styrene arylation (Fig. 2b) indicated the sensitivity of differential regioselectivity to the introduction



(a)

(b)

Fig. 2. Scheme of: (a) reaction of direct arylation of indole,
(b) Mizoroki–Heck reaction with the formation of regioisomeric products.



(a) (b)

Fig. 3. Phase trajectories plotted by using the concentrations of regioisomeric products formed in the following reactions: (a) direct arylation of indole with iodobenzene (Fig. 2a); (b) styrene arylation with 4-bromoacetophenone (Fig. 2b).

of tertiary phosphine additives into the reaction system (Fig. 3b), indicating its entry into the composition active complexes of palladium. In this case, the deviation of the phase trajectory from linearity observed in some cases (Fig. 3b, curves 1, 4, 5) also indicated a change in the composition of such complexes during the reaction.

In special experiments, deviations from linearity were found to be due to a change in the ratio of the concentrations of tertiary phosphine and endogenous halide ions accumulated during the reaction, which compete for inclusion in the composition of active complexes [14].

An assessment of the degree of deviation of the phase trajectory from linearity as a criterion for changing the nature of the active catalyst during the process, which can be carried out both visually and using the tools of linear regression analysis, can be used not only for the case of parallel reactions of catalytic cycle intermediates (Fig. 1b), but also in the case of their competitive transformations in the presence of several substrates/reagents (Fig. 1a). To do this, the change in the concentrations of competing substrates that affect the value of DS in the course of the reaction should be insignificant, that is, to create conditions for the pseudo-zero order reaction to proceed through competing substrates. The traditional technique for implementing pseudo-zero order conditions for substrates involves the use of their excess concentrations. From a mathematical point of view, this means that (as in the case of phase trajectories of parallel reactions of the transformation of a common intermediate) the ratio of the rates of competing reactions of a common intermediate during the reaction, i.e., the slope of the phase trajectory should remain practically unchanged with the constancy of the nature of the intermediate, which should lead to a linear phase trajectory (1).

If the conditions $[S1]_0 >> [P1]$ и $[S2]_0 >> [P2]$ are satisfied, then the equation:

$$\frac{r_{S2}}{r_{S1}} = \frac{d[S2]/dt}{d[S1]/dt} = \frac{k_{S2}[X_{\text{com}}]^{n_{\text{cat}}}[S2]^{n_S}}{k_{S1}[X_{\text{com}}]^{n_{\text{cat}}}[S1]^{n_S}} = \frac{k_{S2}([S2]_0-[P2])^{n_S}}{k_{S1}([S1]_0-[P1])^{n_S}} \approx \frac{k_{S2}}{k_{S1}}\left(\frac{[S2]_0}{[S1]_0}\right)^{n_S}, \qquad (1)$$

where r_{S1} and r_{S2} are the rates of conversion of competing substrates S1 and S2 into the corresponding products P1 and P2 with effective rate constants k_{S1} and k_{S2}, respectively (Fig. 1a); $[X_{\text{com}}]$ is the concentration of the total catalytic cycle intermediate; $[S1]_0$ and $[S2]_0$ are the initial concentrations of competing substrates; n_S and n_{cat} are the reaction orders with respect to the substrate and catalyst, respectively.

For example, in the Suzuki–Miyaura reaction (Fig. 4), the use of a pair of competing aryl chlorides at concentrations exceeding the concentration of their common reagent—arylboronic acid—by a factor of 6 led to linear phase trajectories (Fig. 5a), confirming the value expected based on the equation (1). This result allows us to confidently state that no changes in the nature of the catalytically active compound responsible for the activation of competing aryl halide substrates occur during the reaction. At the same time, under conditions of equimolar ratios of competing aryl chlorides and arylboronic acid (Fig. 5b), the phase trajectory had a typical nonlinear character, which is to be expected for the case of competition of substrates differing in reactivity.

It is not always possible to carry out a reaction with an excess of competing substrates to linearize phase trajectories in order to test the hypothesis of the invariance of the nature of the compounds responsible for catalysis. However, it is also possible to obtain information about the patterns of evolution of the catalytic system for a competitive reaction under conditions of substrate concentrations close to equivalent amounts. In the case of competition between substrates for a common intermediate of the catalytic cycle, the reaction should proceed as one having first order with respect to competing substrates. In this case, integration of Eq. (1) under the condition of the first order in substrates ($n_S = 1$) leads to an equation of the following form:

$$\ln\left(\frac{[S2]}{[S2]_0}\right)=\frac{k_{S2}}{k_{S1}}\ln\left(\frac{[S1]}{[S1]_0}\right)=k_{\mathrm{rel}}\ln\left(\frac{[S1]}{[S1]_0}\right), \qquad (2)$$

where k_{rel} is the relative reactivity of competing substrates.

By using logarithmic coordinates corresponding to Eq. (2) it becomes possible to return to the linear forms of phase trajectories for estimating deviations from linearity as a result of evolutionary changes in the behavior of the catalytic system for most catalytic reactions. The degree of deviation from linearity can be assessed both visually and using linear regression analysis.

If the value of the correlation coefficient of the linear dependence according to Eq. (2) decreases during the reaction, this is unambiguous evidence of the evolution of the catalytic system in a direction not described by this equation. Thus, when performing the Suzuki–Miyaura reaction under the conditions of competition of a pair of arylboronic acids (Fig. 6), a decrease in the value of the correlation coefficient of the linear dependence (2) was found to occur with an increase in the depth of the reaction. The deviation of the experimental phase trajectory from that expected in the approximation of the constant nature of the active catalyst can be demonstrated by comparing it with the phase trajectory obtained by calculation using a constant value of k_{rel}, which is estimated from the slope of linear dependence (2) at the initial stage of the reaction (Fig. 7a). This pattern can also

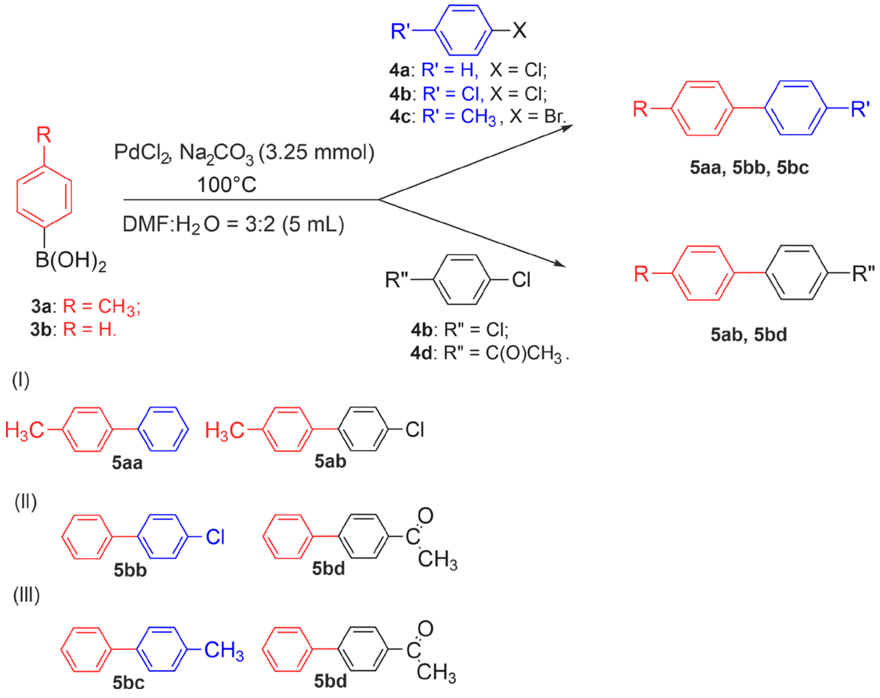
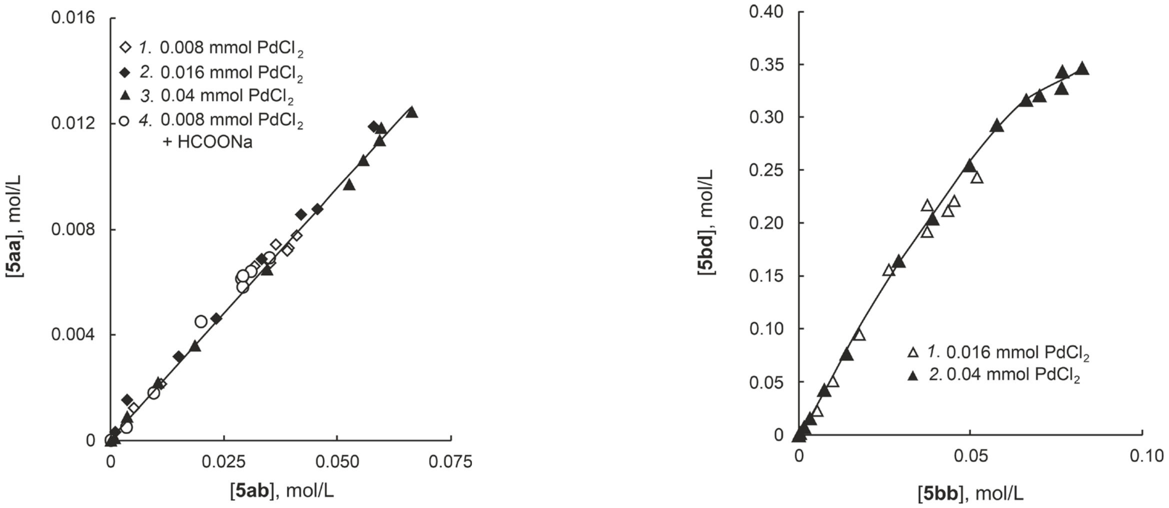


Fig. 4. Suzuki–Miyaura reaction under competition of two aryl halides.
Reaction conditions: (I) **3a** (0.4 mmol), **4a** (2.5 mmol), **4b** (2.5 mmol), $PdCl_2$ (0.008–0.04 mmol), HCOONa (0.1 mmol, if used), 30–140 min, products **5aa**, **5ab**;
(II) **3b** (2.5 mmol), **4b** (2.5 mmol), **4d** (2.5 mmol), $PdCl_2$ (0.016–0.04 mmol), 120–220 min, products **5bb**, **5bd**;
(III) **3b** (2.5 mmol), **4c** (1.25 mmol), **4d** (10 mmol), $PdCl_2$ (0.008 mmol), NBu_4Br (1.15 mmol, if used), 120–230 min, products **5bc**, **5bd**.



(a) (b)

Fig. 5. Phase trajectories of Suzuki–Miyaura reaction with competing:
(a) chlorobenzene and 1,4-dichlorobenzene in the reaction with 4-tolylboronic acid (Fig. 4, conditions (I));
(b) 1,4-dichlorobenzene and 4-chloroacetophenone in the reaction with phenylboronic acid (Fig. 4, conditions (II)).

be visualized by plotting the deviations of the experimentally observed and calculated using the constant k_{rel} value of the concentrations of the product of one of the competing reactions from the concentration of the product of the second competing reaction (Fig. 7b).

The change in the nature of Pd(II) compounds active in the selectivity-determining step [20, 21] was due to a change in the ratio between the concentrations of the base anions capable of coordinating with palladium and the accumulated endogenous halide ions [19].

Evolutionary changes in the catalytic system can also be evaluated for hypotheses of mechanisms that are more complex in comparison with Eq. (2). Under the competition between aryl chloride and aryl bromide in the Suzuki–Miyaura reaction, the kinetics of the reaction are affected by the significant reversibility of the stage in which the competition of substrates occurs [10, 17] (Fig. 8). In this case, the DS is described by Eq. (3) that is more complicated than Eq. (2) and not amenable to linearization. Here, numerical methods for simulating the reaction kinetics can become useful. For example, as the depth of the reaction increases, the phase trajectory (Fig. 9a) is observed to deviate from the calculated dependence obtained by numerical integration of Eq. (3) under the assumption of the unchanged nature of catalytically active species, i.e., unchanged values of the rate constants for the elementary steps presented in Eq. (3)). This is confirmed by the increase in the deviation of the experimental values of the concentrations of one of the competitive reaction products from those calculated by Eq. (3) observed with increasing reaction depth (Fig. 9b).

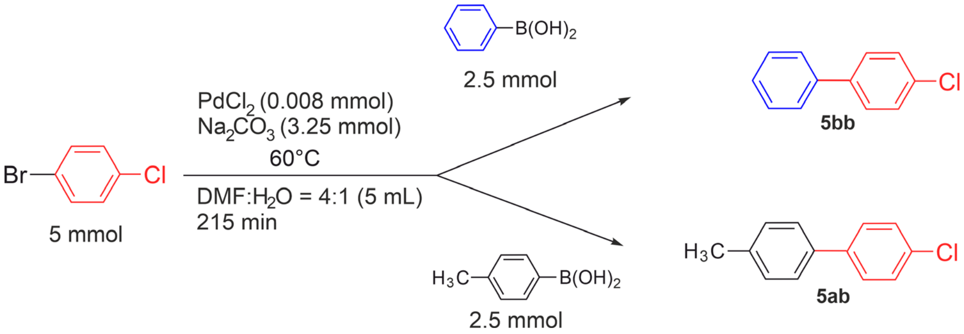
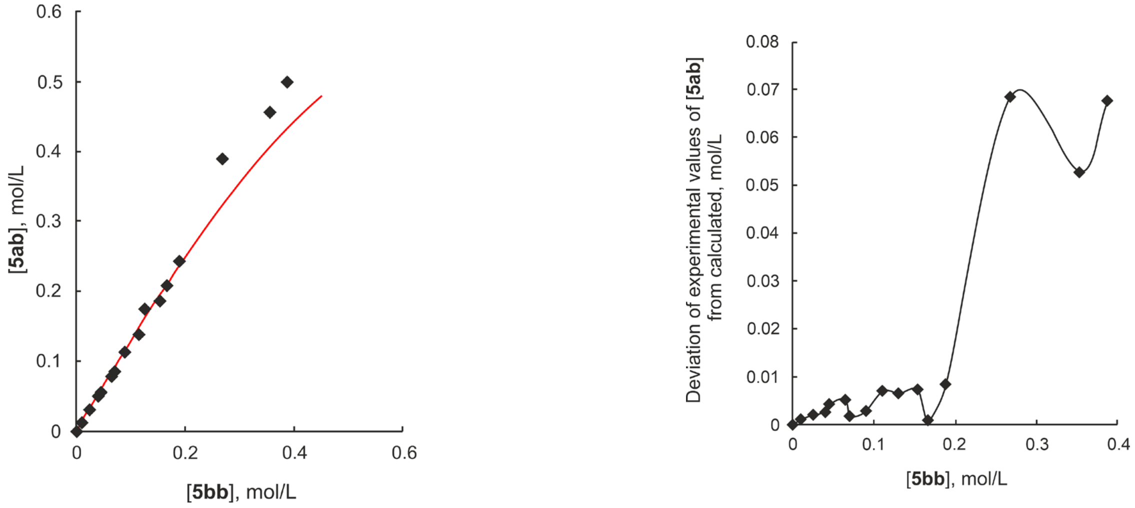


Fig. 6. Suzuki–Miyaura reaction under competition of two arylboronic acids.



(a) (b)

Fig. 7. Experimental (dots) and simulated (red line) phase trajectories of Suzuki–Miyaura reaction with 1-chloro-4-bromobenzene and competing phenyl- and 4-tolylboronic acids (a), and the plot of the deviations between experimental and calculated values of the 1'-chloro-4-methylbiphenyl concentrations (**5ab**) *vs*. increasing 4-chlorobiphenyl concentrations (**5bb**) under the reaction proceeding (b) (Fig. 6).

$$\frac{r_{\mathrm{S2}}}{r_{\mathrm{S1}}}=\frac{(k'_{\mathrm{S2}}k_{\mathrm{S2}})(k'_{-\mathrm{S1}}+k_{\mathrm{S1}}[\mathrm{ArB(OH)_2}])[\mathrm{Ar_2X}]}{(k'_{\mathrm{S1}}k_{\mathrm{S1}})(k'_{-\mathrm{S2}}+k_{\mathrm{S2}}[\mathrm{ArB(OH)_2})[\mathrm{Ar_1X}]}, \qquad (3)$$

where r_{S1}, r_{S2} are the conversion rates of competing aryl halides; $[\mathrm{Ar_1X}]$ and $[\mathrm{Ar_2X}]$ are the concentrations of aryl halides; $[\mathrm{ArB(OH)_2}]$ is the concentration of arylboronic acid. The constants k'_{S1}, $k'_{-\mathrm{S1}}$, k_{S1}, k'_{S2}, $k'_{-\mathrm{S2}}$, k_{S2} correspond to the rate constants of the elementary stages given in Fig. 8. The obtained data represent an additional demonstration of the possibilities of analyzing the nature of catalytically active compounds using phase trajectories under conditions of complex dynamic transformations of the catalyst, which are characteristic of cross-coupling reactions of aryl halides [19, 22–24].

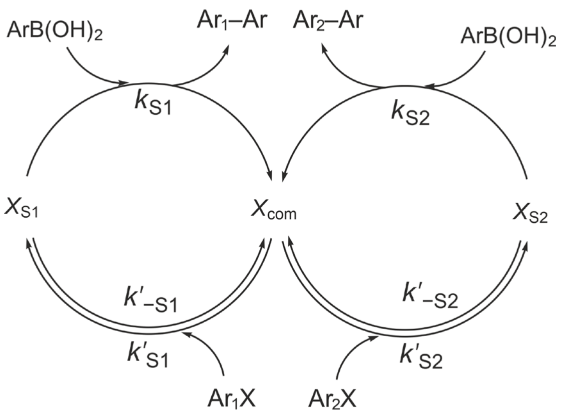


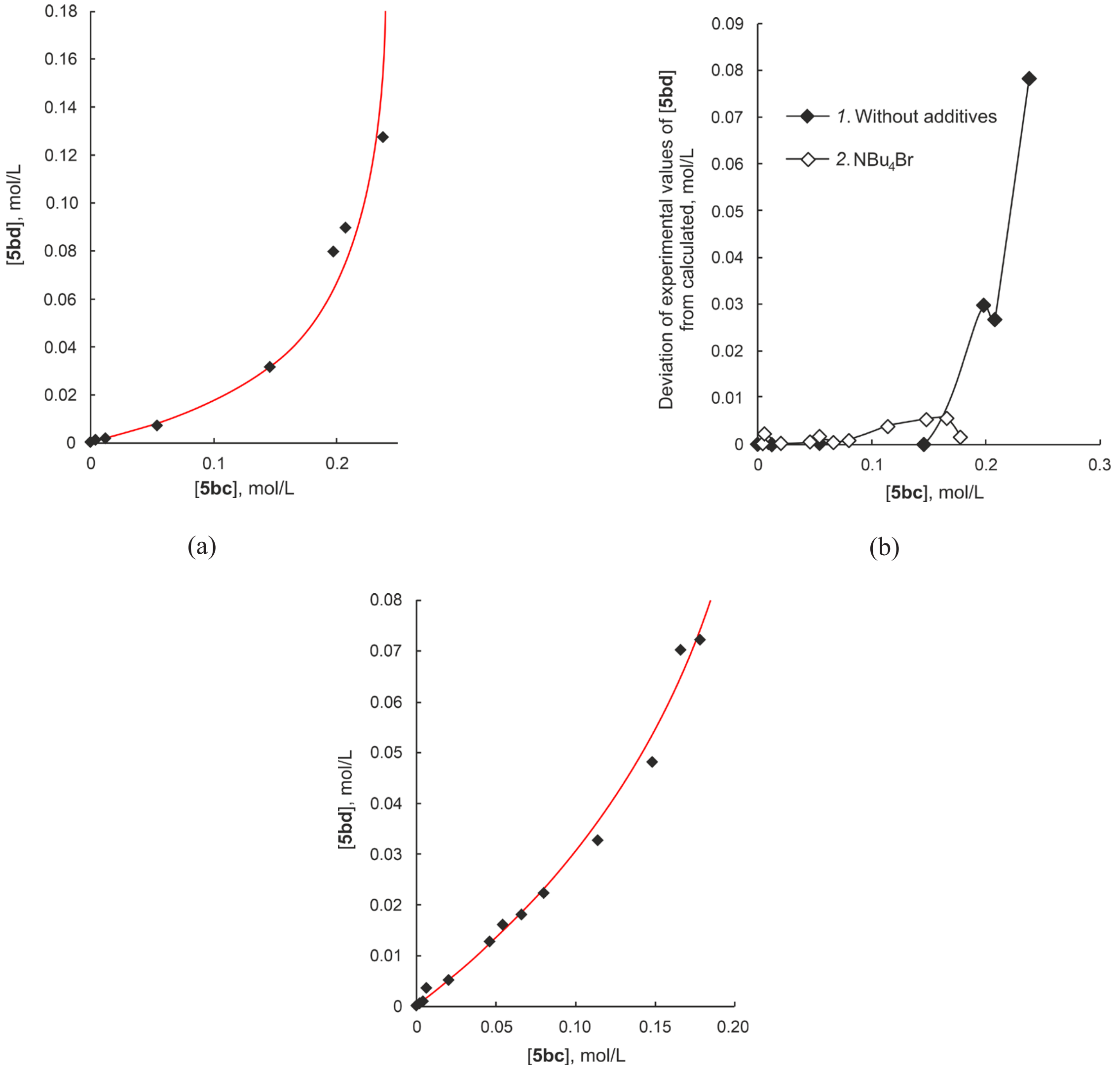
Fig. 8. Scheme of the competitive Suzuki–Miyaura reaction with arylboronic acid, considering reversible character of the elementary step where two aryl halides ($\mathrm{Ar_1X}$, $\mathrm{Ar_2X}$) compete.

The deviations again turned out to be explainable in terms of the accumulation of endogenous halide ions during the reaction [19], leading to a change in the ratio between the catalytically active dissolved and inactive solid forms of the catalyst, which are converted into each other during the reaction [9, 18]. As confirmation of this hypothesis, we can consider the decrease in the deviations of the experimental and calculated phase trajectories at the late stages of the reaction when using additives of halide salts that simulate the effect of endogenous halide ions as significant in terms of reducing the effect of the accumulation of endogenous halogen anions on the distribution of palladium between different types of active particles in the course of the reaction (Fig. 9c).

CONCLUSIONS

The presented examples demonstrate the possibilities of a simple kinetic method using exclusively primary experimental data on the accumulation of products of parallel or competing reactions for studying evolutionary changes during the functioning of catalytic systems.

By constructing phase trajectories of competing or parallel reactions in different coordinates to linearize the dependences of the concentrations



(a)

(b)

(c)

Fig. 9. Experimental (dots) and simulated (red line) phase trajectories of Suzuki–Miyaura reaction with phenylboronic acid and competing 4-chloroacetophenone and 4-bromotoluene with no additives (a), and the plot of the deviations between experimental and calculated values of the 4-acetylbiphenyl concentrations (**5bd**) *vs*. increasing 4-methylbiphenyl concentrations (**5bc**) under the reaction proceeding without additive and with NBu_4Br additive (b). At part (c) the phase trajectories for the reaction with NBu_4Br additive are plotted (Fig. 4, conditions (III)).

of the products of these reactions on each other, it becomes possible to track possible changes in the nature of the active catalyst by visual estimation or linear regression analysis. When the complex nature of the conjugation of the elementary stages of competing catalytic cycles does not permit a linearization of the phase trajectory, the assessment of possible changes in the nature of the catalyst during the reaction can be carried out by simulating phase trajectories using numerical integration procedures for differential equations that describe the ratios of the rates of competing processes.

The analysis of changes in DS or relative reactivity carried out in this way as a result of the spontaneous evolution of the catalytic system can be especially useful for discriminating between possible hypotheses of the mechanism in reactions whose characteristic feature is the dynamic nature of the transformations of various potentially active forms of the catalyst.

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Authors' contribution

All authors equally contributed to the research work.

The authors declare no conflicts of interest.

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About the authors:

Alexander F. Schmidt, Dr. Sci. (Chem.), Full Professor, Professor, Department of Physical and Colloid Chemistry, Rector, Irkutsk State University (1, K. Marksa ul., Irkutsk, 664003, Russia). E-mail: aschmidt@chem.isu.ru. Scopus Author ID 7403416777, ResearcherID M-1405-2013, RSCI SPIN-code 6723-1588, http://orcid.org/0000-0002-1881-7620

Anna A. Kurokhtina, Cand. Sci. (Chem.), Associate Professor, Department of Physical and Colloid Chemistry, Irkutsk State University (1, K. Marksa ul., Irkutsk, 664003, Russia). E-mail: kurokhtina@chem.isu.ru. Scopus Author ID 25221794400, ResearcherID A-6571-2016, RSCI SPIN-code 4477-2786, http://orcid.org/0000-0002-8434-6820

Elizaveta V. Larina, Cand. Sci. (Chem.), Researcher, Institute of Oil and Coal Chemical Synthesis, Irkutsk State University (1, K. Marksa ul., Irkutsk, 664003, Russia). E-mail: tendu90@mail.ru. Scopus Author ID 48761510800, ResearcherID H-2003-2016, RSCI SPIN-code 6947-4160, http://orcid.org/0000-0001-9747-5659

Nadezhda A. Lagoda, Junior Researcher, Institute of Oil and Coal Chemical Synthesis, Irkutsk State University (1, K. Marksa ul., Irkutsk, 664003, Russia). E-mail: nalagoda@yandex.ru. Scopus Author ID 57191614560, ResearcherID S-9020-2017, RSCI SPIN-code 7104-1921, http://orcid.org/0000-0001-9771-8403

Об авторах:

Шмидт Александр Федорович, д.х.н., профессор кафедры физической и коллоидной химии, ректор, ФГБОУ ВО «Иркутский государственный университет» (664003, Россия, г. Иркутск, ул. К. Маркса, д. 1). E-mail: aschmidt@chem.isu.ru. Scopus Author ID 7403416777, ResearcherID M-1405-2013, SPIN-код РИНЦ 6723-1588, http://orcid.org/0000-0002-1881-7620

Курохтина Анна Аркадьевна, к.х.н., доцент, кафедра физической и коллоидной химии, ФГБОУ ВО «Иркутский государственный университет» (664003, Россия, г. Иркутск, ул. К. Маркса, д. 1). E-mail: kurokhtina@chem.isu.ru. Scopus Author ID 25221794400, ResearcherID A-6571-2016, SPIN-код РИНЦ 4477-2786, http://orcid.org/0000-0002-8434-6820

Ларина Елизавета Владимировна, к.х.н., научный сотрудник, Научно-исследовательский институт нефте- и углехимического синтеза, ФГБОУ ВО «Иркутский государственный университет» (664003, Россия, г. Иркутск, ул. К. Маркса, д. 1). E-mail: tendu90@mail.ru. Scopus Author ID 48761510800, ResearcherID H-2003-2016, SPIN-код РИНЦ 6947-4160, http://orcid.org/0000-0001-9747-5659

Лагода Надежда Александровна, младший научный сотрудник, Научно-исследовательский институт нефте- и углехимического синтеза, ФГБОУ ВО «Иркутский государственный университет» (664003, Россия, г. Иркутск, ул. К. Маркса, д. 1). E-mail: nalagoda@yandex.ru. Scopus Author ID 57191614560, ResearcherID S-9020-2017, SPIN-код РИНЦ 7104-1921, http://orcid.org/0000-0001-9771-8403

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RESEARCH ARTICLE

Effect of adsorption-catalytic deformation and partial deactivation on the determination of the absolute activity of a liquid phase hydrogenation catalyst

Andrei V. Afineevskii✉, Dmitriy A. Prozorov, Tatiana Yu. Osadchaya, Natalia E. Gordina

Ivanovo State University of Chemistry and Technology, Ivanovo, 153000 Russia
✉Corresponding author, e-mail: afineevskiy@mail.ru

Abstract

Objectives. *To take into account the change in the number of active sites during the adsorption-catalytic deformation and deactivation of a catalyst surface by means of a catalytic poison when calculating the turnover frequency (TOF) of a hydrogenation catalyst.*
Methods. *The activity was determined by a static method, using a titanium reactor having a volume of 400 mL, an experimental temperature controlled using a liquid thermostat with an accuracy of 0.5 K, with a paddle stirrer rotation speed of 3600 rpm and system hydrogen pressure equal to atmospheric. The consumption of hydrogen used to reduce the model compound was taken into account via the volumetric method. The heats of hydrogen adsorption were determined using a reaction calorimeter with an operating mode close to that of a chemical reactor. After measuring the specific surface area using low temperature nitrogen adsorption, the results were processed using Brunauer–Emmett–Teller theory approximations. Deactivation was carried out by introducing dosed amounts of catalytic poison into the system in titration mode.*

Results. *A kinetic experiment for the reduction of a multiple carbon bond in a sodium maleate molecule using aqueous solutions of sodium hydroxide with additions of monohydric aliphatic alcohols as solvents under conditions of partial deactivation of the catalyst was carried out. The obtained values of heats of hydrogen adsorption on skeletal nickel in the course of the experiment are given. The described approach is used to calculate TOF values taking into account changes in the number of active surface sites during the course of a catalytic reaction and upon the introduction of a deactivating agent. A refined equation for the correct calculation of TOF is proposed along with its mathematical justification. The results of TOF calculations under various assumptions for a number of catalytic systems are shown.*

Conclusions. *When calculating absolute activity values, a change in the number of active sites has a significant effect on the obtained values. The physical meaning of a number of constants in the proposed equation relates the activity of the catalyst to the distribution of hydrogen on its surface in terms of heats of adsorption.*

Keywords: *liquid-phase hydrogenation, active sites, catalyst deactivation, nickel catalyst, bulk catalysts, adsorption-catalytic deformation, TOF*

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НАУЧНАЯ СТАТЬЯ

Влияние адсорбционно-каталитической деформации и частичной дезактивации на определение абсолютной активности катализатора жидкофазного гидрирования

А.В. Афинеевский✉, Д.А. Прозоров, Т.Ю. Осадчая, Н.Е. Гордина

Ивановский государственный химико-технологический университет, Иваново, 153000 Россия

✉*Автор для переписки, e-mail: afineevskiy@mail.ru*

Аннотация

Цели. *Учесть изменение количества активных центров при адсорбционно-каталитической деформации и дезактивации поверхности каталитическим ядом при расчете величин абсолютных активностей (turnover frequency, TOF) катализатора гидрирования.*

Методы. *Определение активности проводили статическим методом, использовали титановый реактор объемом 400 мл, заданную температуру опыта контролировали с помощью жидкостного термостата с точностью до 0.5 K, скорость вращения лопастной мешалки составляла 3600 об/мин, давление водорода в системе равно атмосферному. Расход водорода на восстановление модельного соединения учитывался волюмометрическим методом. Теплоты адсорбции водорода определяли с помощью реакционного калориметра, режим работы которого был близок к режиму работы химического реактора. Удельная площадь поверхности измерялась с помощью низкотемпературной адсорбции* *азота, результаты обрабатывали, используя приближения теории Брунауэра–Эммета–Теллера (БЭТ). Дезактивация проводилась введением в систему дозированных количеств каталитического яда в режиме титрования.*

Результаты. *Получены результаты кинетического эксперимента восстановления кратной углеродной связи в молекуле малеата натрия в растворителях различной природы и состава в условиях частичной дезактивации катализатора. В качестве растворителей использовали водные растворы гидроксида натрия с добавками одноатомных алифатических спиртов. Приведены значения теплот адсорбции водорода на скелетном никеле, полученные в ходе адсорбционно-калориметрического эксперимента. Показан подход, позволяющий учесть изменение количества активных центров поверхности в процессе протекания каталитической реакции и при введении дезактивирующего агента, при расчете значений TOF. Предложено уточненное уравнение для корректного расчета TOF, а также представлено математическое его обоснование. Показаны результаты расчета TOF при различных допущениях для ряда каталитических систем.*

Выводы. *Продемонстрировано, что учет изменения количества активных центров при расчете величин абсолютной активности оказывает значительное влияние на полученные значения. Показан физический смысл ряда констант в предложенном уравнении, связывающем активность катализатора и распределение на его поверхности водорода по теплотам адсорбции.*

Ключевые слова: *жидкофазное гидрирование, активные центры, дезактивация катализатора, никелевый катализатор, массивные катализаторы, адсорбционно-каталитическая деформация, TOF*

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INTRODUCTION

The hypothesis of cyclically activated complexes with alternate rupture and formation of bonds was generalized for the first time in relation to particular cases of individual reactions on the example of a very wide range of chemical processes in the works of Ya.K. Syrkin [1–4]. In heterogeneous catalysis, the adsorption, surface diffusion, chemical rearrangement, reaction, and desorption of the product must occur in such a way that the surface of the catalyst can be replenished with new substrate molecules. The faster such a cycle is carried out, the faster the process progresses. Thus, the turnover rate or turnover frequency (TOF), normalized by the number of active sites and consequently representing the rate at which a full catalytic cycle is performed once, should be considered as one of the best measures of catalytic activity [5–8]. This value, which is also referred to as absolute activity [9], is defined as the maximum number of molecules (N_{mol}) that reacted on one active site (N_{as}) per unit of time τ [9]:

$$\mathrm{TOF} = \frac{N_{\mathrm{mol}}}{N_{\mathrm{as}} \cdot \tau} = [\mathrm{s}^{-1}] \cdot \qquad (1)$$

In order to compare the indicators reported by different research groups, it is necessary to carefully describe the methodology used to determine the number of active sites. The main unsolved problem is that the densities of active sites measured prior to the catalytic reaction are not necessarily identical to those present under reaction conditions. In the case of non-porous catalysts, the values of the working surface and the total surface are almost equal, whereas, in the case of porous catalysts, it is only the surface accessible to the reagents that works. Nevertheless, even on an accessible surface, the number of active sites (in the selected specific reaction) is typically unknown.

Therefore, a different approach is also often used. According to [9], the activity (A) of a catalyst is defined as the difference in reaction rates in the presence of a catalyst (r_{cat}). This is related to the unit of the amount of catalyst (g): mass (m_{cat}), volume, moles, or surface area). In the absence of a catalyst (r_{-cat}), $A = r_{cat}/g - r_{-cat}$. However, since usually $r_{cat} >> r_{-cat}$, the last term in this equation can be disregarded. Thus, the catalytic activity for liquid-phase processes is expressed in terms of the reaction rate, which Syrkin *et al*. proposed to normalize to the amount of catalyst (g) [10]. Thus, in the case of liquid-phase hydrogenation, the activity can be determined as follows (2)–(4) [11]:

$$r = \frac{1}{m_{\text{cat}}}\frac{dV(\text{H}_2)}{d\tau} = \left[\frac{\text{cm}^3}{\text{s}\cdot\text{g}}\right], \qquad (2)$$

$$\alpha = \frac{(\nu_0 - \nu)}{\nu_0} = \frac{(c_0 - c)}{c_0} = \frac{V_0(\text{H}_2)}{V_\infty(\text{H}_2)}, \qquad (3)$$

$$A = r_{\alpha=0\div0.05} = \left[\frac{\text{cm}^3}{\text{s}\cdot\text{g}}\right], \qquad (4)$$

where α is the degree of transformation (conversion); c is the concentration of the substrate to the current time (τ), c_0 is the initial concentration ($\alpha = 0$); r is the conversion rate of the substrate, v is the number of moles of the substrate to the current moment (τ), v_0 is the initial number of moles ($\alpha = 0$); $V_0(H_2)$ is the initial volume of hydrogen ($\alpha = 0$), $V(H_2)$ is the volume of hydrogen absorbed to the current moment, $V_\infty(H_2)$ is the total volume of hydrogen that went into the reaction, at its complete completion ($\alpha = 1$).

The use of Eq. (4) is justified by the fact that the initial rates of the hydrogenation reaction can be considered as objective parameters of the activity of catalysts [12, 13]. For conversions below 0.05, since the hydrogenation rate is directly related to the reactivity of the catalytically active site, the course of side processes has not yet had time to have a significant effect. However, this approach requires that the initial conditions (temperature, hydrogen pressure, reactant concentrations, etc.) are accurately set to be identical each time.

Previously [12–20] it was found that an adsorption-catalytic deformation can in some cases occur during reactions in which the number of active catalyst sites changes. It is therefore necessary to find an approach that allows such changes to be taken into account. It is also known that the action of a catalytic poison is based on its removal of the active site from the reaction zone in some way (blocking, destruction, etc.). That is, the number of active sites should increase during adsorption-catalytic deformation, but when blocked, the number should decrease. The aim of the present work, then, was to find a way to take into account the change in the active sites of the surface during the course of the reaction when calculating the TOF value.

One of the ways to account for the number of active sites removed from the reaction zone can be the analysis of the equation relating the distribution of adsorbed hydrogen by binding energies to the active sites of the catalyst (5)–(7) [21]:

$$A_{\text{calc}} = K_{H\to A}\cdot\Delta_\alpha H^{\text{peak}}_{\text{meas}}(\text{H}_2) - K_{\text{pois}}\cdot n(CDA) + A_{\max}, \qquad (5)$$

$$\begin{aligned}\Delta_\alpha H^{\text{peak}}_{\text{calc}}(\text{H}_2) &= K^{-1}_{H\to A}\cdot A_{\text{meas}} + \\ &+ K_{\text{pois}}\cdot K^{-1}_{H\to A}\cdot n(\text{CDA}) + \Delta_\alpha H^{\text{peak}}_{\max}(\text{H}_2),\end{aligned} \qquad (6)$$

$$\Delta_\alpha H^{\text{peak}}_{\max}(\text{H}_2) = -A_{\max}\cdot K^{-1}_{H\to A}, \qquad (7)$$

where A_{meas} and A_{calc} are the activities of the catalyst measured in kinetic experiment (see Eq. (4)) and calculated from thermochemical data, respectively, [cm^3 · s^{-1}·g^{-1}]; $\Delta_\alpha H^{\text{peak}}_{\text{calc}}(\text{H}_2)$ is the peak position calculated from kinetic data, [kJ·mol^{-1}]; $\Delta_\alpha H^{\text{peak}}_{\text{meas}}(\text{H}_2)$ is the peak position according to the distribution functions (determined in a thermochemical experiment using calorimetric data), [kJ·mol^{-1}]; CDA (cross dehydrogenative arylation) is catalytic poison (deactivating agent for the catalyst); n(CDA) is the amount of catalytic poison introduced into the system per gram of catalyst, [mol·g^{-1}]; $A_{\max}$ is the calculated maximum activity for the recovery of the selected compound on a given catalyst, [cm^3 ·s^{-1}·g^{-1}]; $\Delta_\alpha H^{\text{peak}}_{\max}(\text{H}_2)$ is the limiting heat of hydrogen adsorption (weakly bound hydrogen can participate in hydrogenation, while strongly bound hydrogen cannot); K_{pois}, $K^{-1}_{H\to A}$, $K_{H\to A}$ are constants, the physical meaning of which must be established.

Thus, by using the above equations to determine the physical meaning of a number of constants, it may be possible to determine the number of active sites removed from the reaction zone by the catalytic poison. By taking into account the changes in surface area during the adsorption deformation, as well as the active sites removed from the reaction zone, it will be possible to accurately determine the number of active sites involved in the reaction, which should in turn allow the absolute activity of the catalyst to be accurately calculated.

EXPERIMENTAL

Sodium maleate with a purity of >98% (*Merck*, Germany) was chosen as a hydrogen acceptor: since the mechanism and kinetics of its reduction by hydrogen in the presence of a catalyst are well known and the formation of a minimum number of intermediates and by-products has been recorded, it is often used as a model compound [12, 13, 22, 23].

Skeletal nickel obtained by leaching the Raney alloy (*Merck*, Germany) according to the described method [12, 13] was used as a catalyst. Previously, it was shown that the deactivation of skeletal nickel by the dosed introduction of sulfide ions into the catalytic system, depending on the nature of the solvent, is able to selectively block the active sites of the surface with a given metal-hydrogen bond energy [12].

Hydrogenation was carried out using a static method in a closed system with intensive mixing of the liquid phase to exclude the influence of external mass transfer on the experimental results [12, 13]. The reactor was designed in such a way that the rate of the hydrogenation reaction could be measured by the volume of hydrogen absorbed during the reaction per unit of time. The obtained values were reduced to the standard temperature and pressure (273.15 K, 1 bar). The experimental conditions were as follows: mixing speed is 3600 rpm^{-1}; hydrogen pressure is atmospheric; temperature of the liquid phase is 303 K; mass of the catalyst is $m_{\text{cat}} = 0.5 \pm 0.01$ g; volume of the liquid phase is 100 cm^3; reactor volume is 400 cm^3. The experimental procedure and the reactor diagram are presented in more detail in [12, 13]. The rate of hydrogen uptake, the degree of conversion, and the catalytic activity were calculated according to Eqs. (2)–(4).

Hydrogenate analysis was performed on a Crystallux-4000M gas chromatograph (*META-CHROME*, Russia) with a flame ionization detector. A TRB-PETROL 100 m × 0.25 mm × 0.5 µm capillary column (*Teknokroma Analytica S.A.*, Spain) was used to separate the extractant. The parameters of the analysis program were as follows: analysis time is 60 min; initial temperature of the columns is 35°C; programmed heating to 150°C at a rate of 5°C/min, then to 250°C for the remaining analysis time; detector temperature is 270°C; evaporator temperature is 270°C; volume of sample taken for analysis is 0.4 µL.

RESULTS AND DISCUSSION

In order to obtain a set of data on the activity of the catalyst, nine solvents were considered in the work, including water, sodium hydroxide, and aliphatic monatomic alcohol. The effect of the solvent on the observed kinetic patterns is well documented in the organic synthesis literature [24]. Although similar effects have been described in the literature on heterogeneous catalysis, the chemical basis of the observed effects remains unclear. Solvent effects in heterogeneous catalysis have been rationalized by comparing reaction rates and product distribution with solvent polarity or permittivity [25–28]. Although there is no doubt that such properties of the solvent can affect the kinetics of the reaction, further research is needed in this area to better understand and quantify these effects, which become even more difficult when switching to metal catalysts on a support due to possible solvent/support interactions [29, 30]. The authors associate the solvent effects with the adsorption equilibrium constant and the volume concentration of H_2 [31].

An example of primary data is shown in Fig. 1a. These data were differentiated and then normalized per 1 g of catalyst according to Eqs. (2) and (3) (see example in Fig. 1b).

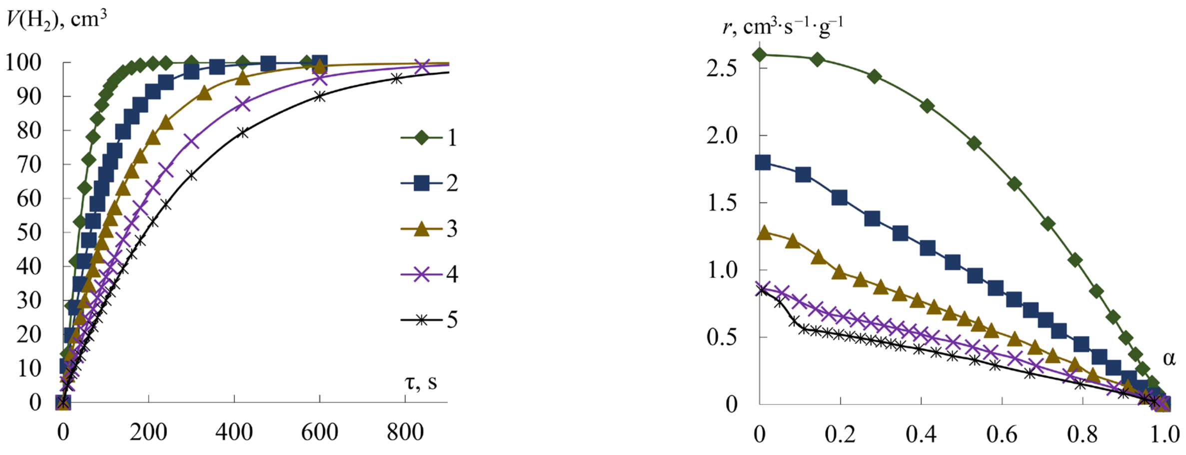
The activity of the catalyst is calculated from Eqs. (2) and (4) and summarized in Table 1.

To calculate the TOF, Eq. (8), obtained from Eqs. (1) and (2), can be used:

$$\text{TOF} = \frac{1}{m_{\text{cat}}} \cdot \frac{dV(\text{H}_2)}{d\tau} \cdot \frac{N_{\text{A}}}{N_{\text{as}}^{\text{norm}} \cdot 1000 \cdot V_{\text{m}}} = \left[\frac{1}{\text{s}}\right], \tag{8}$$

where N_{A} is the Avogadro number (6.02×10^{23} mol^{-1}); $N_{\text{as}}^{\text{norm}}$ is the number of active sites normalized per 1 g of catalyst (g^{-1}); V_{m} is the molar volume of gas (for hydrogen $V_{\text{m}} = 22.43$ dm^3/mol [32]).

According to the definition given in [6–8], the TOF of a catalyst is the maximum number of molecules that reacted on one active site per unit of time. Therefore, this value is determined at the moment when the catalytic reaction reaches its maximum speed. When a reaction is carried out in a batch reactor, the maximum reaction rate is typically observed at the beginning of the



(a) (b)

Fig. 1. Primary data on the absorption of hydrogen during the hydrogenation of sodium maleate in a solution of water–0.01 M NaOH–ethanol 0.11 mole fraction at different amounts of introduced sodium sulfide, mmol (Na_2S)/g (Ni): 1(♦) 0; 2(■) 0.025; 3(▲) 0.075; 4(×) 0.125; 5(∗) 0.175; (a) absorbed hydrogen volume, (b) hydrogen absorption rate.

Table 1. Activity (*A*) of a porous nickel catalyst in aqueous solutions with additions of sodium hydroxide, aliphatic alcohol, and catalyst poison, [cm^3(H_2)/(s·g(Ni))]

Additives to water	***n*(Na_2S), [mmol (Na_2S) · g^{-1} (Ni)]**				
	–	**0.025**	**0.075**	**0.125**	**0.175**
0.01 M NaOH	2.97 ± 0.45	2.23 ± 0.33	1.78 ± 0.27	1.18 ± 0.18	0.90 ± 0.13
0.1 M NaOH	2.82 ± 0.42	2.60 ± 0.38	2.20 ± 0.33	1.48 ± 0.22	1.03 ± 0.15
1 M NaOH	2.32 ± 0.35	2.08 ± 0.32	1.63 ± 0.25	1.18 ± 0.18	0.75 ± 0.12
0.01 M NaOH–MeOH	2.43 ± 0.37	1.68 ± 0.25	1.32 ± 0.20	0.93 ± 0.13	0.38 ± 0.05
0.1 M NaOH–MeOH	2.73 ± 0.42	2.40 ± 0.37	2.22 ± 0.33	1.77 ± 0.27	0.92 ± 0.13
1 M NaOH–MeOH	2.05 ± 0.30	1.73 ± 0.27	1.53 ± 0.23	1.45 ± 0.22	1.15 ± 0.17
0.01 M NaOH–EtOH	2.62 ± 0.38	1.80 ± 0.27	1.28 ± 0.20	0.87 ± 0.13	0.85 ± 0.13
0.1 M NaOH–EtOH	2.88 ± 0.43	3.13 ± 0.47	2.48 ± 0.37	1.77 ± 0.27	1.43 ± 0.22
1 M NaOH–EtOH	1.63 ± 0.25	1.83 ± 0.28	1.57 ± 0.23	1.50 ± 0.23	1.28 ± 0.20

Note: MeOH is methanol; EtOH is ethanol.

reaction. In the present work, the maximum speed occurred at the beginning of the process in all cases (see Fig. 1b). The TOF is thus determined at the same time as the catalyst activity. Thus, with some assumptions about the hydrogenation reactions of the model compounds considered, the absolute activity can be expressed by Eq. (9):

$$\mathrm{TOF} \approx \frac{A \cdot N_A}{N_{as}^{norm} \cdot 60 \cdot 1000 \cdot V_m} = \left[\frac{1}{s}\right]. \qquad (9)$$

G.D. Zakumbaeva *et al.* [33] found that $1.5 \cdot 10^{19}$ nickel atoms are located on 1 m^2 of the surface of skeletal nickel, that is, $N_{as}^{1\,m^2} = 1.5 \cdot 10^{19}$.

Consequently, the normalized number of active sites per 1 g of catalyst can be expressed by Eq. (10):

$$N_{\mathrm{as}}^{\mathrm{norm}} = S_{\mathrm{sp}} \cdot N_{\mathrm{as}}^{1\,\mathrm{m}^2}, \tag{10}$$

where S_{sp} is the specific surface area of the catalyst.

Combining Eqs. (9) and (10) gives Eq. (11):

$$\mathrm{TOF} \approx A \cdot \frac{N_{\mathrm{A}}}{S_{\mathrm{sp}} \cdot N_{\mathrm{as}}^{1\,\mathrm{m}^2} \cdot 1000 \cdot V_{\mathrm{m}}} = \frac{A \cdot \psi}{S_{\mathrm{sp}} \cdot 1000} = \left[\frac{1}{\mathrm{s}}\right], \tag{11}$$

where, for skeletal nickel, $\psi = 1789$.

Using Eq. (11), absolute activities (TOF) were calculated and summarized in Table 2.

Analyzing the data presented in Table 2, it can be seen that the TOF values decrease monotonically. However, this should not be the case. It is logical to assume that there should be changes upon initial introduction of the catalytic poison, since the energy profile of the surface changes and the binding energies of hydrogen with the surface begin to increase [12]. However, further values should change slightly, since additional introduction of the catalytic poison should only change the number of active sites available to the reactants, not their nature.

When calculating TOF according to the above Eq. (11), S_{sp} was considered as a constant. However, as mentioned above, the specific surface area will change due to the adsorption deformation that occurs when the catalyst is poisoned. It was therefore decided to measure the specific surface area (low temperature nitrogen adsorption by the Brunauer–Emmett–Teller (BET) method) in order to take its changes into account for a more accurate calculation of the TOF.

The data shown in Fig. 2 are in good agreement with the data published in [20]. There, an initial increase in specific surface area is also followed by

Table 2. Absolute activity (TOF) of a porous nickel catalyst in aqueous solutions with various additives of sodium hydroxide, aliphatic alcohol, and catalytic poison, without taking into account adsorption deformation or blocking of active sites by catalytic poison, 100/s

Additives to water	***n*(Na_2S), [mmol (Na_2S) · g^{-1} (Ni)]**				
	–	**0.025**	**0.075**	**0.125**	**0.175**
0.01 M NaOH*	5.90	4.44	3.55	2.35	1.79
0.1 M NaOH*	5.60	5.17	4.37	2.95	2.05
1 M NaOH*	4.61	4.14	3.25	2.35	1.49
0.01 M NaOH–MeOH**	7.14	4.94	3.86	2.74	1.12
0.1 M NaOH–MeOH**	8.02	7.04	6.50	5.18	2.69
1 M NaOH–MeOH**	6.01	5.08	4.50	4.25	3.37
0.01 M NaOH–EtOH**	7.67	5.28	3.76	2.54	2.49
0.1 M NaOH–EtOH**	8.46	9.19	7.28	5.18	4.20
1 M NaOH–EtOH**	4.79	5.38	4.60	4.40	3.76

* Specific surface area of the catalyst (S_{sp}) = 90 m^2/g;

** Specific surface area of the catalyst (S_{sp}) = 61 m^2/g.

a decrease as the level of poisoning increases. In [20], such a change in specific surface area is explained by the initial adsorption deformation, where the catalyst particles fall apart into smaller particles, leading to an increase in specific surface area. This is also reflected in the increased activity of the catalyst, which occurs despite the poisoning of its catalytic poison in a number of solvents. Taking into account the obtained data, a new calculation of TOF was made, where S_{sp} is no longer a constant, but is measured for all cases. The data are presented in Table 3.

In Table 3, the TOF for poisoned catalysts is less dependent on the solvent and the values are close, whereas, without taking into account the adsorption deformation, there is practically no correlation of similar values. It is therefore advisable to use the proposed approximation to calculate the TOF. However, this approximation does not take into account the reduction in the number of active sites due to blocking by a catalytic poison. Consequently, with this approach to calculating TOF, the resulting value also decreases as the level of poisoning increases. However, in some cases (solutions of H_2O–EtOH–0.1 M NaOH and H_2O–EtOH–1 M NaOH), a promotional effect was observed: in order to correctly calculate TOF, it is necessary to somehow take into account changes in the number of active sites during partial poisoning. This requires further research.

To account for the number of active sites removed from the reaction zone, it is necessary to reveal the physical meaning of K_{pois} in Eq. (5). According to [21] for skeletal nickel, A_{max} = 196 cm^3·s^{-1}·g^{-1}, = −247.76·10^3 kJ·mol^{-1}, and K_{pois} = 509887 s^{-1}; Eqs. (5) and (6) take the form (12) and (13), respectively:

$$A_{calc} = 8.11 \cdot 10^{-4} \cdot \Delta_{\alpha} H^{peak}_{meas}(H_2) - \\ - 5.09887 \cdot 10^{5} \cdot n(Na_2S) + 196, \quad (12)$$

$$\Delta_{\alpha} H^{peak}_{calc}(H_2) = 1.2335 \cdot 10^{3} \cdot A_{meas} + \\ + 6.2894 \cdot 10^{8} \cdot n(Na_2S) - 241.76 \cdot 10^{3}. \quad (13)$$

If expressed $K_{H \rightarrow A}$ from Eq. (7) and substituted into Eq. (5), we get the following Eq. (14):

$$A_{calc} = \frac{-A_{max}}{\Delta_{\alpha} H^{peak}_{max}(H_2)} \cdot \Delta_{\alpha} H^{peak}_{meas}(H_2) - \\ - K_{pois} \cdot n(Na_2S) + A_{max}. \quad (14)$$

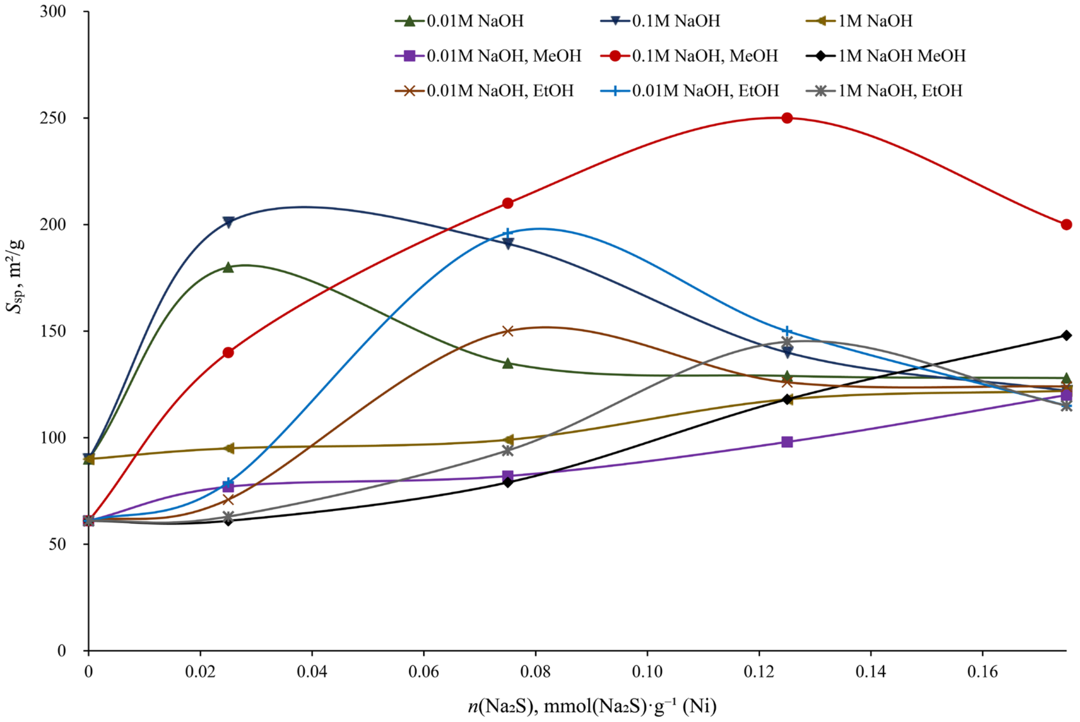


Fig. 2. Influence of the amount of introduced catalytic poison on the specific surface area of the catalyst.

Table 3. Absolute activity (TOF) of a porous nickel catalyst in aqueous solutions with various additions of sodium hydroxide, aliphatic alcohol, and catalytic poison, taking into account adsorption deformation, but without blocking of active sites by catalytic poison, 100/s

Additives to water	**n(Na$_2$S), [mmol (Na$_2$S) · g^{-1} (Ni)]**				
	–	**0.025**	**0.075**	**0.125**	**0.175**
0.01 M NaOH	5.90	2.22	2.36	1.64	1.26
0.1 M NaOH	5.60	2.31	2.06	1.90	1.52
1 M NaOH	4.61	3.92	2.95	1.79	1.10
0.01 M NaOH–MeOH	7.14	4.24	1.57	1.33	0.55
0.1 M NaOH–MeOH	8.02	5.44	2.02	2.11	1.43
1 M NaOH–MeOH	6.01	4.92	2.92	1.79	1.79
0.01 M NaOH–EtOH	7.67	4.18	2.80	1.58	1.27
0.1 M NaOH–EtOH	8.46	4.00	2.12	1.26	1.28
1 M NaOH–EtOH	4.79	5.38	3.55	2.27	1.55

Now let us try to group this equation into a different form (15):

$$A_{\text{calc}} = A_{\text{max}}\left(1-\frac{\Delta_\alpha H^{\text{peak}}_{\text{meas}}(\text{H}_2)}{\Delta_\alpha H^{\text{peak}}_{\text{max}}(\text{H}_2)}-\frac{K_{\text{pois}}}{A_{\text{max}}}\cdot n(\text{Na}_2\text{S})\right). \qquad (15)$$

Based on Eq. (15) and the information that the dimension K_{pois} = [cm^3(H$_2$)·s^{-1}·mol^{-1}(S^{2-})], Eq. (16) is:

$$K_{\text{pois}} = \frac{A_{\text{max}}\cdot N_A\cdot K_{\text{S-Ni}}}{N^{\text{norm}}_{\text{as}}}. \qquad (16)$$

Substituting the figures obtained for skeletal nickel into this equation, we get $K_{\text{S–Ni}}$ = 8. Thus, $K_{\text{S–Ni}}$ can be assumed to be the coordination number for sulfide with respect to nickel, which is in good agreement with the previously obtained data [12, 13]. As a result, Eq. (15) can be expressed in a finite general form (17):

$$A_{\text{calc}} = A_{\text{max}}\left(1-\frac{\Delta_\alpha H^{\text{peak}}_{\text{meas}}(\text{H}_2)}{\Delta_\alpha H^{\text{peak}}_{\text{max}}(\text{H}_2)}-\frac{N_{\text{A}}\cdot K_{\text{S-Ni}}}{N^{\text{norm}}_{\text{as}}}\cdot n(\text{Na}_2\text{S})\right). \qquad (17)$$

It is clear that one sulfur atom blocks eight nickel atoms. Thus, it is possible to set a limit at which all nickel atoms will be blocked, as well as taking into account the number of unblocked atoms $N^{\text{norm}}_{\text{as}_{\text{unblock}}}$ (18):

$$N^{\text{norm}}_{\text{as}_{\text{unblock}}} = N^{\text{norm}}_{\text{as}} - N_{\text{A}}\cdot K_{\text{S-Ni}}\cdot n(\text{Na}_2\text{S}). \qquad (18)$$

Based on the equations given above, it becomes clear that K_{pois} represents the degree of blocking of active sites multiplied by the maximum possible activity for the selected catalyst. Based on this, the following Eq. (19) was obtained for calculating TOF:

$$\begin{aligned}\mathrm{TOF} &\approx A\cdot\frac{N_\mathrm{A}}{\left(S_\mathrm{sp}\cdot N_\mathrm{as}^{1\,\mathrm{m}^2}-N_\mathrm{A}\cdot K_{\mathrm{S-Ni}}\cdot n(\mathrm{Na_2S})\right)\cdot 1000\cdot V_\mathrm{m}}=\\ &=A\cdot\left(\frac{N_\mathrm{A}}{S_\mathrm{sp}\cdot N_\mathrm{as}^{1\,\mathrm{m}^2}\cdot 1000\cdot V_\mathrm{m}}-\frac{1}{K_{\mathrm{S-Ni}}\cdot n(\mathrm{Na_2S})\cdot 1000\cdot V_\mathrm{m}}\right)= \\ &=A\cdot\left(\frac{\psi}{S_\mathrm{sp}\cdot 1000}-\frac{1}{K_{\mathrm{S-Ni}}\cdot n(\mathrm{Na_2S})\cdot 1000\cdot V_\mathrm{m}}\right).\end{aligned} \tag{19}$$

The results of calculating the absolute error taking into account the adsorption deformation and deactivation of the catalyst are shown in Table 4.

As shown in Table 4, the data show close values of absolute activity in all the considered systems, having already introduced the catalytic poison. Thus, taking into account the adsorption deformation and the physical blocking of the active sites by the catalytic poison, the TOF values begin to depend less on the amount of catalytic poison to instead primarily depend on the fact of its introduction. Thus, with the exception of a few cases related to severe selective poisoning (e.g., with a solution of MeOH–0.01 M NaOH) [12,13], a further decrease in TOF after blocking 16% of the active atoms is already insignificant, which was expected since TOF shows the activity of an active site. The obtained deviations can be explained by an increase in the heat of adsorption with an increase in the amount of catalytic poison injected.

CONCLUSIONS

The studies carried out allow us to take into account the number of atoms currently available for the reaction (Eq. (18)).

Table 4. Absolute activity (TOF) of a porous nickel catalyst in aqueous solutions with various additives of sodium hydroxide, aliphatic alcohol, and catalytic poison, taking into account adsorption deformation and blocking of active sites by catalytic poison, 100/s

Additives to water	**Degree of blocking nickel atoms**				
	0%	**11%**	**16%**	**32%**	**45%**
0.01 M NaOH	5.9	2.3	2.9	2.4	2.2
0.1 M NaOH	5.6	2.4	2.4	2.7	2.8
1 M NaOH	4.6	4.3	3.9	2.7	2.0
0.01 M NaOH–MeOH	7.1	4.8	1.9	1.9	1.0
0.1 M NaOH–MeOH	8.0	6.1	2.3	2.9	2.8
1 M NaOH–MeOH	6.0	5.6	3.9	2.5	3.5
0.01 M NaOH–EtOH	7.7	4.7	4.0	2.7	2.4
0.1 M NaOH–EtOH	8.5	4.2	2.4	1.5	1.8
1 M NaOH–EtOH	4.8	6.2	5.1	3.4	2.5

The physical meaning of K_{pois} is established to represent the product of the maximum possible activity for the selected catalyst by the degree of blocking of active sites (Eq. (16)). It is shown that the lack of consideration of adsorption-catalytic deformation and blocking of active sites leads to an incorrect calculation of the TOF. With this calculation, the absolute activity decreases evenly. Moreover, when these two processes are taken into account, it can be seen that the absolute activity initially drops sharply with the initial introduction of the catalytic poison, since the energy profile of the surface changes along with an increase in the binding energies of hydrogen with the surface. However, with an increased amount of catalytic poison in the system, the values further change insignificantly, since additional poisoning of the catalyst only changes the number of active sites available to the reactants, but not their nature.

Equation (19) allows the absolute activity of a liquid phase hydrogenation catalyst to be calculated taking into account the adsorption catalytic deformation.

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Authors' contribution

All authors equally contributed to the research work.

The authors declare no conflicts of interest.

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About the authors:

Andrey V. Afineevskii, Cand. Sci. (Chem.), Senior Researcher, Research Laboratory for Synthesis, Research and Testing of Catalytic and Adsorption Systems for Hydrocarbon Processing, Ivanovo State University of Chemistry and Technology (7, pr. Sheremetevskii, Ivanovo, 153000, Russia). E-mail: afineevskiy@mail.ru. Scopus Author ID 55798461600, ResearcherID E-6432-2017, RSCI SPIN-code 5815-6489, http://orcid.org/0000-0001-6933-5130

Dmitry A. Prozorov, Dr. Sci. (Chem.), Senior Researcher, Research Laboratory for Synthesis, Research and Testing of Catalytic and Adsorption Systems for Hydrocarbon Processing, Ivanovo State University of Chemistry and Technology (7, pr. Sheremetevskii, Ivanovo, 153000, Russia). E-mail: prozorovda@mail.ru. Scopus Author ID 55770115900, ResearcherID U-3788-2019, RSCI SPIN-code 1500-1202, http://orcid.org/0000-0002-1749-2828

Tatyana Yu. Osadchaya, Cand. Sci. (Chem.), Researcher, Research Laboratory for Synthesis, Research and Testing of Catalytic and Adsorption Systems for Hydrocarbon Processing, Ivanovo State University of Chemistry and Technology (7, pr. Sheremetevskii, Ivanovo, 153000, Russia). E-mail: osadchayatyu@gmail.com. Scopus Author ID 56587842300, ResearcherID AAB-1677-2020, RSCI SPIN-code 4802-2816, http://orcid.org/0000-0003-0280-0960

Natalya E. Gordina, Rector, Ivanovo State University of Chemistry and Technology (7, pr. Sheremetevskii, Ivanovo, 153000, Russia). E-mail: gordinane@mail.ru. Scopus Author ID 6506079434, ResearcherID S-8639-2017, RSCI SPIN-code 6821-0739, http://orcid.org/0000-0002-1067-4688

Об авторах:

Афинеевский Андрей Владимирович, к.х.н., старший научный сотрудник, лаборатория синтеза, исследований и испытания каталитических и адсорбционных систем для процессов переработки углеводородного сырья, ФГБОУ ВО «Ивановский Государственный химико-технологический университет» (153000, Россия, Иваново, Шереметевский пр., д. 7). E-mail: afineevskiy@mail.ru. Scopus Author ID 55798461600, ResearcherID E-6432-2017, SPIN-код РИНЦ 5815-6489, http://orcid.org/0000-0001-6933-5130

Прозоров Дмитрий Алексеевич, д.х.н., старший научный сотрудник, лаборатория синтеза, исследований и испытания каталитических и адсорбционных систем для процессов переработки углеводородного сырья, ФГБОУ ВО «Ивановский Государственный химико-технологический университет» (153000, Россия, Иваново, Шереметевский пр., д. 7). E-mail: prozorovda@mail.ru. Scopus Author ID 55770115900, ResearcherID U-3788-2019, SPIN-код РИНЦ 1500-1202, http://orcid.org/0000-0002-1749-2828

Осадчая Татьяна Юрьевна, к.х.н., научный сотрудник, лаборатория синтеза, исследований и испытания каталитических и адсорбционных систем для процессов переработки углеводородного сырья, ФГБОУ ВО «Ивановский Государственный химико-технологический университет» (153000, Россия, Иваново, Шереметевский пр., д. 7). E-mail: osadchayatyu@gmail.com. Scopus Author ID 56587842300, ResearcherID AAB-1677-2020, SPIN-код РИНЦ 4802-2816, http://orcid.org/0000-0003-0280-0960

Гордина Наталья Евгеньевна, д.т.н., ректор, ФГБОУ ВО «Ивановский Государственный химико-технологический университет» (153000, Россия, Иваново, Шереметевский пр., д. 7). E-mail: gordinane@mail.ru. Scopus Author ID 6506079434, ResearcherID S-8639-2017, SPIN-код РИНЦ 6821-0739, http://orcid.org/0000-0002-1067-4688

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RESEARCH ARTICLE

Palladium-catalyzed allylation of norbornadiene: Experimental and quantum chemical research

Sergey A. Durakov, Karen T. Egiazaryan, Ravshan S. Shamsiev, Vitaly R. Flid✉

MIREA – Russian Technological University (M.V. Lomonosov Institute of Fine Chemical Technologies), Moscow, 119571 Russia
✉*Corresponding author, e-mail: vitaly-flid@yandex.ru*

Abstract

Objectives. *Catalytic processes involving norbornadiene (NBD) and norbornene (NBN) derivatives provide exceptional opportunities for the synthesis of a wide range of carbocyclic hydrocarbons. By significantly expanding this range, it becomes possible to obtain materials offering a wide variety of predictable properties. The aim of the present review is to summarize the latest achievements in the creation of novel processes catalyzed by palladium compounds. Considerable attention is paid to the study of the mechanisms of NBD allylation reactions by a combination of experimental and theoretical methods.*
Results. *Various strategies of the molecular design of palladium catalysts for syntheses based on NBN and NBD are considered. The possibility of implementing various directions of NBD allylation is demonstrated. Factors influencing the direction of the reactions, by which means individual products can be selectively obtained, are discussed.*

Conclusions. *The effective development of new catalytic processes involving NBD and NBN derivatives requires the complex application of synthetic, kinetic, isotopic, and quantum chemical approaches. By combining instrumental and theoretical methods with constant feedback, it becomes possible to optimize the search for original catalytic systems, obtain information about the mechanisms of their action, and influence technological parameters in a targeted manner.*

Keywords: *norbornene, norbornadiene, allylation, catalysis, kinetics, quantum chemical calculations, reaction mechanism, transition metals, palladium, strained carbocyclic compounds*

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ОБЗОРНАЯ СТАТЬЯ

Палладий-катализируемое аллилирование норборнадиена: Экспериментальные и квантово-химические исследования

С.А. Дураков, К.Т. Егиазарян, Р.С. Шамсиев, В.Р. Флид✉

МИРЭА – Российский технологический университет (Институт тонких химических технологий им. М.В. Ломоносова), Москва, 119571 Россия
✉*Автор для переписки, e-mail: vitaly-flid@yandex.ru*

Аннотация

Цели. *Каталитические процессы с участием норборнадиена (НБД) и производных норборненового (НБН) ряда открывают исключительные возможности для синтеза широкого круга карбоциклических углеводородов. Значительное расширение их ассортимента позволяет впоследствии получать материалы с широким спектром прогнозируемых свойств. Целью обзора является обобщение последних достижений в области создания новых процессов, катализируемых соединениями палладия. Значительное внимание уделено исследованию механизмов группы реакций аллилирования НБД совокупностью экспериментальных и теоретических методов.*

Результаты. *Рассмотрены различные стратегии молекулярного дизайна палладиевых катализаторов для синтезов на основе НБН и НБД. Показана возможность реализации различных направлений аллилирования НБД. Обсуждены факторы, влияющие на направление реакций и позволяющие селективно получать индивидуальные продукты.*

Выводы. *Разработка новых каталитических процессов с участием НБД и НБН-производных требует комплексного применения синтетических, кинетических, изотопных и квантово-химических подходов. Совокупность инструментальных и теоретических методов, имеющих обратные связи, позволяет оптимизировать поиск оригинальных каталитических систем, получать информацию о механизмах их действия и направленно влиять на технологические параметры.*

Ключевые слова: *норборнен, норборнадиен, аллилирование, катализ, кинетика, квантово-химические расчеты, механизм реакции, переходные металлы, палладий, напряженные карбоциклические соединения*

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INTRODUCTION

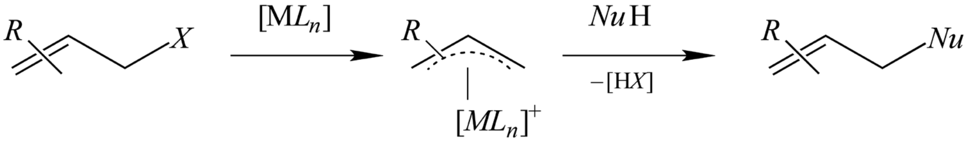
Allyl addition and substitution reactions catalyzed by transition metals attract considerable research attention due to their utility in the synthesis of numerous drugs, semi-product, and materials. Since the pioneering work of Tsuji and Trost in this area, new approaches have been created to form C–C, C–N, C–H, C–O, C–S, C–P, and C–B bonds with high regio- and enantio- control [1, 2]. At the same time, it is worth noting the high functional tolerance of such reactions and the consequent possibility of their implementation under "mild" conditions. Quite typically, the addition of the allyl fragment proceeds without the formation of by-products at high rates of substrate conversion and selectivity for target products.

Such reactions predominantly occur with the participation of allylic substrates (allyl alcohols, allyl carboxylates, allylamines, etc.), a transition metal used as a catalyst (usually nickel or palladium), and a nucleophile attacking allyl complex (Fig. 1). If the substrate is insufficiently reactive, it is possible to provide for its additional activation using the right selection of the metal-catalyst, ligands, solvent and auxiliary activators (for example, Lewis acids).

With the optimal choice of conditions, the possibility of stereoselective allylation of substrates may in some cases arise [3–5]. Compared to most similar reactions catalyzed by metals, asymmetric allyl substitution proceeds at sp^3 rather than sp^2 hybridized centers. Allylation reactions are also used to build cycles, transfer 1,3-chirality, separate racemates, desymmetrize meso substrates, and so on [6].

In recent years, great progress has been achieved in the field of allyl substitution reactions using metal complex catalysts, as summarized in reviews [1–3, 5, 7, 8]. Approaches have been developed for the use of various substrates: allyl ethers, alcohols, and allylamines [1]. Methods for their additional activation along with new generation of ligands for conducting enantioselective synthesis of important natural compounds or drugs have been proposed [9]. Among the various substrates capable of supporting reactions, compounds of the norbornene (NBN) and norbornadiene (NBD) series, representing important objects of organic synthesis, are of particular interest [10–12]. The unconventional nature of the allylation reaction with the participation of these compounds is associated with the structure of the resulting products and the mechanism of their formation. During addition to a nucleophile, the allyl fragment can undergo significant transformations: C–C bond cleavage in the allyl fragment itself with the formation of methylene-vinyl (**1**) and methylenecyclobutane (**2**) derivatives, the formation of methylenecyclopentane cycles (**3**), or addition to the alkene (**4**). In addition, the formation of several isomeric products is possible (Fig. 2).

The possibility of NBN allylation was first demonstrated in 1979 by M. Catellani *et al.* using Ni^0 complexes as catalyst [13]. The reaction products, representing compounds having a type **1** and type **2** *exo* structure, are formed along various routes along which the process conditions are controlled by varying selectivity. Later, along with a demonstration of the universality of the method for NBN substrates, it was shown that effective catalysts for this and related reactions can be formed from various nickel compounds [14, 15]. In the course of further studies, the use of NBD was found to significantly expand the synthetic possibilities of this reaction [16]. The reason of these significant differences lies in the NBD property of chelate-type coordination to the metal, resulted in a more diverse structure of products than for NBN. In addition to compounds of types **1** and **2**, the formation of nortricyclane isomers, compound **3**, is also observed. In addition, double allylation products **6**–**11** and **6'**–**11'** are often observed in the presence of an excess of the allylating agent due to the presence of a second double NBN bond in the NBD molecule.



where *R* is substituent, *M* is transition metal, *L* is ligand, *Nu* is nucleophile, *X* = OAc, OCO_2R, etc.

Fig. 1. Transition metal-catalyzed allylic substitution with activated allylic substrates.

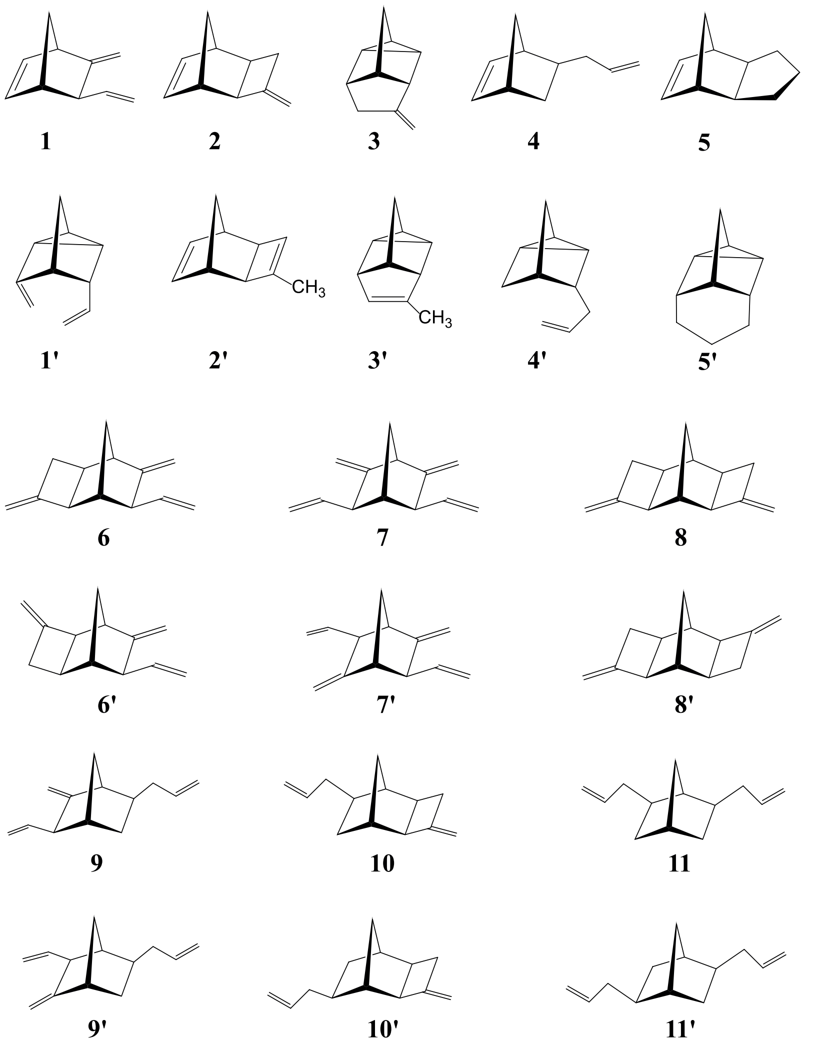


Fig. 2. Products of NBD allylation.

Thus, allylation of NBD leads to a number of products with different structures, which indicates the multipath nature of the process. These compounds have a high potential for use as monomers for obtaining materials with desired properties or components for rubbers of the EPDM type (synthetic ethylene propylene diene monomer rubber). However, the practical use of the NBD allylation reaction is currently quite limited. The structure of the carbocyclic skeleton of the NBD molecule leads to all types of isomerism in the resulting products—regio-, stereo, enantio-, which often produces a mixture that is difficult to separate and adversely affects the selectivity of process. In this regard, it became necessary to conduct regular research to understand the mechanisms of allylation and develop new catalysts. In practical terms, a reasonable selection of a catalyst and reaction conditions is impossible without a deep understanding of the nature of catalytically active particles. An examination of the structure and energy parameters of the intermediates that form the catalytic cycle, informs an understanding of the nature of the rate-determining stages and the roots of different levels of isomerism. The most rational way to solve these key problems of catalysis is associated with the complex application of experimental synthetic, kinetic, isotope, and quantum chemical methods and approaches. Such studies have been carried out for a number of years at the Ya.K. Syrkin Department of Physical Chemistry of the M.V. Lomonosov Institute of Fine Chemical Technologies of RTU MIREA.

Over the past decades, a sufficient amount of kinetic and spectral data has been collected during the research of the stoichiometric and catalytic interaction of NBD with allyl complexes of transition metals and allylcarboxylates. Proposed schemes of mechanisms for these reactions help to qualitatively explain the structure of the resulting products[1]. However, since nickel systems are sensitive even

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[1] Flid V.R. *Physical and chemical bases of catalytic syntheses involving norbornadiene and allyl derivatives*. Dr. Sci. Thesis (Chem.). Moscow; 2000. 250 p. (in Russ.).

to trace amounts of oxygen, obtaining accurate information about these transformation mechanisms turned out to be a very difficult task.

In previous work, we have used an integrated approach in the study of various directions of allylation, consisting in the joint application of modern experimental methods, the rational use of physicochemical methods for the analysis of reaction systems, as well as quantum chemistry approaches, in order to obtain elusive information about highly reactive intermediates. The only currently realistic alternative to nickel in NBD allylation reactions takes the form of palladium-based catalyst systems. Due to the special properties of the latter, not only the main intermediates of the process were investigated, but also a new synthetic direction was discovered, leading to the development of the first heterogeneous catalysts.

Thus, the aim of the present review is to summarize the results of recent research in the field of palladium-catalyzed NBD allylation. The important feature of this process approach consists in the unity of theoretical and experimental approaches with constant feedback, which has been successfully used to carry out molecular design of catalysts and develop highly efficient homogeneous and heterogeneous catalytic systems for allylation reactions of NBD and NBN compounds.

EXPERIMENTAL RESEARCH OF PALLADIUM-CATALYSED ALLYLATION OF NBD

At the first stage of research, in order to identify new—in addition to nickel-based—catalytic systems, the stoichiometric interaction of NBD with homoligand η^3-allyl complexes of other metals, Co, Fe, Ni, Rh, Pd, and Pt, was studied [17]. The reaction was found to proceed quantitatively at 25°C in just a few minutes, yielding a wide range of products. The general nature of the reaction, which is associated with the transfer of hydrogen between η^3-allyl ligands, was established for all metals. When using complexes of nickel, palladium, and platinum, compounds with a double bond in the norbonene ring are predominantly formed. This fact illustrates the monodentate nature of NBD coordination in transition metal complexes of the nickel subgroup. Noting the closeness of the ratio of products for these metals, an assumption was made about the similarity of their coordination capabilities. It is noted that the activity of the metals significantly decreases from nickel to platinum.

Since the stoichiometric model of a single catalytic cycle turned out to be convenient in establishing the main directions of the addition of the allyl fragment to NBD and revealing the details of the mechanism, in 1991 a hypothesis was put forward about the possibility of developing similar catalysts based on other transition metals [17]. However, it was only in 2000 that a catalytic process using palladium compounds could be implemented [18]. When NBD is allylated with allyl acetate, almost the same set of products is formed as for nickel [19]. For various palladium precursors: $Pd(dba)_2$+$2PPh_3$, $Pd(OAc)_2$+$2PPh_3$, $PdCl_2(PPh_3)_2$, $[(C_3H_5)Pd]NO_3$+$2PPh_3$, similar activity values and product ratios are observed. The composition of products is similarly affected by temperatures and the ratio of reagents. Thus, at 25–60°C, compounds **1** and **2** are formed in high yields, while at temperatures above 80°C, the relative amount of compound **3** increases. The selectivity for individual isomers does not exceed 50–60%. With an excess of allyl acetate, as in the case of nickel catalysts, secondary allylation of the unsubstituted NBN double bond in compounds **1** and **2** occurs, leading to a large quantity of isomeric products **6**–**8** and **6'**–**8'**.

Thus, qualitative analogy was established in the behavior of Ni- and Pd-catalytic systems during the allylation of NBN and NBD substrates, on which basis we can assume a similar structure of key intermediates. Despite the fact that the reaction rate for palladium-based systems is somewhat lower than for their nickel-based counterparts, the former tend to be more stable and exhibit activity under normal conditions in air. By greatly simplifying the technological aspects of the process itself, this allows the application of new tools to the study of its mechanism. In this regard, further studies on optimizing the conditions for obtaining individual products were carried out using palladium systems.

Palladium catalysts containing phosphines have a high group selectivity with respect to compounds **1**–**3**; in most cases, however, the yield of individual products does not exceed 50%. An exception is the nanocluster system consisting of $Pd_{55/147}$ and triphenylphosphine in the $[bmim][BF_4]$ ionic liquid medium, when the only product **1** is formed [20]. Apparently, this is one of the few examples of the fact that the Pd_{147} cluster is not destroyed in the medium of an ionic liquid. Indirectly, this experiment anticipated a new direction: the development of heterogeneous catalytic systems for supporting this reaction.

An interesting direction of the reaction was discovered when using a new allylating agent, allyl formate (AF). Although AF is not used for nickel catalysts due to the consequent instability, the same catalytic system is formed in NBD and AF media for ligand-free catalytic systems and various palladium precursors (Pd^0, Pd^{2+}), heteronuclear carboxylate complexes of the composition $[PdM(\mu\text{-}R\text{COO})_m L_n]_x$, where M = Zn, Co, Ni, Mn, and rare earth elements; R = Me, *tert*-Bu; m = 4.5; x = 1, 2, and $Pd_2Cu(\mu\text{-OAc})_6$, as well as giant $Pd_{55/147}$ clusters [21]. The main reaction product in all cases is 5-allylnorbornene-2 (5-allylbicyclo[2.2.1]-heptene-2) **4**, which was previously unavailable when using nickel catalysts. Products **1**–**3** under similar conditions are formed only in trace amounts.

Substituted AFs, which also enter the reaction, selectively add to the double bond of NBD with an unsubstituted carbon atom. The differences between the processes described earlier and this reaction are that, in the first case, the allyl group, in adding to NBD, loses the H atom (oxidative allylation), while in the second case, it adds it (reductive allylation). Thus, palladium compounds are catalysts for both oxidative and reductive NBD allylation. Previously, the formation of reductive NBD allylation products was observed only in stoichiometric interactions [22].

It was shown that for Pd^{2+} precursors, the process begins after a long induction period. As a result of kinetic and electrochemical experiments, it was established that Pd^{2+} is reduced to Pd^0 during this period under the action of the components of the reaction mixture. The process can be accelerated by the right choice of base.

The proposed mechanism of NBD hydroallylation is based on the totality of all experimental and spectral data (Fig. 3). After the formation of the Pd^0 complex at the initial stage, AF is oxidatively added to it. This is followed by the insertion of NBD, coordinated in the *trans* position relative to the substituent R, at the palladium-allyl bond. The structure of such relatively stable complexes has been studied by X-ray diffraction analysis[2]. As a result of decarboxylation at the subsequent stage, a palladium hydride complex is most likely formed. Although this has not yet been observed directly in this reaction, the possibility of the formation of similar complexes in other catalytic processes has already been experimentally demonstrated [23]. This is followed by the stage of reductive elimination with the formation of compound **4** and regeneration of the original Pd^0 form.

The formation of hydride complexes of palladium as a result of decarboxylation of formate ions has long been known [24]. It can be assumed that NBD and a neutral ligand on palladium, for example, dibenzylideneacetone (dba) or phosphine, play an important role in the stabilization of Pd^0 formed as a result of the reductive elimination of the product at the final stage of the catalytic cycle. Further, due to the greater prevalence and commercial availability, we used palladium acetate as a catalyst precursor.

By analogy with nickel systems, it was assumed that greater selectivity in the formation of products **1**–**3** could be achieved by varying the phosphine/palladium ratio. In the course of the studies, however, we found that varying the amount of the phosphine ligand has practically no effect

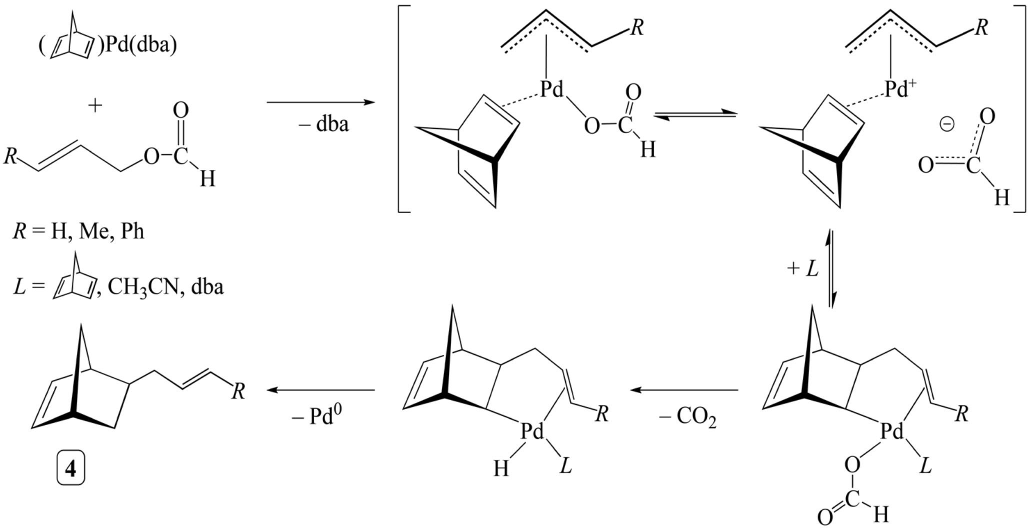

Fig. 3. Mechanism of catalytic hydroallylation of NBD.

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[2] Evstigneeva E.M. *Electronic structure, spectral and catalytic properties of allyl complexes of palladium*. Dr. Sci. Thesis (Chem.). Moscow; 2011. 259 p. (in Russ.).

on the ratio between products **1**–**3**. However, in the case of carrying out the reaction in acetonitrile and using AF as an allylating agent, the direction of the process changes with an increase in the amount of phosphine ligand towards an increase in the amount of oxidative allylation products and a decrease in compound **4** [25].

To explain this phenomenon using a combination of physicochemical methods of analysis, we studied the stages of formation of palladium intermediates in solutions of various compositions. The study was carried out using the methods of cyclic voltammetry (CV), high-resolution mass spectrometry, nuclear magnetic resonance spectroscopy (NMR) and by gas chromatography-mass spectrometric (GC-MS) control of products and intermediates in various model systems and in the reaction itself.

The complex formation reactions in solutions necessary for the formation of catalytically active complexes proceed by the substitution mechanism, in which the ligand and/or reagents replace the solvate molecules of the solvent. The nature of the solvent also affects the kinetics and mechanism of such transformations. The rate of its exchange with another ligand depends on the strength of interaction between a metal cation and a coordinated solvent molecule. This means that at each stage of the reaction it is necessary to take into account the role of stabilization of key intermediates by solvent molecules. Solvents with a wide range of physicochemical properties were studied as reaction media. In addition, all components of the catalytic system of the reaction under study should be soluble in them. Although the properties of a solvent are characterized by many parameters, the main contribution is usually determined under conditions of homogeneous metal complex catalysis by the ability of the solvent to form hydrogen bonds with substrates and intermediates, as well as the degree of polarity, polarizability, and coordinating ability with respect to transition metals. The totality of these relative characteristics correlates with the statistical probability of solvent coordination to transition metal complexes and reflects its ability to solvate and stabilize them.

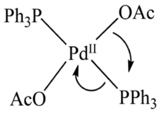
When studying the effect of solvents, two series of experiments were carried out: without additional introduction of ligands and with the use of PPh_3. At the first stage, the interaction of palladium acetate with NBD with AF in a ligand-free system was studied. The data obtained confirmed that the very possibility of a reaction between NBD and AF under the indicated conditions really depends on the solvent used. For a significant number of non-polar or low-polar solvents, the reaction is practically absent. An increase in the conversion of reagents, on the contrary, is observed when using solvents capable of coordination (acetonitrile, dimethyl sulfoxide), and, to a lesser extent, for water and ethanol. The complete absence of reaction when using pyridine, despite its higher ability to coordinate, is obviously associated with the difficulties of replacing it with reagents in palladium complexes during the formation of intermediates. In general, in the medium of coordinating solvents, the reaction proceeds with the predominant formation of **4**, compounds **2'** and **3** are observed in insignificant amounts. In some cases, products of double allylation of NBD **11** and **11'** are formed (Fig. 2).

During the formation of catalytically active complexes from $Pd_3(OAc)_6$ in solutions in the presence of phosphine ligands, it was found that upon addition of PPh_3 ($^{31}P = -5.81$ ppm), a brown solution becomes yellow. The resulting complex is characterized by the signals $E^{p}_{red} = -1100$ mV and $^{31}P = 14.67$ ppm. (14.84 ppm in $CDCl_3$), which corresponds to the $Pd(OAc)_2(PPh_3)_2$ compound (1). According to [26–29], this complex undergoes intramolecular rearrangement (2), during which Pd^{2+} is reduced to Pd^0, while PPh_3 (3) is oxidized to triphenylphosphine oxide ($O{=}PPh_3$) $^{31}P = 26.41$ ppm (29.50 ppm in $CDCl_3$).

In the case of an excess of phosphine, the $Pd^0(PPh_3)(OAc)^-$ complex associated with the acetate ion and characterized by the peak of $E^{p}_{ox} = +190$ mV and the signal of $^{31}P = 17.94$ ppm (15.95 ppm in $CDCl_3$), in accordance with reactions (4) and (5) forms complexes $Pd(PPh_3)_4$, $Pd(PPh_3)_3$, giving a broadened peak $E^{p}_{ox} = +580$ mV, signals $^{31}P = 15.31$ ppm (15.39 ppm in $CDCl_3$) and $^{31}P = 20.80$ ppm (20.18 ppm in $CDCl_3$). 14-Electron particles of the $Pd(PPh_3)_2$ type are not observed in model systems.

For the ligand-free system, as a result of the CV analysis, the addition of AF to $Pd_3(OAc)_6$ was found to lead to the gradual formation of two Pd^0 complexes. Most likely, these are $Pd(CH_3CN)(OAc)^-$

$$Pd(OAc)_2 + 2PPh_3 \longrightarrow Pd(OAc)_2(PPh_3)_2 \qquad (1)$$



$$\longrightarrow Pd^0(PPh_3)(OAc)^- + AcO\text{–}PPh_3^+ \qquad (2)$$

$$AcO\text{–}PPh_3^+ + H_2O \longrightarrow AcOH + O{=}PPh_3 + H^+ \qquad (3)$$

$$\mathrm{Pd^0(PPh_3)(OAc)^-} + \mathrm{2PPh_3} \longrightarrow \mathrm{Pd^0(PPh_3)_3} + \mathrm{OAc^-} \tag{4}$$

$$\mathrm{Pd^0(PPh_3)_3} + \mathrm{2PPh_3} \rightleftarrows \mathrm{Pd^0(PPh_3)_4} \tag{5}$$

and $Pd(CH_3CN)_2$, which are characterized by broad peaks E^p_{ox} = –20 mV and E^p_{ox} = 700 mV, respectively. In the NBD–$Pd_3(OAc)_6$ system, such interactions are not observed.

The formation of a complex of palladium with NBD and an acetate moiety, solvent, and NBD was registered by high-resolution mass spectrometry with electrospray ionization (ESI-MS). The 14-electron complexes $Pd^0(CH_3CN)_2$ and $Pd^0(CH_3CN)(AcO)^-$ were not found in the solution. The $Pd^0(NBD)_2$ complex, which is responsible for the formation of insignificant amounts of NBD dimerization products, was detected only when AF was depleted [30].

When PPh_3 is added to the system, the situation changes dramatically. The ligand actively competes with the solvent for the coordination site on palladium, as a result of which both reductive and oxidative allylation of NBD becomes possible. For solvents incapable of coordination, the direction of reductive allylation is almost completely suppressed; in this case, compounds **1**, **2**, and **3** become the main reaction products. PPh_3 in the active complex as it is oxidized.

In the presence of PPh_3, in addition to the compounds described above, the solution contained a complex characterized by a signal in the NMR spectrum ^{31}P = 18.58 ppm. Based on the data of works [26–29, 31] and the classical work of Yamomoto [32], an allyl derivative of composition $Pd^{2+}(PPh_3)(OAc)^-(\eta^3\text{-}C_3H_5)(OCOH)$ can be concluded to result from the oxidative addition of AF to the spontaneously formed $Pd^0(PPh_3)(OAc)^-$ complex. Similarly, for a ligand-free system, the formation of the compound $Pd^{2+}(CH_3CN)(OAc)^-(\eta^3\text{-}C_3H_5)(OCOH)$ was assumed.

When PPh_3 is used, NBD allylation occurs in both polar and weakly polar solvents with high polarizability. The GC-MS analysis of the reaction mixtures indicates the presence of 14-electron palladium complexes of the anionic form $(PPh_3)Pd^0(OAc)^-$ and $(PPh_3)_2Pd^0(OAc)^-$, stabilized by induced and permanent dipoles of the solvent. Such interactions have been well studied for the closely related system $Pd_3(OAc)_6$+PPh_3 [28].

In some cases, a small amount of double allylation, hydrogenation, and hydroformylation products accumulate in the system, whose formation was described in our earlier works [21, 25, 30, 35, 36].

Thus, it is experimentally confirmed that (depending on the nature of the solvent and the presence of a ligand) two different types of precursors can form in the system, preceding the stage of oxidative addition of AF to the palladium atom (Fig. 4). In the absence of PPh_3, the role of the ligand is taken simultaneously by NBD and the coordinating solvent.

The presence of anionic palladium complexes during the formation of the catalytic system with PPh_3 and at the first stage of reduction in the ligand-free system is confirmed by the CV data. It is known that the formed anionic complexes of zerovalent palladium are much more active in the oxidative addition of allyl carbonates. If they are not sufficiently stabilized by solvent molecules or if they are strongly coordinated by two solvent molecules (for example, pyridine), the catalytic system is destroyed with the formation of propene observed in some cases.

Evidence of the influence of the proton solvent, which is expressed in the stabilization of palladium intermediates by additional hydrogen bonds, was not found.

The mechanism of the reduction of palladium acetate in a ligand-free system followed by the oxidative addition of AF is still not completely clear. Traces of water present in the solution or formic acid can act as a reducing agent for palladium. The involvement of AF itself cannot be ruled out: the formyl hydrogen atom can transfer to acetate groups from the complex, releasing CO_2 and forming CH_3COOH.

According to the GC analysis, it was found that during the induction period associated with the formation of the active complex, the response of two signals increases, the intensity of which is proportional to the concentration of palladium acetate. It was shown by NMR and GC-MS that they are products of the addition of acetate groups to the NBD **12** and **12'** molecule (Fig. 4). It is important to note that model experiments with acetic acid under conditions of NBD catalytic allylation at T = 20–60°C and in the absence of a catalyst or AF do not lead to the formation of these products, which can be obtained without a catalyst, but only at much higher temperatures [33].

Experiments with the use of deuterated AF indicate the formation of products with a molecular weight of 153. A deuterium atom was found in the norborene ring; it is obvious that it gets there when transferred from the formyl group. This suggests the formation of the

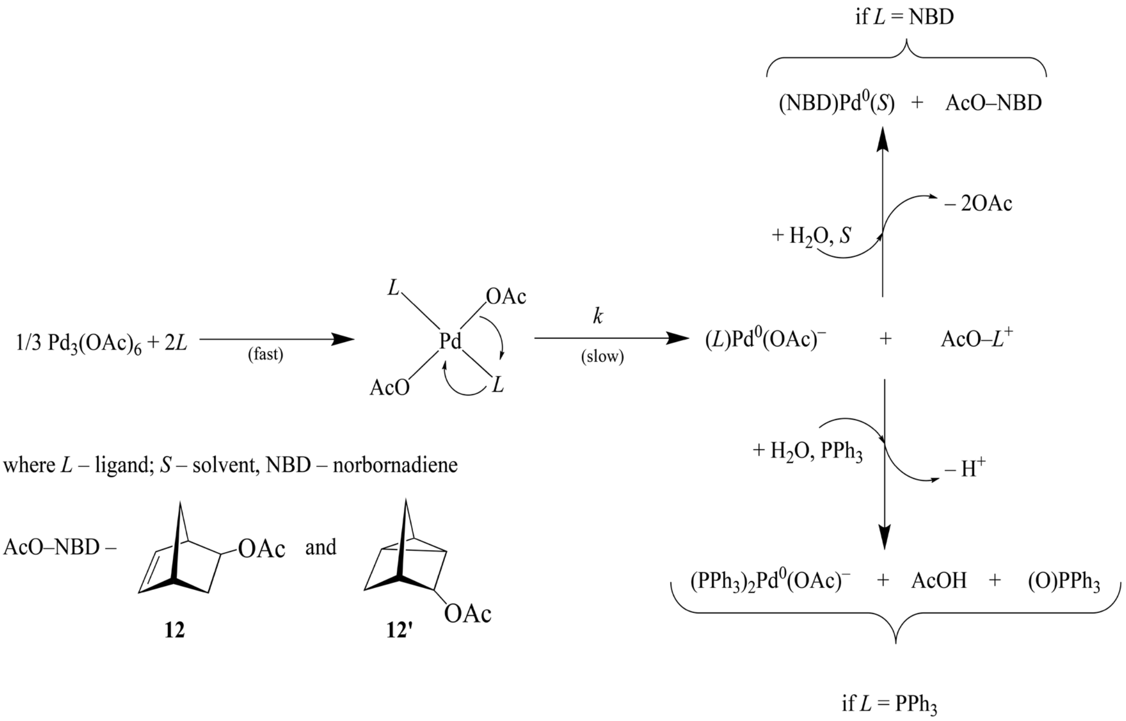


Fig. 4. Scheme of the reduction of palladium acetate to Pd^0 with the formation of active intermediates of neutral and anionic nature.

Pd^{2+}(η^2-*exo*-NBD)(OAc)$^-$(η^3-C$_3$H$_5$)(OCOH) intermediate. At one of the stages of the mechanism, after coordination of NBD on the Pd complex, theaddition of the acetate ion to NBD occurs, culminating in β-hydride elimination with the formation of compounds **12-D$_1$** and **12'-D$_1$** (Fig. 5).

Following removal of the acetate groups, the interaction of Pd*L*$_2$ with AF and NBD leads to the Pd(η^2-*exo*-NBD)(η^3-C$_3$H$_5$)(OCOH) intermediate. The Pd^{2+}(PPh^3)(OAc)$^-$(η^3-C$_3$H$_5$)(OCOH) complex formed as a result of the oxidative addition of AF is capable of exchanging a phosphine ligand for an *exo*-coordinated NBD molecule. As a result, as in the ligand-free system, the Pd(η^2-*exo*-NBD)(η^3-C$_3$H$_5$)(OCOH) complex is formed, whose further transformations lead to NBD allylation products.

During the CV analysis of the NBD+AF+Pd$_3$(OAc)$_6$+PPh$_3$ system, not only the Pd^0(PPh$_3$)(OAc)$^-$ complex is observed, but also a signal in the $E^{\mathrm{p}}_{\mathrm{ox}}$ = 0 mV region; this probably belongs to Pd^0(CH$_3$CN)(OAc)$^-$ formed as a result of stabilization of the system by the solvent.

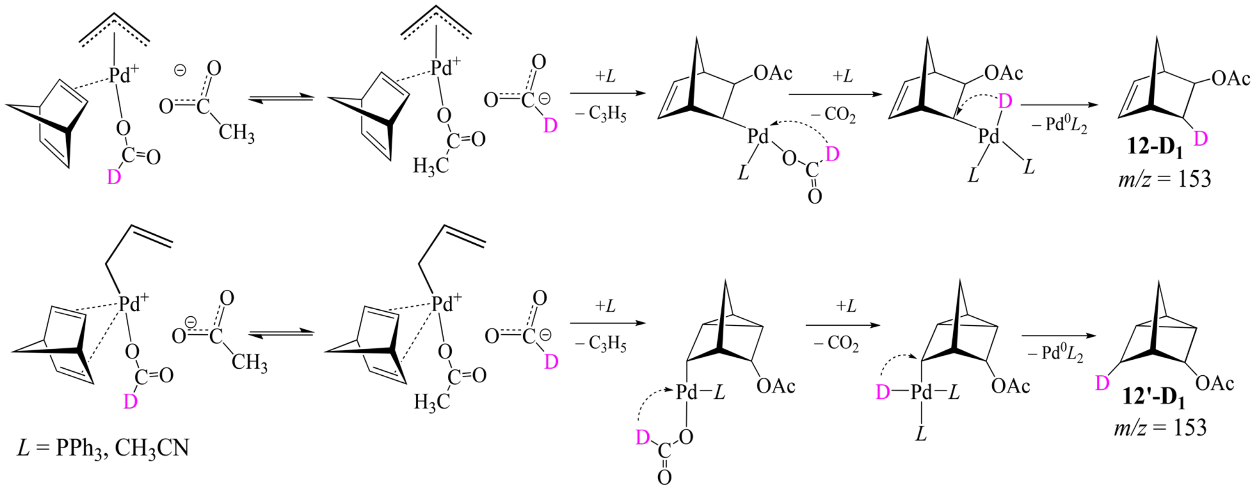


Fig. 5. Mechanism of formation of NBD acetylation products.

Thus, in a catalytic system based on palladium acetate and PPh_3, phosphine molecules, having a higher affinity for palladium, are initially coordinated. After that, intermediates are formed into which the AF molecule is embedded. This is followed by the coordination and implementation of the NBD molecule. The process ends with the transfer of acetyl moieties to NBD. After that, palladium intermediates containing an NBD molecule, as well as allyl and formyl fragments, are again formed.

Acetonitrile or phosphine ligands stabilize the palladium complexes formed after the formation of the C–C bond (^{31}P = 23.14 ppm), occupying the coordination sites released during the reaction. The ligand present in the coordination sphere actively participates in the process. Its properties affect the directions of interaction between AF and NBD, leading to products of various structures.

In the case of η^2-*exo*-coordination of NBD, only one site for the ligand is vacant in the intermediate, which is confirmed by experiments with bi- and tridentate ligands. Thus, when diphenylphosinomethane (dppm), diphenylphosinoethane (dppe), diphenylphosinopropane (dppp), diphenylphosphinobutane (dppb), and terpyridine (terpy) are used, only the corresponding palladium complexes are formed regardless of the temperature and type of solvent [34]. Although these reactions are accompanied by a color change and/or precipitation, no catalytic transformations are observed (Fig. 6).

The described facts confirm the square-planar configuration of palladium complexes throughout the entire reaction, indicating that the chelate ligand, occupying two coordination sites on the palladium atom, blocks the further course of the reaction.

The catalytic cycle is accompanied by the regeneration of various Pd^0 complexes with phosphine or NBD in the coordination sphere. As the reagents are consumed, they are accumulated. With an excess of NBD at the end of the process, its cyclodimerization is possible.

From the obtained data, it becomes clear why it is not possible to radically change the ratio of products **1**–**3** in nonpolar media by varying the amount of PPh_3 in the allylation reaction of NBD with AF. Based on the available ideas, for this purpose, an approach was taken to use sterically bulky tertiary phosphines. Such phosphines can facilitate the oxidative addition of the substrate to palladium, which, due to their structure, then affects other stages. Oxidative addition is accelerated by ligands with strong electron-donating properties, which increase the electron density at the metal center. This effect is clearly manifested in reactions involving allylcarboxylates. Smaller ligands, such as PPh_3, can form active diphosphine complexes ($Pd(PR_3)_2$). In some cases, sterically bulky ligands promote β-hydride elimination, especially when this step is limiting.

It was concluded that phosphines with electron-withdrawing substituents promote the formation of NBD **1**–**3** oxidative allylation products. Such ligands facilitate β-hydride elimination involving the hydrogen atom of the NBN ring. The steric factor also plays an important role in the process. Thus, the use of ligands with a small cone angle ($\theta < 145°$) causes β-hydride elimination in the formyl fragment with the formation of propene. Bulky ligands direct the process towards the production of NBD allylation products. However, it should be taken into account that an excessively large value of the phosphine cone angle, for example, in the case of trimesitylphosphine ($P(Mes)_3$) with $\theta > 212°$, leads to inhibition of the reaction, probably due to steric hindrances arising in the coordination of substrates.

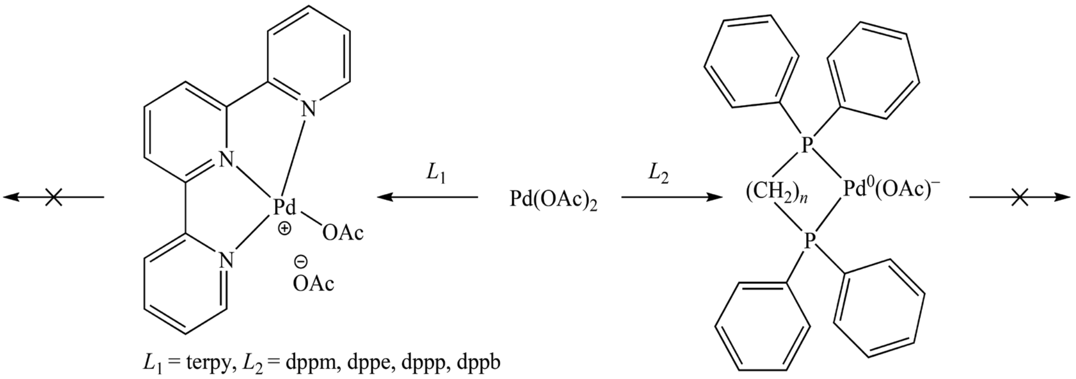


Fig. 6. Palladium complexes with polydentate ligands.

Thus, the best rates of conversion and selectivity for products **1**–**3** are achieved when using phosphines with a conical angle θ close to 145°, whose electronic parameters are higher than 2065 cm^{-1}, to achieve a selectivity of more than 65% in obtaining isomer **1** and maintaining a high catalyst activity.

Interesting information was obtained using isotopically substituted AFs with different degrees of substitution of protium for deuterium [35] (Fig. 7).

An analysis of the mass spectra of the products showed that the use of AF with a deuterated label in the formyl group resulted in the formation of allylation products **1**–**3**, **4**, and **4-D$_1$** with molecular weights of 132, 134, and 135, respectively. For AF deuterated at the allyl moiety, the masses of products **1-D$_5$**, **2-D$_4$**, **3-D$_4$**, and **4-D$_5$** of single allylation are 137, 136, 136, and 139. Using fully deuterated AF gives products **1-D$_5$**, **2-D$_4$**, **3-D$_4$**, and **4-D$_6$** with molecular weights 137, 136, 136, and 140. Depending on the composition of the deuterated AF, isomers of compounds **1** and **4** are formed in small amounts, namely: **1'**, **1'-D$_5$**, **4'**, **4'-D$_1$**, **4'-D$_5$**, **4'-D$_6$**. For compound **2**, these are derivatives **2'** and **2'-D$_4$**, probably formed as a result of double bond migration. Compound **15** and its deuterated analogues **5-D$_1$**, **5-D$_5$**, and **5-D$_6$** were discovered for the first time (Fig. 8). Small amounts of C_3H_6, C_3H_5D, C_3HD_5, and C_3D_6 propene are also formed, whose composition depends on the AF structure.

A number of important conclusions can be formulated according to a structural analysis of the products as follows:

1. The products of catalytic reactions and the position of deuterium atoms in them are similar to the compounds obtained by the stoichiometric interaction of NBD with deuterium-substituted bis(η^3-allyl)nickel.

2. The structure of all NBD **1**–**3** oxidative allylation products is the same for various allylating agents, as well as for nickel and palladium.

3. The reductive NBD allylation product **4** in the catalytic version is formed only when AF and palladium complexes are used. This compound

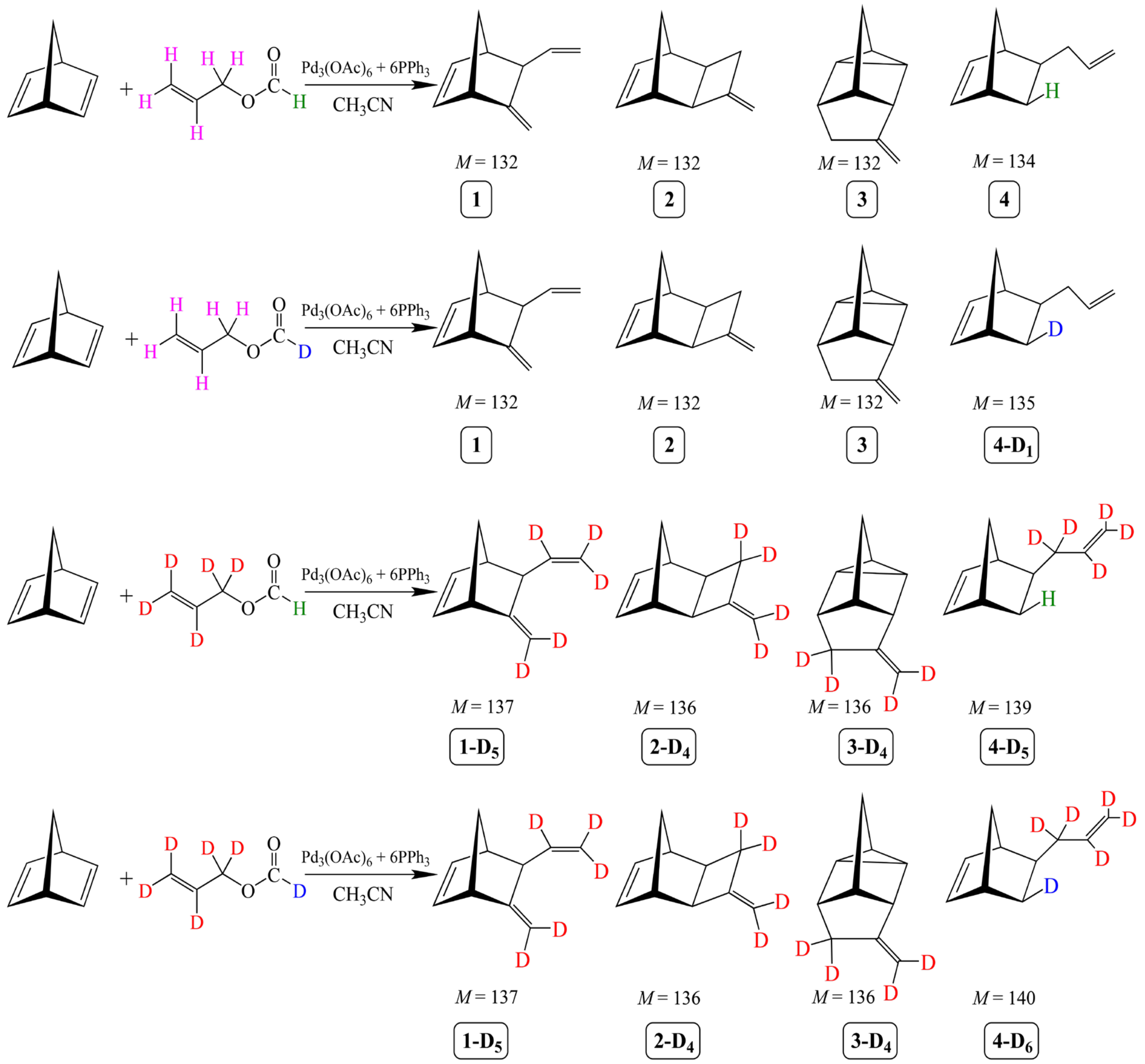


Fig. 7. Catalytic NBD allylation under the action of the $Pd_3(OAc)_6$+6PPh_3 system using a series of isotopically substituted allyl formats.

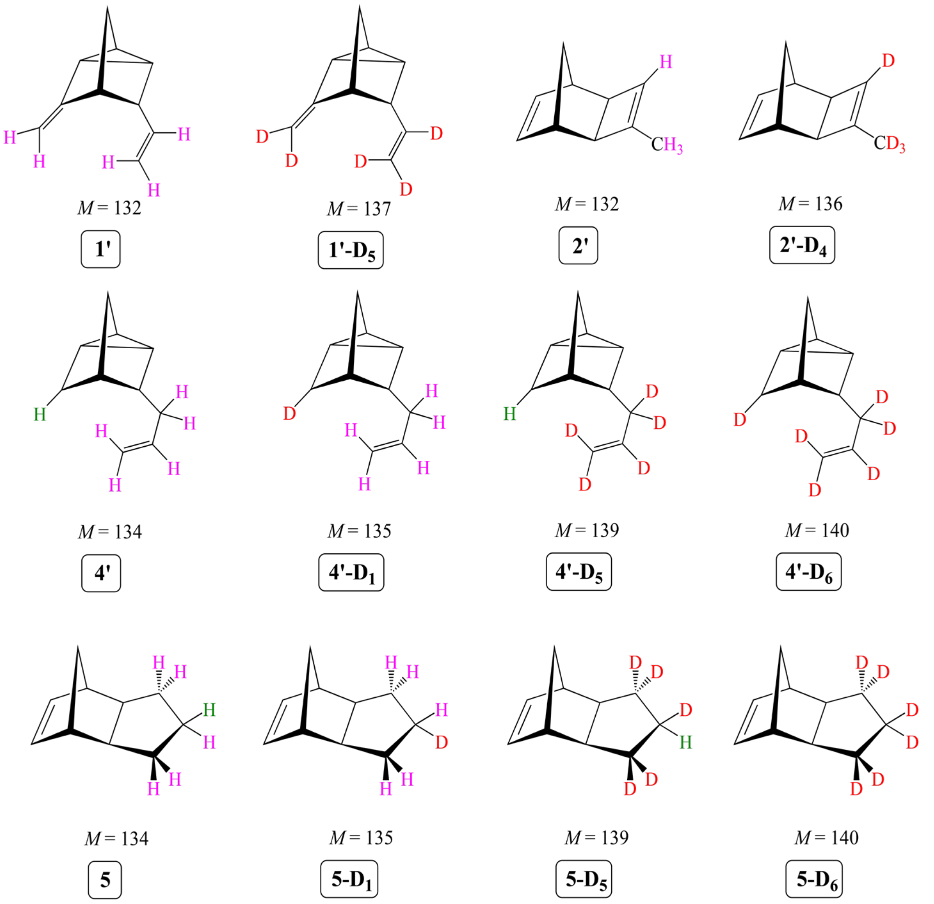


Fig. 8. Structure of side-produced analogs of NBD allylation products.

is also observed in the stoichiometric interaction of NBD with homoligand allyl complexes of transition metals. The stereochemistry of compound **4** is determined by the *exo* direction of attack of the hydride transfer and allyl with respect to the NBN ring.

4. The direction of hydride transfer for all products, which is of a general nature, is associated with the breaking of the C–H β-bond with respect to the metal atom. This stage can proceed with the participation of allyl, norbornenyl, or formyl fragments.

5. The formation of products **1** and **5** suggests the formation of an intermediate with the cyclopentane fragment and the presence of formyl hydrogen in the palladium complex.

6. Compounds **1'**, **3**, **3'**, **4'**, and their deuterated analogs are formed as a result of η^4-coordination of NBD on the palladium atom, which activates the second double bond in the molecule and leads to nortricyclane products.

7. Compounds **2** and **3** are formed as a result of the rearrangement of the allyl fragment at the stages of [2+2]- or [2+4]-addition.

8. The formation of isomers **2'** and **3'** occurs as a result of double-bond migration in the allyl fragment coordinated on the palladium atom at the stage of β-hydride transfer.

9. The formyl fragment is retained in the coordination sphere of the palladium complex throughout the entire catalytic cycle up to the stage of β-hydride transfer, whose direction determines the structure and ratio of products (Fig. 9).

The information obtained with the use of deutero-substituted AFs is still insufficient for discussing the nature of the rate-limiting step. Given the variability of hydride transfer, the rate-determining steps may differ for products **1**–**4**. Therefore, additional kinetic studies were carried out with AF-D_1 deuterated at the formyl group. The first series of experiments consisted of the combined use of AF and AF-D_1 to create competitive conditions. The kinetic isotope effect (KIE) was estimated by comparing the concentrations of products **4** and its deuterated analog **4-D$_1$**, which are formed in parallel using the $Pd_3(OAc)_6$ catalytic system and using the same amounts of AF and AF-D_1. Assuming that the reaction mechanism does not change for different isotopes, the formation of products **4** and **4-D$_1$** should

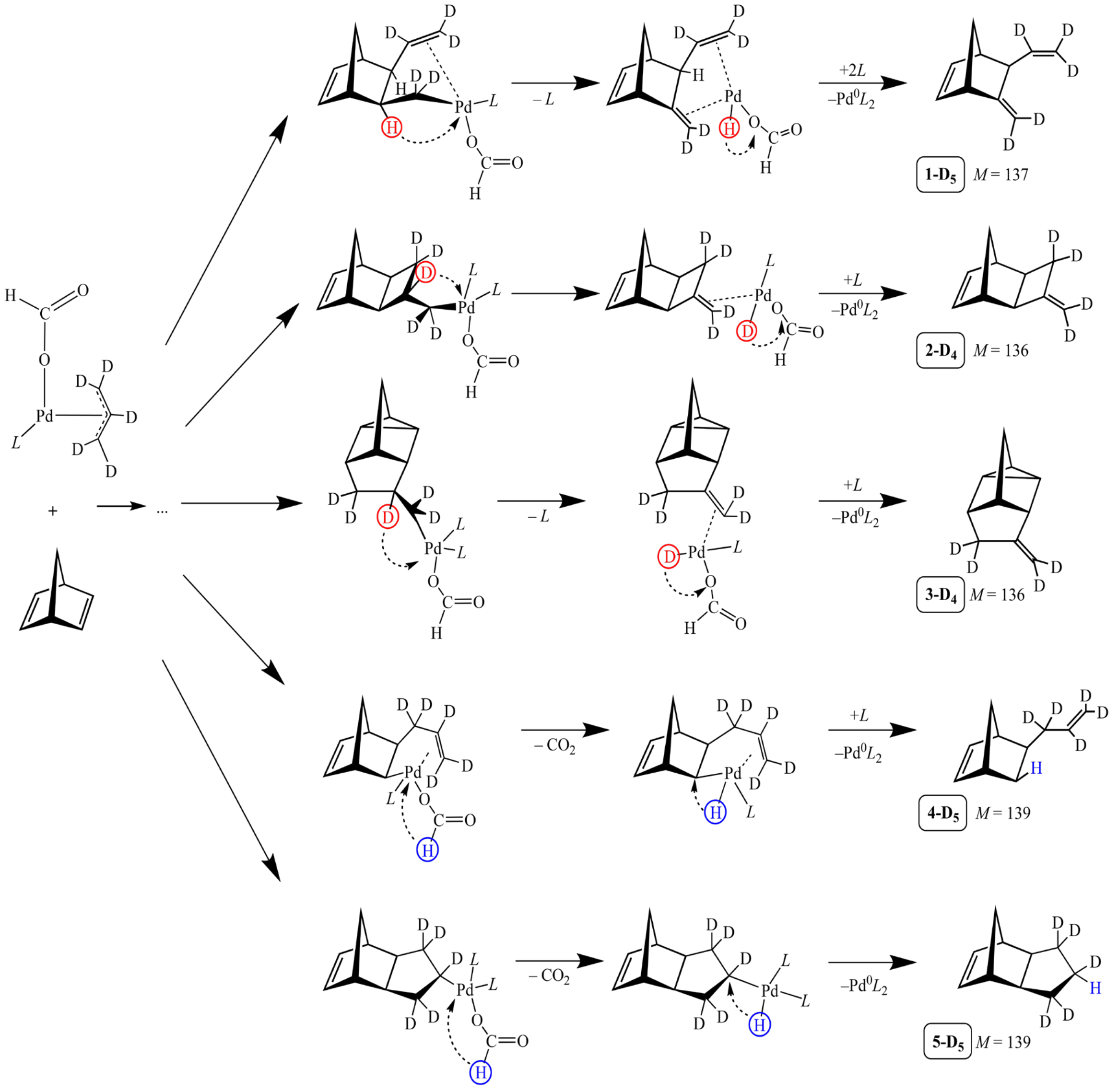


Fig. 9. Options for the direction of the β-hydride transfer step for key intermediates in the catalytic NBD allylation reaction.

have the same kinetic description. Then the ratio of the concentrations of the products will be constant in time and equal to the ratio of the observed rate constants.

The second series of experiments involving AF and AF-D$_1$ was carried out separately under identical conditions, minimizing the formation of by-products. For this, AF was taken in deficiency (10%) in relation to NBD. Taking into account the low reaction rate at 25°C, the concentrations of the products were similarly determined at low conversions of the reagents (not higher than 5%). The time was counted after the end of the induction period (Fig. 10).

The KIE values obtained in two series of experiments completely coincide: $K_{KIE} = 2.2 \pm 0.2$. A rather high KIE value excludes isotope insensitive steps, such as trans-metalation and product dissociation, from consideration [36]. It is very likely that the formation of a C–H bond (β-hydride transfer or reductive elimination) occurs at the limiting stage of the process. The assumption of β-hydride transfer as a limiting step in the catalytic cycle of the NBD hydroallylation mechanism was also considered in our theoretical works [37].

Thus, all compounds formed during NBD allylation can formally be considered as NBD adducts with [C_3H_4], [C_3H_6], [H], and [COOH] fragments. The source of these hypothetical particles or molecules are the allyl fragments and the formyl group, which are originally part of the AF. For the reaction to proceed, it is necessary that allyl derivatives (All–X) with an activated All–X bond oxidatively add to Pd^0 complexes to form an

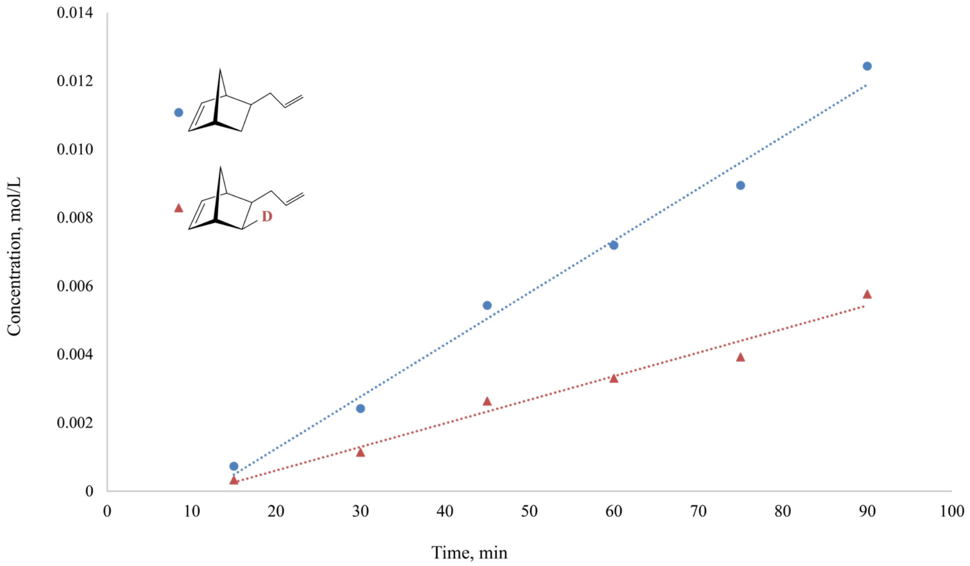


Fig. 10. Time dependence of the ratio of NBD **4** and **4-D$_1$** hydroallylation products.

allyl-palladium intermediate. Then the NBD molecule is coordinated on the metal atom, causing η^3–η^1 isomerization of the allyl ligand, and is introduced into the η^1-allyl–metal bond. The different directions of cyclization occurring in the resulting intermediate depend on the type of the ligand coordinated on the palladium atom. The catalytic cycle is completed with β-hydride transfer, product formation, and regeneration of Pd^0L_2 particles. Here, hydride transfer can proceed in different directions.

The totality of our experimental data suggests a consistent mechanism of the process that explains the formation of all NBD allylation products when AF is used as an allylating agent (Figs. 11 and 12).

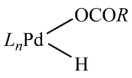
The formation of secondary NBD allylation products occurs according to a similar mechanism. The substrates are mono-adducts containing an active intracyclic NBN bond capable of being coordinated on the palladium atom in the allyl complex (Fig. 12). The yield of products depends on the activity of the double bond in the corresponding mono-adduct. Since in this case the η^4-coordination of the reagents is impossible, no products having a nortricyclane structure are formed.

The reduction of double bonds is probably associated with the formation of formic acid, which acts as a hydrogenating agent in the reaction mixture. One of the possible ways of its decomposition in the presence of a palladium catalyst is associated with the formation of carbon dioxide and hydrogen. These assumptions were confirmed by an analysis of the gas phase in the reactor attesting to the formation of carbon dioxide. Additional experiments testify to the stability of the catalytic system under study. The resulting formic acid enters into further transformations without having a deactivating effect, probably due to its decomposition on palladium (6).

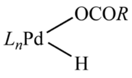
$$\mathrm{HCOOH} \xrightarrow{[\mathrm{Pd}]} \mathrm{CO_2} + 2[\mathrm{H}] \qquad (6)$$

This transformation is associated with the formation of a certain amount of NBD hydrogenation products. Thus, under the conditions of the process, AF simultaneously acts as an allylating and hydrogenating agent.

In accordance with the mechanism (Fig. 12), the formation of compounds **1**–**3** in the presence of AF proceeds similarly to other allyl ethers. The key role in the formation of hydrogenation and hydroformylation products of NBD and compounds **1**–**4** is played by the hydride complex formed at the stage


$L_nPd\begin{matrix}\diagup \mathrm{OCO}R \\ \diagdown \mathrm{H}\end{matrix}$

of β-hydride transfer. For all R that are alkyl or aryl radicals, the decomposition of this intermediate as a result of reductive elimination leads to the formation of the acid RCOOH. In the case of R = H, however, the situation is fundamentally different. All directions are implemented simultaneously, their ratio depends on many factors, including NBD conversion. It can be assumed that the complex


$L_nPd\begin{matrix}\diagup \mathrm{OCO}R \\ \diagdown \mathrm{H}\end{matrix}$

is involved in the following transformations (Fig. 13 and 14).

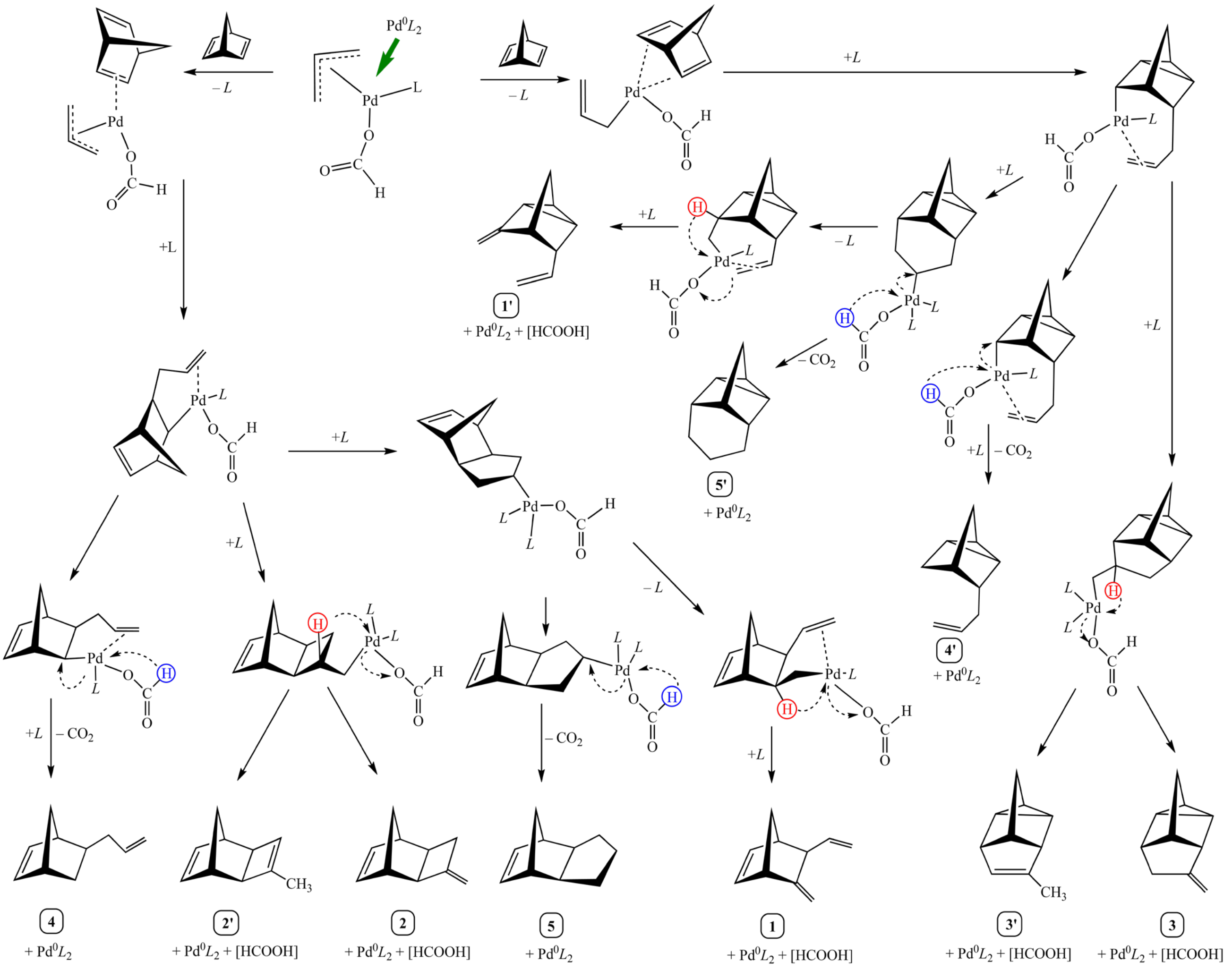


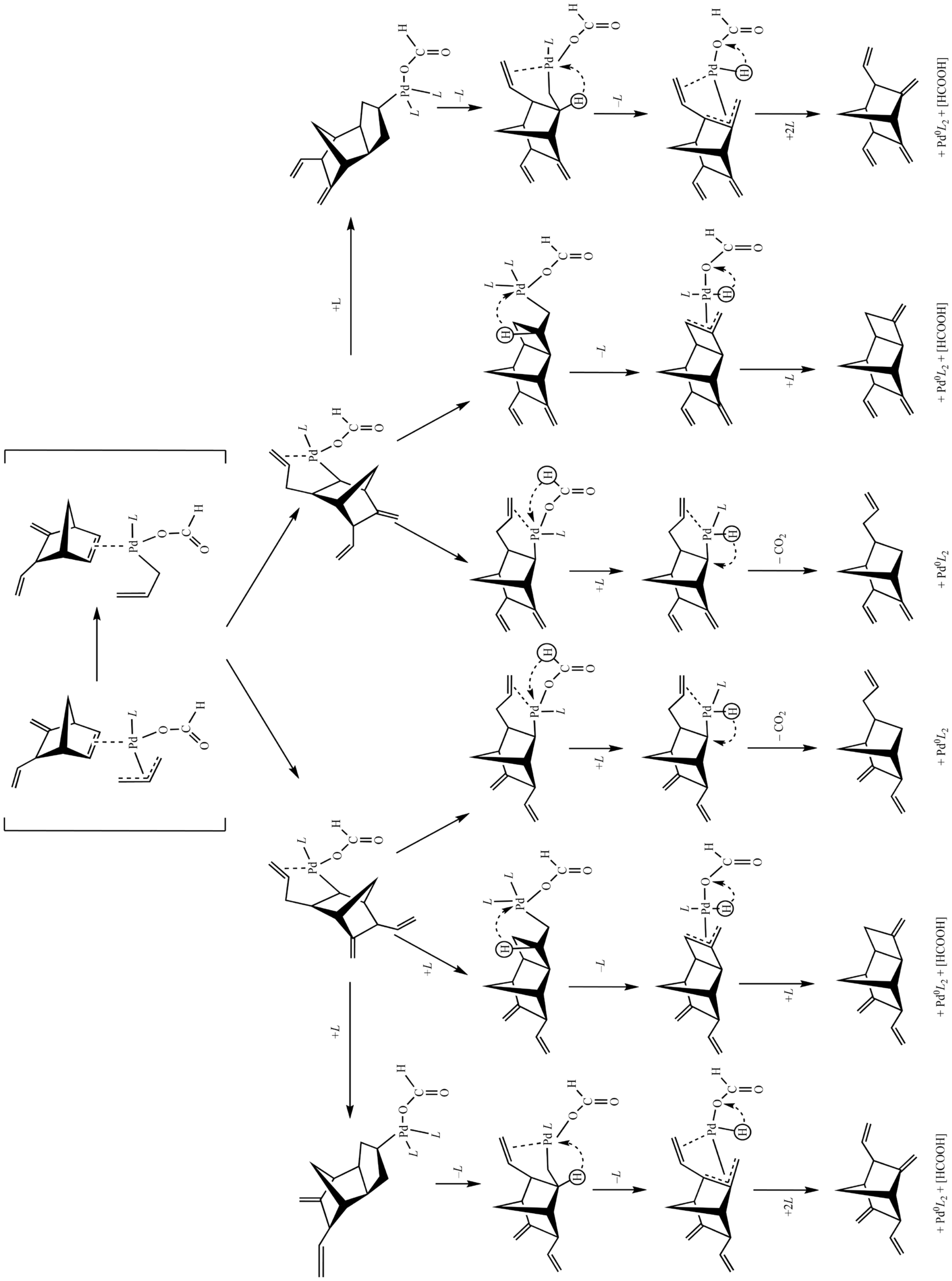
Fig. 11. Mechanism of catalytic NBD allylation with allyl formate on palladium catalysts.

Based on the totality of the data obtained, and taking into account the previously proposed reaction mechanisms for palladium and nickel catalytic systems, it is shown that palladium complexes can be effectively used to develop and vary the composition of a catalytic system, as well as the conditions of its operation, to achieve high values of the conversion of the reagents for the selective preparation of compounds **1** and **4**. At the same time, the efficient preparation of products **2** and **3** is possible only in the case of the use of nickel catalysts having a different coordination polyhedron and broader possibilities for coordinating additional molecules of phosphorus-containing ligands. This understanding of the catalytic NBD allylation mechanism was used to inform the first successful prototypes of heterogeneous catalysts based on the immobilization of metal complexes on various supports with the preservation of the structure of active sites in the selective preparation of products **1**–**4** [38].

QUANTUM-CHEMICAL SIMULATION OF NBD ALLYLATION

In addition to experimental research carried out at the Ya.K. Syrkin Department of Physical Chemistry, theoretical studies of reactions involving NBD have been undertaken, in particular, concerning oxidative and reductive NBD allylation with AF. Quantum-chemical modeling was used in a number of cases to explain the experimental facts, clarify the reaction mechanism, identify key stages and intermediates, as well as to predict the effect of chiral ligands on the enantioselectivity of NBD allylation.

The calculations were performed in the scalar-relativistic approximation of the density functional theory (DFT) using the Priroda [39, 40] and ORCA 5.0.3 [41, 42] programs. Geometry optimization of all reactants, products, transition states (TS), and intermediates was carried out in the



7 6' 9' 9 6 7'

Fig. 12. Mechanism of formation of double NBD allylation products.

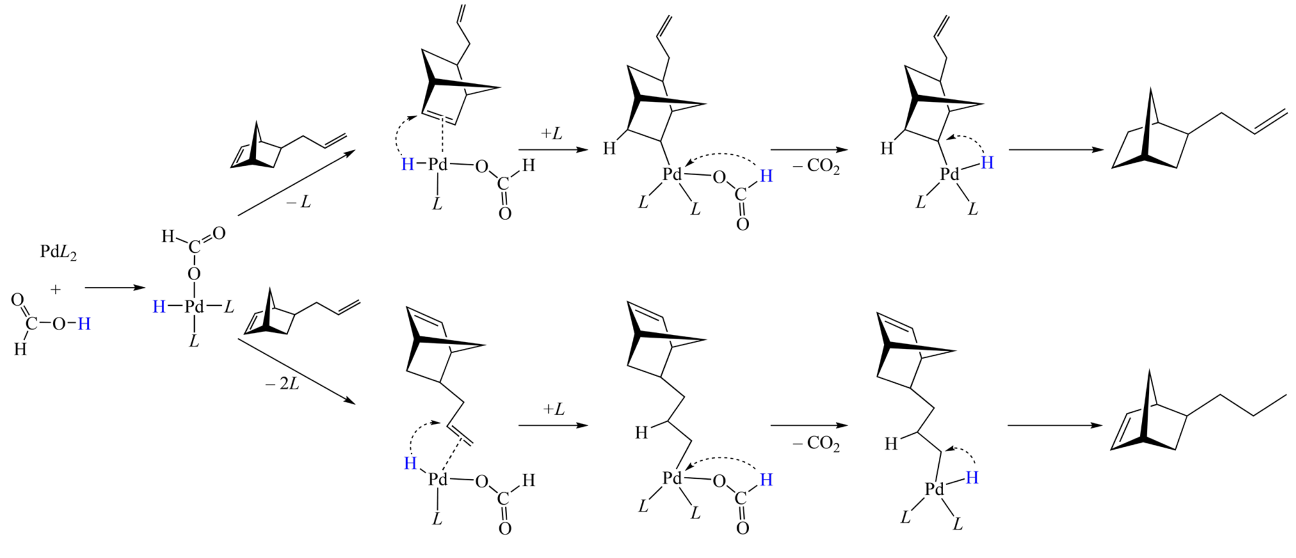


Fig. 13. Mechanism of formation of NBD allylation product with simultaneous hydrogenation.

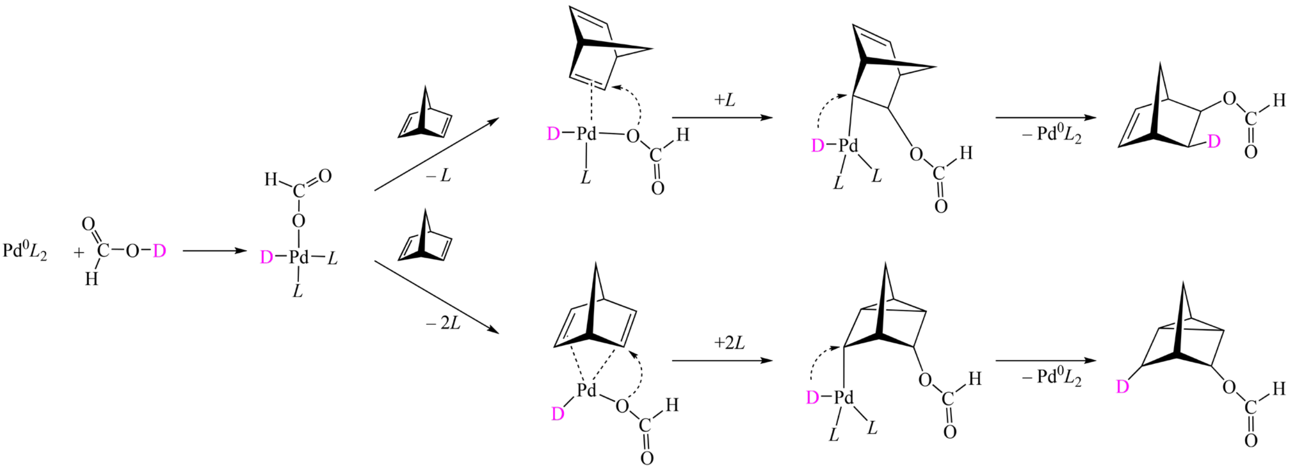


Fig. 14. Mechanism of formation of NBD hydroformylation products.

PBE[3] exchange-correlation functional [43] to set the full-electron L11[4] basis [44]. The calculations described in the section on evaluating enantioselectivity were further refined in the ωB97X-D3(BJ)[5] long-range-corrected hybrid functional [45] and the ZORA-def2-TZVP[6] all-electron basis [46] for P, O, C, H, and SARC-ZORA-TZVP[7] [47] for Pd. The correspondence of the optimized structures to minima or TS was confirmed by analysis of vibration frequencies. To check the relationship of localized TSs with the products and reagents of the stage, the internal reaction coordinate (IRC) was calculated. Thermodynamic parameters were calculated for 25°C. Corrections to solvation energies were obtained within the PCM-SMD[8] model [48] for acetonitrile (ε = 35.7).

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[3] PBE is Perdew-Burke-Ernzerhof exchange-correlation functional.

[4] L11 is all electron double zeta basis set, built according to the type of correlation-consistent polarization valence-split Dunning basis set cc-pCVDZ.

[5] ωB97X-D3(BJ) is hybrid exchange-correlation functional corrected for long-range interaction with the inclusion of Grimme dispersion corrections.

[6] ZORA-def2-TZVP is valence triple zeta polarization basis set for calculations in zero regular approximation (ZORA).

[7] SARC-ZORA-TZVP is valence triple zeta polarization basis set for calculations in zero regular approximation (ZORA) taking into account relativistic corrections for heavy elements.

[8] PCM-SMD is Polarizable Continuum Model and Solvation Model of Density.

In a phosphine-free catalytic system with a high selectivity of up to 95% [21], the product of reductive NBD allylation with 5-allyl-2-norbornene AF (**4**) is formed. Quantum-chemical calculations made it possible to identify two most probable routes for the formation of product **4**. Figure 15 shows the results of modeling the mechanism of reductive allylation for two types of NBD coordination aimed at elucidating the stereostructure of the product.

The initial stages of the mechanism are associated with the formation of catalytically active Pd(AF)(CH_3CN) (**H1**) and Pd(AF)(NBD) (**H2**, **H3**) complexes from Pd(CH_3CN)$_3$ and AF and NBD molecules. This is followed by the stage of oxidative addition (**H2→H4**, **H3→H5**), which, as shown by calculations [49], can have two TSs. The difference between them lies in the number of atoms involved in the TS formation. In one TS, one O atom is involved, while in the other, more preferably, both O atoms are involved.

Since an intramolecular change in the η^2-*exo*/η^2-*endo* orientation of the NBD ligand is impossible, the stereostructure of the product is predetermined at the stage of NBD coordination on the Pd atom: *exo* (**4**) or *endo* (**4'**).

This is followed by the formation of a C–C bond between the allyl ligand and NBD (**H4→H6**, **H5→H7**), which is associated with a noticeable decrease in the Gibbs free energy of the system. This stage is also characterized by the highest activation energy over the entire reaction path: 22.1 and 23.9 kcal/mol, respectively, for the routes of formation of products **4'** and **4**. Taking into account the possibility of isomerizing the **H5** complex into the more stable **H5.1**, the activation energy of the route of product **4'** formation will be equal to 24.8 kcal/mol, which exceeds the energy for **4** by 0.9 kcal/mol. Taking into account the solvation energy, the energy difference between the energies of the rate-determining TSs decreases to 0.1 kcal/mol, indicating the possibility of observing a mixture of stereoisomers **4** and **4'**.

Subsequent steps involve hydride transfers (**H8→H10→H12** and **H9→H11→H13**) from the formate ligand to the Pd atom and back from the Pd atom to the allylnorbornene derivative. As in the case of the stage of C–C bond formation, the stages of hydride transfer involving the *exo*- and *endo*- NBN fragment have similar activation energies. At the final stage, the formed product is

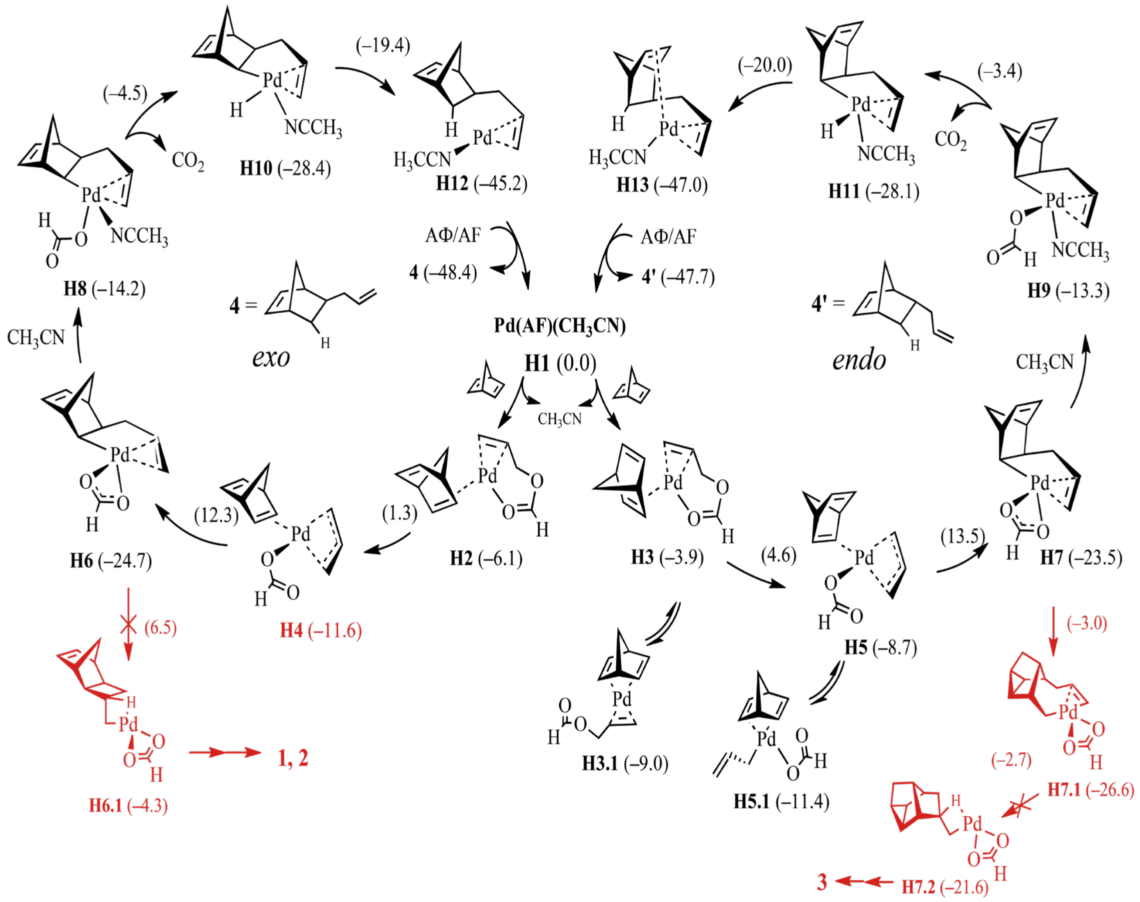

Fig. 15. Catalytic cycles for the formation of stereoisomers of 5-allyl-2-norbornene **4** and **4'**. Gibbs energies are indicated in parentheses (ΔG_{298}, $\Delta G^{\neq}_{298}$, kcal/mol).

replaced by an AF molecule to form a catalytically active complex **H1**, which is returned to the next catalytic cycle.

Detailed quantum chemical calculations do not rule out an alternative route for the formation of *exo*-product **4**, in which β-hydride elimination precedes the stage of C–C bond formation (mechanism **B**, Fig. 16). Mechanism **B** branches off immediately after the oxidative addition step. As a result of the C–H bond cleavage in the formate ligand in **H14**, a hydride intermediate **H15** is formed, which can be converted along the following route: first, the C–C bond is formed (**H15→H16**), then the CH$_3$CN molecule is added (**H16→H10**), then hydride transfer occurs with a Pd atom to the NBD fragment (**H10→H12**) and, finally, the product is cleaved off.

As in the case of mechanism **A**, the maximum activation barrier to the reaction proceeding via mechanism **B** is at the stage of C–C bond formation. Allowing for solvation within the framework of SMD and the inclusion of two solvent molecules (acetonitrile) leads to activation energies of this stage equal to 21.0 and 20.8 kcal/mol for routes **A** and **B**, respectively. Thus, according to the results of theoretical studies, product **4** is formed via two routes with almost equal contributions to the reaction mechanism (Fig. 16).

Quantum-chemical calculations were carried out to clarify the nature of the KIE manifested in this reaction. The experimental estimate of the KIE [36] of allylation is 2.2, possibly indicating that the stage of C–H bond cleavage during hydride transfer is rate-determining. However, according to the quantum chemical calculation data [50], the KIE should be significantly larger than 4.7 in this case. The difference is explained by the fact that, according to [51], the KIE depends not only on the rate constant (*k*) of the rate-determining stage (which, according to calculations, is the C–C bond cleavage stage, but in this case, KIE = ~1), but also on *k* stage preceding or following the rate-determining. In both mechanisms, the stage of hydride transfer from the formyl ligand is irreversible; in this case, the experimentally observed value of KIE is an average value determined by *k* stages of C–H and C–C bond cleavage.

The high selectivity for product **4** in the phosphine-free system can be explained by kinetic obstacles ($\Delta\Delta G^{\neq}_{298}$ = 24–31 kcal/mol) during the formation of subsequent C–C bonds (**H6→H6.1** and **H7→H7.1→H7.2**) required to obtain allylation products **1**–**3**. In the presence of phosphines, in particular PPh$_3$, the activation barriers of this stage are noticeably lowered to form all possible products **1**–**4**.

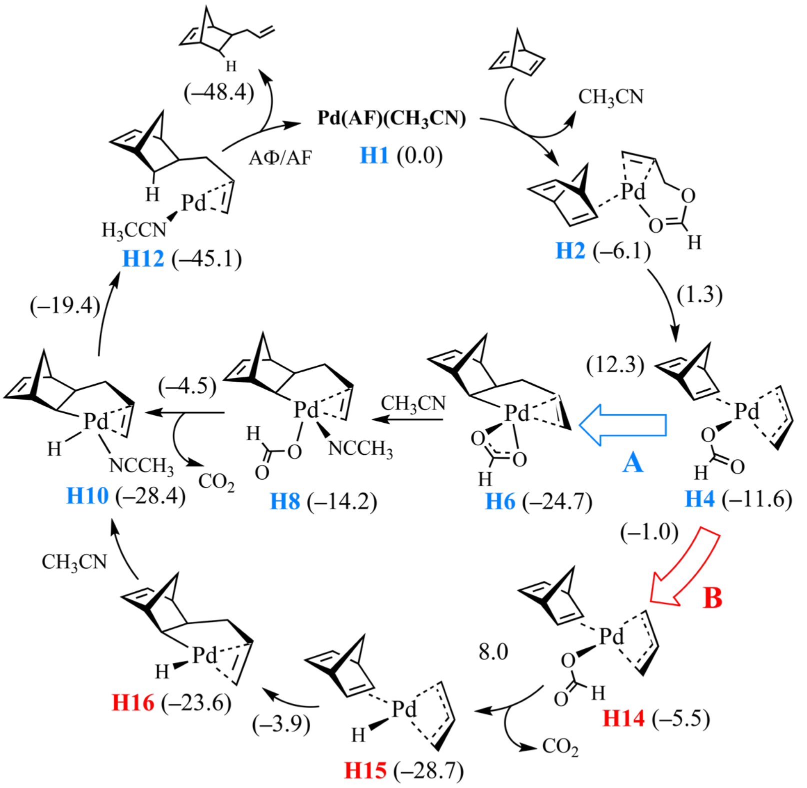

Fig. 16. Routes of formation of *exo*-5-allyl-2-norbornene (**4**) according to mechanisms **A** and **B**. Gibbs energies (ΔG_{298}, $\Delta G^{\neq}_{298}$, kcal/mol) relative to **H1** are given in parentheses.

The performed quantum-mechanical calculations of the stability of compounds **2** and **3** and their isomeric analogs show that isomer **2'** is thermodynamically preferable to isomer **2** by 0.73 kcal/mol (ΔG°_{298}). Isomer **3** is thermodynamically preferable to **3'** by 1.27 kcal/mol (ΔG°_{298}). This conclusion is in complete agreement with the yields of these isomers for phosphine-free systems. However, the real yield of compound **2** increases with the introduction of phosphine into the system, which indicates the influence of kinetic factors.

Figure 17 shows the mechanism of formation of product **3**. $Pd(\eta^2\text{-}C_3H_5COOH)(PPh_3)_2$ (**A1**) can be considered as a catalytically active complex. As a result of the oxidative addition steps (**A2→A3**) and NBD coordination, the key intermediate Pd(η^2-*endo*-NBD)(C_3H_5)(OCOH) (**A4**) is formed. Since NBD coordination predetermines the stereostructure of the product, further transformations of intermediate **A4** lead to *endo*-structure product **3**.

The structure of product **3** suggests the sequential formation of three C–C bonds. Various routes of formation of the first and subsequent carbon bonds are considered. In the case of preliminary η^2/η^4 isomerization of the NBD ligand and addition of the PPh_3 ligand, the activation energy for the formation of the first C–C bond turns out to be the lowest possible (**A5→A6**, $\Delta G^{\neq}_{298}$ = 25.4 kcal/mol). Alternative routes for the formation of the first C–C bond are associated with overcoming much higher activation barriers. Therefore, the C–C bond between the allyl and NBD ligands is formed first.

The lowest energy, and therefore the most probable route for the formation of the second C–C bond is associated with the formation of a cyclopropane fragment in the NBN derivative (**A6→A7**). The stage is characterized by a noticeable activation barrier ($\Delta\Delta G^{\neq}_{298}$) of 18.7 kcal/mol, but also accompanied by a noticeable decrease in energy. The presence of the PPh_3 ligand in the Pd coordination sphere noticeably lowers the activation barrier during the formation of the third C–C bond, which leads to the formation of the cyclopentane fragment (**A7→A8**). For example, this stage for the phosphine and phosphine-free systems is characterized by an activation barrier of 14.0 and 23.9 kcal/mol, respectively [52].

An interesting feature of this route is the formation of intermediate **A9** with C–H agostic interaction with Pd. At the final stages, the *endo*-allylation product **3** and the HCOOH molecule are eliminated by adding PPh_3 and AF molecules. Thus, the **A1** complex is returned to the catalytic cycle.

Figure 18 shows the mechanism of formation of the reductive allylation product **4** in the presence of phosphines. Of the allylation mechanisms in the presence of PPh_3, mechanism **A** is the most probable. However, in contrast to the previously described mechanism **A**, the formation of a C–C bond occurs in the presence of phosphine between the η^1-allylic and NBD ligands. This is facilitated by the preliminary coordination of PPh_3 and η^3-η^1 isomerization of the allyl groups (**A11→A12→A13**). Further hydride transfers (**A13→A17→A18**) proceed with sufficiently low activation barriers to form product **4** and CO_2.

Intermediate **A13**, which is formed in the route of formation of product **4**, is the key one in relation to the regioselectivity of the allylation reaction. Its various transformations lead either to the reductive allylation product **4** or to the oxidative

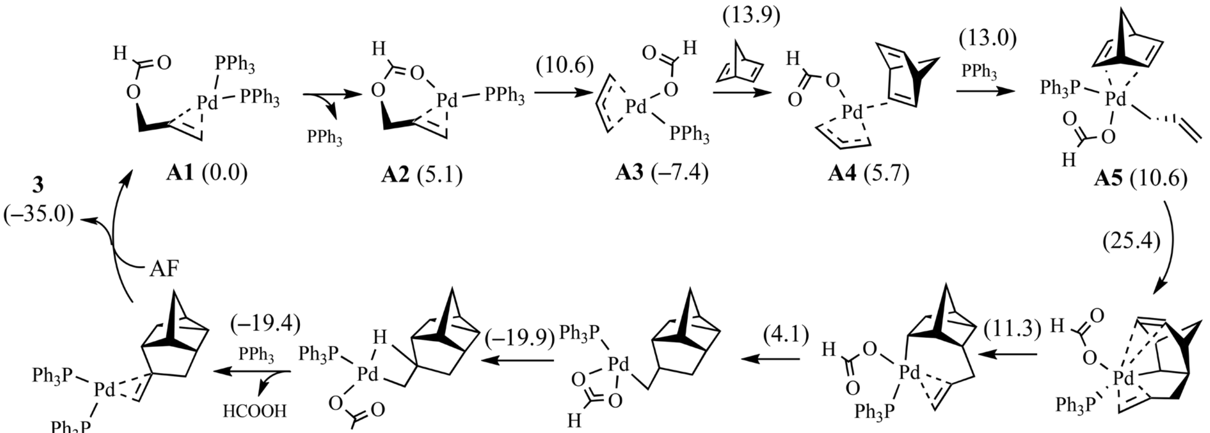

Fig. 17. Mechanism of formation of NBD *endo*-allylation product with indication of key intermediates. The Gibbs energies (ΔG_{298}, $\Delta G^{\neq}_{298}$, kcal/mol) relative to **A1** are given in parentheses.

allylation products **1** and **2**. The latter are obtained during the formation of the second C–C bond with the formation of an NBN derivative with a four-membered cyclic fragment (**A14**). Thus, it is due to the presence of phosphine that the activation barrier of this transformation noticeably decreases ($\Delta G^{\neq}_{298}$ = 12.6 kcal/mol).

Another important key intermediate, **A14**, determines the selectivity of the reaction with respect to products **1** and **2**. Depending on the bond being broken, C–H or C–C, product **1** or **2** is formed, respectively, ($\Delta\Delta G^{\neq}_{298}$ = 4.5 kcal/mol), but subject to the preliminary formation of the **A15** agostic complex.

An additional route for **A14** transformation leads to product **1**. A specific feature of the formation of **1** is the need to break the C–C bond in the $C_7H_8C_3H_5$ fragment. Detailed quantum chemical calculations made it possible to explain the mechanism of this transformation, which proceeds via the mechanism of β-carbon elimination. The most probable cause is the cleavage of the bond in the methylenecyclobutane fragment of intermediate **A14**. In this case, C–C cleavage and the formation of new Pd–C bonds occur in one stage, i.e., consistent with an activation barrier of 20.0 kcal/mol. The subsequent stages of the mechanism for the formation of product **1** are associated with intramolecular isomerization and hydride transfer from the NBN derivative to the formate ligand without the direct involvement of the Pd atom (**A19**→**A20**). Closing of the catalytic cycle occurs when the reaction products are replaced by PPh_3 and AF molecules.

At all key stages of the reaction, the coordination sphere of the metal contains no more than one PPh_3 molecule. This is due to a significant increase in the Gibbs energy of the system upon coordination of the second phosphine molecule due to steric repulsions within the complex. Therefore, there will be no direct correlation between the ratio of phosphines and the selectivity of the formation of allylation products. This explains the weaker effect of the P/Pd molar ratio on the reaction selectivity compared to the Ni-containing catalytic system [25].

In the final part, we present the results of theoretical modeling of the enantioselective sensitivity of NBD allylation. Each of products **1**–**4** has enantiomers due to the presence of chiral centers. Due to the fact that one of the coordination sites in the reagent of the stage of formation of the first C–C bond (Fig. 19) is occupied by a phosphine ligand, it is logical to assume that the structure of this phosphine affects the enantioselectivity of allylation.

Our calculations [53] used four model phosphines: methylisopropylphenylphosphine PPh(^{i}Pr)(Me), isopropylisobutylphenylphosphine PPh(^{i}Bu)(^{i}Pr), methylisopropylisobutylphosphine P(^{i}Bu)(^{i}Pr)(Me), and cyclohexylphenyl(*p*-tolyl)phosphine P(*p*-Tol)(Cy)(Ph).

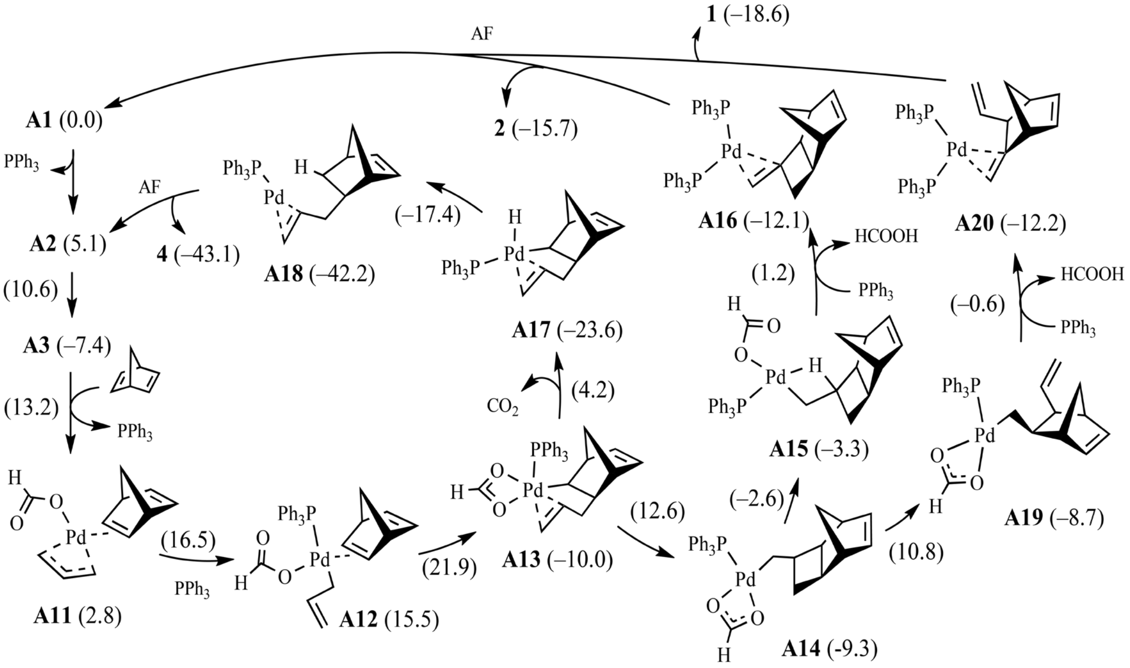

Fig. 18. Mechanism of formation of NBD *exo*-allylation product with indication of key intermediates. he Gibbs energies (ΔG_{298}, $\Delta G^{\neq}_{298}$, kcal/mol) relative to **A1** are given in parentheses.

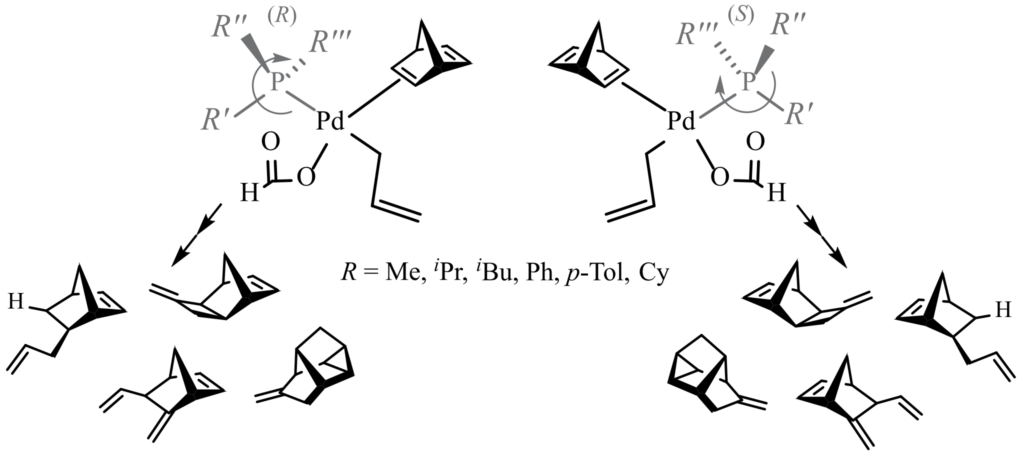

Fig. 19. Structure of enantiomers of allylation products (**1–4**) depending on the nature of the phosphine ligand in the reagent of the stage of formation of the first C–C bond.

Table. Theoretical evaluation of the regio- and enantioselectivity of NBD allylation in the presence of chiral phosphines

Phosphine	**Ratio of regioisomers, %**		**Ratio of enantiomers, %**	
	exo	***endo***	***exo***	***endo***
PPh_3	81	19	50:50	50:50
PPh(^{i}Bu)(^{i}Pr)	99.7	0.3	91:9	91:9
PPh(^{i}Pr)Me	99	1	98:2	98:2
P(^{i}Bu)(^{i}Pr)Me	93/99.9*	7/0.1*	19:81	94:6
P(*p*-Tol)(Cy)(Ph)	18/80*	82/20*	96:4	60:40

*depending on the configuration of the initial phosphine.

Since the enantiomeric excess is associated with the difference in the energies of TSs with different (*R*/*S*) configurations of the phosphine, the presence of only one aryl group in the chiral phosphine is desirable. According to the table, two aryl groups or their absence leads to a decrease in the enantiomeric excess. The calculations performed predict the fundamental possibility of obtaining enantiomerically pure NBN derivatives.

CONCLUSIONS

Until recently, the synthesis of carbocyclic compounds based on NBN and NBD was mainly carried out empirically by intuitive iterating of catalysts, ligand environment, and reaction conditions. Over the last 15–20 years, however, systematic studies of the kinetics and mechanisms of reactions involving NBN and NBD have begun, as well as the application of quantum chemistry methods for such objects and processes. The synergy between these intensively developing areas already now allows targeted development and optimization of reaction conditions to obtain individual products and materials having valuable properties. On the example of our research of the NBD allylation reaction, carried out in recent years at the Ya.K. Syrkin Department of Physical Chemistry of the M.V. Lomonosov Institute of Fine Chemical Technologies of RTU MIREA, the advantages of the constant feedback between theoretical and experimental approaches have been demonstrated. We believe that the further development of such strategy will not only reduce the total cost and complexity of research into optimizing the total experimental cycle, but also help to develop a better and deeper understanding of the mechanisms of the investigating reactions. Using this strategy, for example, new homogeneous and heterogeneous catalytic systems based on nickel and palladium complexes have been already developed for the reactions of NBD allylation and hydroallylation, on which basis the conditions for the selective production of 5-allylnorbornene-2 and 5-methylene-6-vinylnorbornene-2 have been optimized. All the necessary prerequisites have been also created for optimization of methods and approaches in the direction of carrying out enantioselective syntheses of NBN derivatives. Obtaining compounds with enantiomeric purity will open up new possibilities for their application in medicine and polymer chemistry through the development of materials offering valuable properties. It also seems promising to continue research on the development of new heterogeneous catalytic systems that have undoubted technological advantages over homogeneous one.

Acknowledgments

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Authors' contributions

Sergey A. Durakov – search for publications on the topic of the review, analysis of literary sources, writing the text of the review on experimental studies of norbornadiene allylation;

Karen T. Egiazaryan – search for publications on the topic of the review, analysis of literary sources, writing the text of the review on quantum chemical studies of norbornadiene allylation;

Ravshan S. Shamsiev – systematization of publications, scientific and technical editing, design of bibliography and illustrative materials;

Vitaly R. Flid – conceptualization of the idea of the review, scientific editing of the work, critical evaluation of the article materials, formulation of conclusions.

The authors declare no conflicts of interest.

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About the authors:

Sergey A. Durakov, Cand. Sci. (Chem.), Associate Professor, Department of Analytical Chemistry and Senior Researcher, Department of Physical Chemistry, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (86, Vernadskogo pr., Moscow, 119571, Russia). E-mail: s.a.durakov@mail.ru. Scopus Author ID 57194217518, ResearcherID AAS-6578-2020, RSCI SPIN–code 9420-3916, https://orcid.org/0000-0003-4842-3283

Karen T. Egiazaryan, Postgraduate Student, Department of Physical Chemistry, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (86, Vernadskogo pr., Moscow, 119571, Russia). E-mail: mccubas369@gmail.com. Scopus Author ID 57222128479, SPIN-код РИНЦ 7855-7507, https://orcid.org/0000-0002-7942-4011

Ravshan S. Shamsiev, Dr. Sci. (Chem.), Professor of the Department of Physical Chemistry, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (86, Vernadskogo pr., Moscow, 119571, Russia). E-mail: shamsiev.r@gmail.com. Scopus Author ID 6506076152, ResearcherID L-4526-2016, SPIN-код РИНЦ 1741-4076, https://orcid.org/0000-0002-0473-770X

Vitaly R. Flid, Dr. Sci. (Chem.), Professor, Head of the Department of Physical Chemistry, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (86, Vernadskogo pr., Moscow, 119571, Russia). E-mail: vitaly-flid@yandex.ru. Scopus Author ID 6602997346, ResearcherID H-1781-2017, RSCI SPIN–code 8790-3380, https://orcid.org/0000-0001-6559-5648

Об авторах:

Дураков Сергей Алексеевич, к.х.н., доцент кафедры аналитической химии им. И.П. Алимарина, старший научный сотрудник кафедры физической химии им. Я.К. Сыркина Института тонких химических технологий им. М.В. Ломоносова, ФГБОУ ВО «МИРЭА – Российский технологический университет» (119571, Россия, Москва, пр-т Вернадского, д. 86). E-mail: s.a.durakov@mail.ru. Scopus Author ID 57194217518, ResearcherID AAS-6578-2020, SPIN–код РИНЦ 9420-3916, https://orcid.org/0000-0003-4842-3283

Егиазарян Карен Тигранович, аспирант кафедры физической химии им. Я.К. Сыркина Института тонких химических технологий им. М.В. Ломоносова ФГБОУ ВО «МИРЭА – Российский технологический университет» (119571, Россия, Москва, пр-т Вернадского, д. 86). E-mail: mccubas369@gmail.com. Scopus Author ID 57222128479, SPIN-код РИНЦ 7855-7507, https://orcid.org/0000-0002-7942-4011

Шамсиев Равшан Сабитович, д.х.н., профессор кафедры физической химии им. Я.К. Сыркина Института тонких химических технологий им. М.В. Ломоносова ФГБОУ ВО «МИРЭА – Российский технологический университет» (119571, Россия, Москва, пр-т Вернадского, д. 86). E-mail: shamsiev.r@gmail.com. Scopus Author ID 6506076152, ResearcherID L-4526-2016, SPIN-код РИНЦ 1741-4076, https://orcid.org/0000-0002-0473-770X

Виталий Рафаилович Флид, д.х.н., профессор, заведующий кафедрой физической химии им. Я.К. Сыркина Института тонких химических технологий им. М.В. Ломоносова, ФГБОУ ВО «МИРЭА – Российский технологический университет» (119571, Россия, Москва, пр-т Вернадского, д. 86). E-mail: vitaly-flid@yandex.ru. Scopus Author ID 6602997346, ResearcherID H-1781-2017, SPIN–код РИНЦ 8790-3380, https://orcid.org/0000-0001-6559-5648

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CHEMISTRY AND TECHNOLOGY OF MEDICINAL COMPOUNDS AND BIOLOGICALLY ACTIVE SUBSTANCES

ХИМИЯ И ТЕХНОЛОГИЯ ЛЕКАРСТВЕННЫХ ПРЕПАРАТОВ И БИОЛОГИЧЕСКИ АКТИВНЫХ СОЕДИНЕНИЙ

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RESEARCH ARTICLE

Synthesis and biological activity of 5-acetyl- and 5-hydroxyalkyl-1,3-dioxane derivatives

Airat I. Musin[1], Yulianna G. Borisova[1,✉], Shakhobiddin Sh. Dzhumaev[1], Nailya S. Khusnutdinova[1,2], Gul'nara Z. Raskil'dina[1], Rimma M. Sultanova[1], Semen S. Zlotskii[1]

[1] *Ufa State Petroleum Technological University, Ufa, 450064 Russia*
[2] *Bashkir State Medical University, Ufa, 450008 Russia*
✉ *Corresponding author, e-mail: yulianna_borisova@mail.ru*

Abstract

Objectives. *To synthesize derivatives of 5-acetyl- and 5-hydroxyalkyl-1,3-dioxanes and evaluate their effect on platelet aggregation and plasma hemostasis.*

Methods. *To determine the qualitative and quantitative composition of the reaction masses, gas chromatography-, chromate mass spectrometry-, and* ^{1}H *and* ^{13}C *nuclear magnetic resonance spectrometry methods were used.*

Results. *Derivatives of 5-acetyl- and 5-hydroxyalkyl-1,3-dioxanes were obtained under thermal heating conditions in order to evaluate their effect on platelet aggregation and plasma hemostasis.*

Conclusions. *Derivatives of 5-acetyl- and 5-hydroxyalkyl-1,3-dioxanes were synthesized in high yields. Their effect on platelet aggregation and plasma hemostasis was established.*

Keywords: *5-acyl-1,3-dioxane, alkylation, ethers, isoniazid, 2,4-dinitrophenyl hydrazine*

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НАУЧНАЯ СТАТЬЯ

Синтез и биологическая активность производных 5-ацетил- и 5-оксиалкил-1,3-диоксанов

А.И. Мусин[1], Ю.Г. Борисова[1,✉], Ш.Ш. Джумаев[1], Н.С. Хуснутдинова[1,2], Г.З. Раскильдина[1], Р.М. Султанова[1], С.С. Злотский[1]

[1]Уфимский государственный нефтяной технический университет, Уфа, 450064 Россия
[2]Башкирский государственный медицинский университет, Уфа, 450008 Россия
✉Автор для переписки, e-mail: yulianna_borisova@mail.ru

Аннотация

Цели. *Синтезировать производные 5-ацетил- и 5-оксиалкил-1,3-диоксанов и оценить их влияние на агрегацию тромбоцитов и плазменное звено гемостаза.*
Методы. *Для определения качественного и количественного состава реакционных масс были использованы газовая хроматография, хромато-масс-спектрометрия и спектроскопия ядерного магнитного резонанса ^{1}H и ^{13}C.*
Результаты. *В условиях термического нагрева получены производные 5-ацетил- и 5-оксиалкил-1,3-диоксанов, произведена оценка их влияния на агрегацию тромбоцитов и плазменное звено гемостаза.*
Выводы. *С высокими выходами синтезированы производные 5-ацетил- и 5-оксиалкил-1,3-диоксанов, установлено их влияние на агрегацию тромбоцитов и плазменное звено гемостаза.*

Ключевые слова: *5-ацил-1,3-диоксан, алкилирование, простые эфиры, изониазид, 2,4-динитрофенил-гидразин*

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INTRODUCTION

Substituted cyclic acetals and their analogs are known to support a wide spectrum of biological activity [1–5]. Thus, 5-hydroxymethi-1,3-dioxanes obtained from commercial 1,1,1-trioxymethylalkanes and their derivatives exhibit herbicidal, anticoagulant, and other activities [6–11].

In previous work we demonstrated the possibility of reducing that available 5-acyl-1,3-dioxanes to the corresponding secondary alcohols using metal-containing catalysts [12]. According to this approach, a highly efficient heterogeneous Pd/Al_2O_3 catalyst (0.25% Pd; hydrogenation temperature 40–90°C) was studied at the Ya.K. Syrkin Department of Physical Chemistry of RTU MIREA by the research group led by V.R. Flid [13].

In this connection, the synthesis of new reagents of the class of cyclic acetals based on available petrochemical products seems important and promising.

MATERIALS AND METHODS

The analysis of the reaction masses of the compounds was carried out on the Chromatec-Crystal 5000M hardware-software complex (*Chromatec*, Russia) with the installed base NIST MS Search 2020 (*National Institute of Standards and Technology*, USA). A CR-5ms capillary quartz column (*Chromatec*, Russia) of 30 m length, 0.25 mm diameter, and 0.25 µm phase thickness was used under the following analysis conditions: duration of analysis is 20 min; temperature of ion source is 260°C; temperature of the transition line is 300°C; pressure is 37–43 mTorr; carrier gas is helium; heating rate is 20°C/min). The mass spectra of the compounds were obtained using the electron impact ionization method with an ionization energy of 70 eV; the scanning range was 30–300 Da. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AM-500 spectrometer (*Bruker Corporation*, USA) with operating frequencies of 500 and 125 MHz, respectively; the solvent used was $CDCl_3$. Chemical shifts are given in δ (ppm) scale relative to tetramethylsilane as an internal standard. The spin-spin coupling constants (*J*) are given in Hz.

Compounds **1a** and **1b** were obtained according to the procedure described in [14]. The physicochemical characteristics correspond to those previously presented in work [14].

Compounds **3a** and **3b** were obtained according to the procedures listed in [15, 16].

***N*-[1-(5-isopropyl-1,3-dioxan-5-yl)ethylidene]-benzohydrazone (3a).** White powder. $T_{m.p.}$ = 138–140°C. Yield 90%. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 1.13 (t, 6H, 2 CH_3, *J* = 8.8 Hz), 2.13 (s, 3H, CH_3), 2.65 (q, 1H, CH, *J* = 7.03, 14.0 Hz), 3.51 (d, 2H, CH_a, *J* = 12 Hz), 4.35 (d, 2H, CH_b, *J* = 11.52 Hz), 4.47 (d, 1H, CH, *J* = 6.11 Hz), 4.90 (d, 1H, CH, *J* = 6.05 Hz), 7.50–9.00 (5H, Ph-). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 17.93 (CH_3), 17.95 (CH_3), 31.29 (CH), 42.39 (CH_3), 72.95 (2 CH_2), 94.16 (CH_2), 120.91–150.45 (Ph-), 162.37 (N=C).

1-(5-isopropyl-1,3-dioxan-5-yl)ethanone (2,4-dinitrophenyl)(methyl)hydrazone (3b). Light yellow powder. $T_{m.p.}$ = 138–140°C. Yield 88%. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 1.43 (t, 6H, 2 CH_3, *J* = 7.3 Hz), 2.13 (s, 3H, CH_3), 2.51 (q, 1H, CH, *J* = 7.06, 13.8 Hz), 3.88 (d, 2H, CHa_a, *J* = 12 Hz), 4.24 (d, 1H, CH_b, *J* = 11.88 Hz), 4.47 (d, 1H, CH, *J* = 6.02 Hz), 4.90 (d, 1H, CH, *J* = 6.01 Hz), 7.50–9.00 (5H, Ph-). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 19.68 (CH_3), 19.87 (CH_3), 31.22 (CH), 42.23 (CH_3), 73.63 (2 CH_2), 94.24 (CH_2), 120.91–145.28 (Ph-), 162.39 (N=C).

The basic deacetalization technique is presented in the work [17].

3,3-bis-(hydroxymethyl)-4-methylpentan-2-one (3c). Colorless liquid. Yield 89%. $T_{b.p.}$ = 108–110°C (2 mm Hg). ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 1.02 (t, 6H, 2 CH_3, *J* = 7.1 Hz), 1.88 (q, 1H, CH, *J* = 7.01, 13.2 Hz), 2.23 (s, 3H, CH_3), 3.96 (d, 2H, CH_a, *J* = 10.55 Hz), 4.02 (d, 1H, CH_b, *J* = 10.43 Hz). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 19.69 (CH_3), 19.88 (CH_3), 22.51 (CH_3), 30.83 (CH), 63.49 (2 CH_2), 207.23 (C=O).

Mass spectrum *m*/*z*, (I_{rel}, %): (159)/(14), (145)/(60), (99)/(76), (41)/(100).

The basic acylation procedure is presented in the work [18].

1-(5-isopropyl-1,3-dioxan-5-yl)-ethylchloroacetate (7a). Colorless viscous liquid. Yield 90%. $T_{b.p.}$ = 125–127°C (5 mm Hg). ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 0.95 (t, 6H, 2 CH_3, *J* = 7.75 Hz), 1.35 (t, 3H, CH_3, *J* = 7.01 Hz), 1.88–1.98 (m, 1H, CH), 3.66 (d, 2H, CH_a, *J* = 11 Hz), 3.99 (d, 2H, CH_b, *J* = 11 Hz), 4.05 (s, 2H, CH_2), 4.15 (d, 1H, CH, *J* = 6 Hz). 4.66 (d, 1H, CH, *J* = 6 Hz), 4.92 (d, 1H, CH, *J* = 6 Hz). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 15.94 (CH_3), 21.49 (CH_3), 21.68 (CH_3), 29.69 (CH), 40.77 (CH_2), 68.21 (2 CH_2), 71.26 (CH), 93.87 (CH_2), 166.94 (C=O).

Mass spectrum *m*/*z*, (I_{rel}, %): (251/253)/(5/2), (99)/(30), (87)/(100), (43)/(60).

Bis-[1-(5-isopropyl-1,3-dioxan-5-yl)ethyl]-terephthalate (7b). Colorless viscous liquid. Yield 70%. $T_{b.p.}$ = 131–133°C (1 mm Hg). ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 0.99 (t, 12H, 4 CH_3, *J* = 11.67 Hz), 1.23 (t, 6H, 2 CH_3, *J* = 10 Hz), 1.73–1.84 (m, 2H, 2 CH), 3.74 (d, 4H, 4 CH_a, *J* = 11.3 Hz), 3.99 (d, 4H, 4 CH_b, *J* = 11.04 Hz), 4.43 (d, 2H, 2 CH, *J* = 6 Hz), 4.59 (d, 2H, 2 CH, *J* = 6 Hz). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 14.12 (2 CH_3), 21.42 (2 CH_3), 21.47 (2 CH_3), 31.66 (CH), 68.91 (4 CH_2), 71.23 (2 CH), 92.99 (2 CH_2), 121.49–153.41 (Ph-), 171.03 (C=O).

Mass spectrum *m*/*z*, (I_{rel}, %): (487/1), (335)/(20), (87)/(100), (77)/(50), (51)/(10).

The basic alkylation procedure is presented in the work [18].

5-[1-(allyloxy)ethyl]-5-isopropyl-1,3-dioxane (8a). Colorless viscous liquid. Yield 98%. $T_{b.p.}$ = 131–133°C (1 mm Hg). ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 0.98 (t, 6H, 2 CH_3, *J* = 7 Hz), 1.35 (d, 3H, CH_3, *J* = 7 Hz), 1.82–1.93 (m, 1H, CH), 3.28 (d, 1H, CH, *J* = 7 Hz), 3.74 (d, 2H, CH_a, *J* = 10.2 Hz), 3.83 (d, 2H, CH_b, *J* = 11 Hz), 3.94 (d, 1H, CH, *J* = 7 Hz), 4.04 (d, 1H, CH, *J* = 7.4 Hz), 4.63 (d, 1H, CH, *J* = 6 Hz), 4.88 (d, 1H, CH, *J* = 6 Hz), 5.74 (d, 1H, CH, *J* = 10.2 Hz), 5.81 (d, 1H, CH, *J* = 7 Hz), 5.83–5.91 (m, 1H, CH). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 15.92 (CH_3), 21.42 (CH_3), 21.46 (CH_3), 29.67 (CH), 68.27 (2 CH_2), 71.44 (CH), 73.39 (CH_2), 93.89 (CH_2), 113.99 (CH_2), 136.73 (CH).

Mass spectrum *m*/*z*, (I_{rel}, %): (213/1), (186)/(30), (157)/(80), (87)/(100), (41)/(40).

5-[1-(benzyloxy)ethyl]-5-isopropyl-1,3-dioxane (8b). Colorless liquid. Yield 83%. $T_{b.p.}$ = 122–123°C (1 mm Hg). ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 0.97 (t, 6H, 2 CH_3, *J* = 7.8 Hz), 1.30 (d, 3H, CH_3, *J* = 8 Hz), 1.76–1.83 (m, 1H, CH), 3.05 (d, 1H, CH, *J* = 10 Hz), 3.59 (d, 2H, CH_a, *J* = 10 Hz), 3.74 (d, 2H, CH_b, *J* = 11 Hz), 4.75 (s, 2H, CH_2), 4.89 (d, 1H, CH, *J* = 6 Hz), 4.95 (d, 1H, CH, *J* = 6 Hz), 7.05–7.94 (Ph-). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 15.87 (CH_3), 21.39 (CH_3), 21.41 (CH_3), 29.49 (CH), 68.22 (2 CH_2), 71.41 (CH_2), 72.31 (CH), 92.05 (CH_2), 126.99–139.93 (Ph-).

Mass spectrum *m*/*z*, (I_{rel}, %): (263/1), (187)/(50), (91)/(30), (87)/(100), (77)/(60), (51)/(30).

The basic procedure for condensation with phenyl isocyanate is presented in the work [18].

1-(5-isopropyl-1,3-dioxan-5-yl)ethylcarbamate (5a). White powder. Yield 92%. $T_{m.p.}$ = 101–103°C. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 0.90 (t, 6H, 2 CH_3, *J* = 8 Hz), 1.17 (d, 3H, CH_3, *J* = 8 Hz), 1.73–1.86 (m, 1H, CH), 3.67 (d, 2H, CH_a, *J* = 11 Hz), 3.78 (d, 2H, CH_b, *J* = 11 Hz), 4.01 (d, 1H, CH, *J* = 8 Hz), 4.93 (d, 1H, CH, *J* = 6.3 Hz), 4.96 (d, 1H, CH, *J* = 6.6 Hz), 7.05–7.92 (Ph-). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 15.77 (CH_3), 21.41 (CH_3), 21.44 (CH_3), 29.41 (CH), 68.12 (2 CH_2), 75.33 (CH), 91.09 (CH_2), 127.92–138.91 (Ph-), 163.66 (C=O).

The method for the condensation of alcohol **1b** with vinyl ethyl ether **10** is presented in [19].

5-[1-(1-diethoxy]ethyl-5-isopropyl-1,3-dioxane (11a). Colorless liquid. Yield 65%. $T_{b.p.}$ = 134–135°C (2 mm Hg). ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 0.96 (t, 6H, 2 CH_3, *J* = 8 Hz), 1.01 (t, 3H, CH_3, *J* = 9 Hz), 1.12 (s, 3H, CH_3), 1.28 (t, 3H, CH_3, *J* = 8.1 Hz), 1.62–1.73 (m, 1H, CH), 3.63 (d, 1H, CH, *J* = 9.1 Hz), 3.69 (d, 2H, CH_a, *J* = 11.7 Hz), 3.92 (d, 2H, CH_b, *J* = 11.5 Hz), 4.02 (d, 1H, CH, *J* = 9.2 Hz), 4.12 (d, 1H, CH, *J* = 6.4 Hz), 4.23 (d, 1H, CH, *J* = 6.3 Hz). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 15.18 (CH_3), 17.73 (CH_3), 20.99 (CH_3), 21.44 (CH_3), 29.32 (CH), 64.55 (CH_2), 68.37 (2 CH_2), 76.31 (CH), 93.21 (CH_2), 99.21 (CH).

5,5-[ethane-1,1-diylbis(oxyethane-1,1-diyl)]-bis-(5-isopropyl-1,3-dioxane) (11b). Colorless liquid. Yield 65%. $T_{b.p.}$ = 154–156°C (1 mm Hg). ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 0.96 (t, 12H, 6 CH_3, *J* = 8.1 Hz), 1.01 (t, 6H, 2 CH_3, *J* = 9.5 Hz), 1.18 (t, 3H, CH_3, *J* = 8.9 Hz), 1.71–1.81 (m, 2H, 2 CH), 3.69 (d, 2H, 2 CH, *J* = 9.1 Hz), 3.78 (d, 2H, CH_a, *J* = 11 Hz), 3.83 (d, 2H, CH_b, *J* = 11 Hz), 4.28 (d, 2H, 2 CH, *J* = 8 Hz), 4.32 (d, 2H, 2 CH, *J* = 6.4 Hz). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 15.54 (CH_3), 17.33 (CH_3), 20.92 (CH_3), 21.31 (CH_3), 29.49 (CH), 64.23 (CH_2), 68.85 (2 CH_2), 76.98 (CH), 93.96 (CH_2), 99.21 (CH).

Methodology for conducting a biological experiment

The basic method for determining anticoagulant and aggregation activity is presented in [19].

Optical measurements. The results were recorded by optical density with the calculation of hemolysis according to the formula: % of hemolysis = $((E_{op} - E_c)/E_{100}) \times 100$, where E_{op} is the optical density of the experimental sample; E_c is the optical density of the control sample; E_{100} is the optical density of water with a suspension of erythrocytes with 100% hemolysis (optical density: 0.8–1.0).

Statistical processing. The check for the normality of the distribution of actual data was performed using the Shapiro–Wilk test. Analysis of variance was performed using the Kruskal–Wallis test. The critical significance level *p* for statistical tests was taken as equal to 0.05.

RESULTS AND DISCUSSION

Previously, we showed [12] that the condensation of methyl isobutyl ketone with paraform leads to ketone **1a** in high yield. By carrying out hydrogenation of **1a** under homo- and heterogeneous conditions, it is possible to pass to cyclic alcohol **1b** [12]. Continuing these studies, we obtained some derivatives of ketone **1a** and alcohol **1b**, as well as determining the assessment of their effect on platelet aggregation and plasma hemostasis.

By breaking the ring in compound **1a** with refluxing in 2% sulfuric acid, ketodiol **3c** was obtained in 60% yield. Condensation of ketone **1a** with compounds containing a primary amino group, isoniazid **2a** and 2,4-dinitrophenylhydrazine **2b**, gave Schiff bases **3a** and **3b** in quantitative yields (Fig. 1).

The corresponding complex mono-**7a** and di-**7b** esters were obtained *via* esterification of secondary alcohol **1b** with mono-**6a** and di-**6b** acid chlorides (Fig. 2).

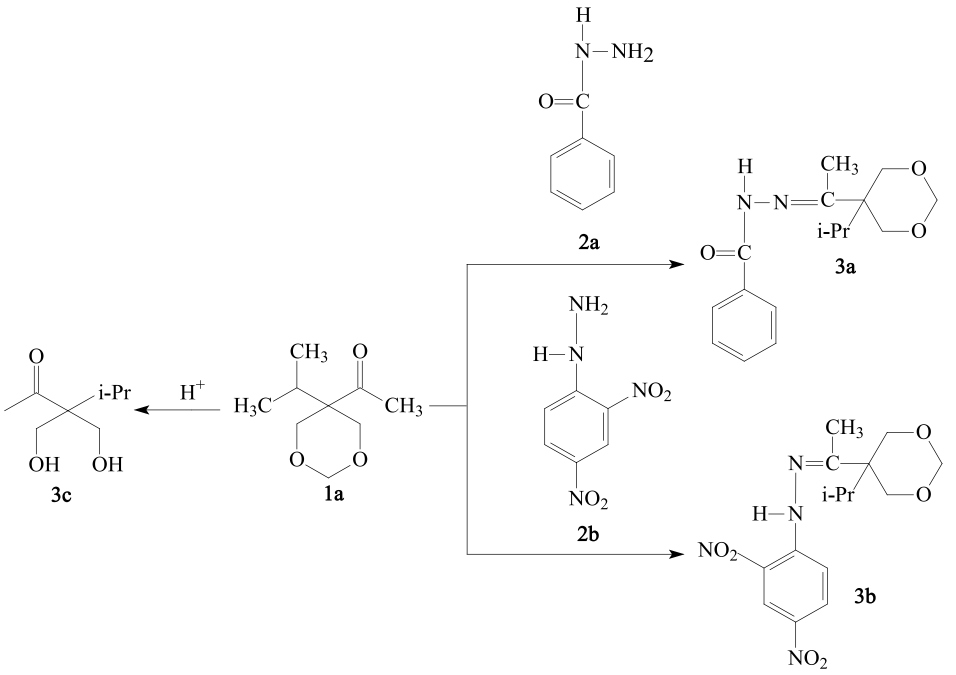

Fig. 1. Scheme of reactions of 1-(5-isopropyl-1,3-dioxan-5-yl)ethanone **1a**.

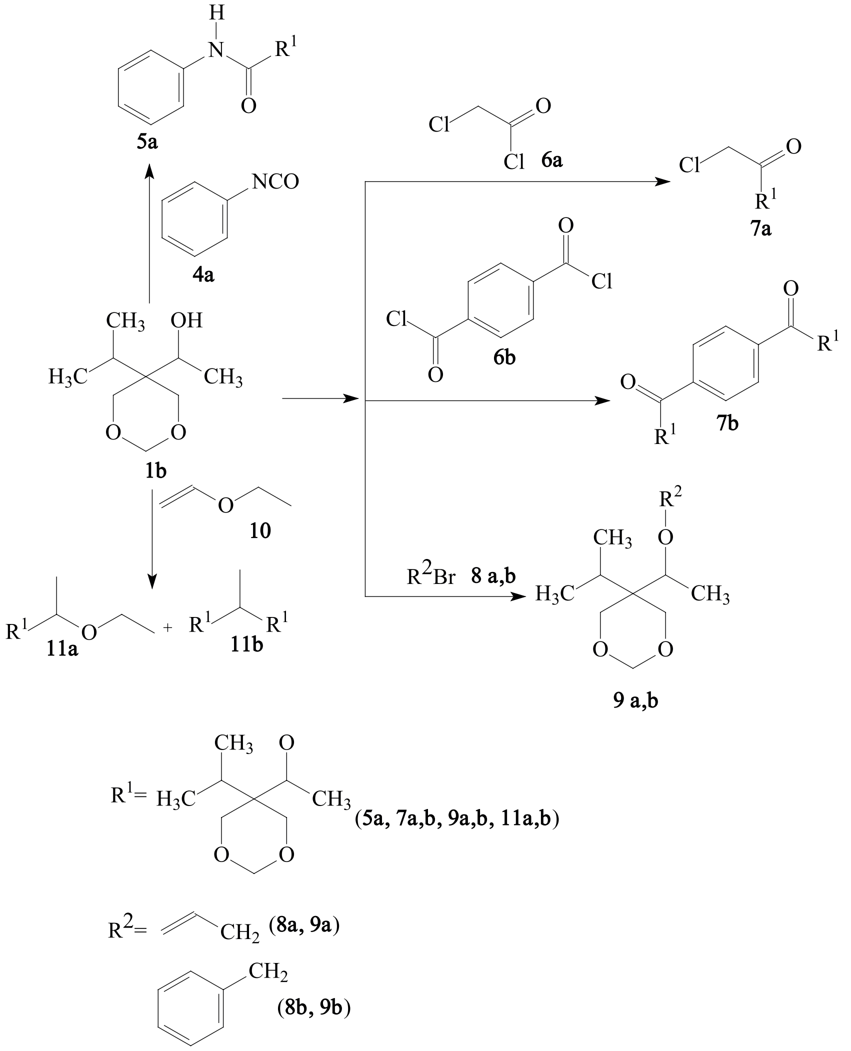

Fig. 2. Scheme of reactions of 1-(5-isopropyl-1,3-dioxan-5-yl)ethanol **1b**.

Table 1. Effect of the ether : alcohol molar ratio on the yield of reaction products (0.5 wt % KU-2-8, 0–5°C, 3 h)

Ether : alcohol mole ratio	Yield of acetals, %
10 : **1b** = 1 : 10	**11a** = 12%, **11b** = 72%
10 : **1b** = 10 : 1	**11a** = 70%, **11b** = 15%
10 : **1b** = 1 : 1	**11a** = 30%, **11b** = 65%

Ethers **9a** and **9b** were obtained by alkylation of alcohol **1b** allyl-**8a** and benzyl-**8b** bromides (70–90% yield of the corresponding derivatives).

The addition of 1-(5-isopropyl-1,3-dioxan-5-yl)ethanol **1b** to ethyl vinyl ether **10** resulted in a mixture of mono-**11a** and di-**11b** acetals (Table 1).

At a 10-fold excess of alcohol **1b**, almost complete substitution of the ethoxy group is observed with a more than 70% yield of symmetrical acetal **11b**. In the absence of alcohol, the main product is unsymmetrical acetal **11a** at a yield 4–5 times higher than that of acetal **11b**. The equimolar ratio of the reactants ether : alcohol leads to a mixture of unsymmetrical and symmetrical acetals **11a** and **11b**, the latter being dominant.

It was of interest to determine the effect of the synthesized compounds on anticoagulation and antiaggregation activity *in vitro* according to the method presented in the recommendation [20].

The indicators of the effect of compounds on the hemostasis system under *in vitro* conditions are presented in Table 2.

Table 2. Effect of newly synthesized compounds and reference drugs on platelet aggregation, Me (0.25–0.75)

Compound	Latent period, % to control	Maximum amplitude, % to control	Aggregation rate, % to control	Time to reach maximum amplitude, % to control
1a	+4.7 (3.8–5.8)††, #	−6.3 (5.2–7.4)*, ††, ##	−3.2 (2.6–4.1)††, #	+11.5 (10.3–12.4)*, †
1b	+15.1 (13.4–16.5)*, †, ##	−3.4 (2.3–5.6)††, #	−11.4 (9.6–12.5)*, ††	−17.4 (15.7–18.6)*, ††, ##
7a	−2.3 (0.5–3.1)††	−1.2 (0.6–1.8) ††, #	−3.9 (1.4–5.2)††, ##	−8.1 (5.8–9.1)*, ††, ##
7b	+14.7 (14.3–18.1)*, †, ##	−19.4 (16.5–20.2)**, ††, #	−13.6 (12.8–17.4)*, †, #	−23.0 (22.6–27.8)**, ††, ##
Acetylsalicylic acid	−2.1 (1.1–2.6)††	−13.7 (10.8–16.4)*, ††	−10.5 (7.6–12.3)*, ††	+10.5 (8.7–13.4)*, ††
Pentoxifylline	+32.4 (28.7–35.6)**, ##	−48.4 (42.7–56.5)**, ##	−34.9 (28.7–39.6)**	+32.1 (27.6–36.4)**, #

Note: $^{*}p \le 0.05$; $^{**}p \le 0.001$ in comparison with the control; † $p \le 0.05$, †† $p \le 0.001$ in comparison with pentoxifylline; # $p \le 0.05$, ## $p \le 0.001$ in comparison with acetylsalicylic acid, $n = 6$.

Table 3. Influence of the newly synthesized compounds and the reference drug on the parameters of the plasma hemostasis link, Me (0.25–0.75)

Compound	Elongation of activated partial thromboplastin time, % to control	Elongation of prothrombin time, % to control	Change in fibrinogen concentration, g/L
1a	+ 10.2 (9.4–11.4)	0.0 (0.0–0.0)	0.0 (0.0–0.0)
1b	+ 11.7 (9.2–12.3)	0.0 (0.0–0.0)	0.0 (0.0–0.0)
7a	+ 9.3 (8.1–11.9)	0.0 (0.0–0.0)	0.0 (0.0–0.0)
7b	+ 12.4 (9.5–12.9)	0.0 (0.0–0.0)	0.0 (0.0–0.0)
Sodium heparin	20.3 (19.7–21.4)	0.0 (0.0–0.0)	0.0 (0.0–0.0)

Note: † $p > 0.05$ in comparison with the control; compounds versus sodium heparin at $p \leq 0.05$, $n = 6$.

Ester **7a** exhibited antiaggregation activity exceeding the values of acetylsalicylic acid (Table 2). At the same time, **7a** significantly prolonged the latent period, lengthening the reaction of platelet release relative to the control. It should be noted that compounds **1a** and **1b** also reduce the rate of platelet aggregation; however, they are inferior to acetylsalicylic acid in terms of antiaggregation activity, and their antiaggregation activity values are in the range of 3.4–10.4%. Among the studied derivatives of this series, no compounds with a proaggregant effect were found.

All compounds induced hypocoagulation, increasing the activated partial thromboplastin time (APTT) by 6.2–12.4% compared with the control (Table 3); however, the fibrinogen concentration and prothrombin time were not affected. The severity of the effect of the studied compounds was significantly inferior to the effect of heparin, which increased APTT by 20.3%.

CONCLUSIONS

After obtaining derivatives of 5-acetyl- and 5-hydroxyalkyl-1,3-dioxanes under thermal heating conditions, their antiaggressive and anticoagulant activity was studied. Among the synthesized series of compounds, the ester of monochloroacetic acid was found to have the maximum effect on platelet aggregation and the plasma link of hemostasis.

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Authors' contributions

A.I. Musin – conducting research;

G.Z. Raskil'dina – literature review on the topic of the article;

Sh. Sh. Dzhumaev – conducting research;

N.S. Khusnutdinova – processing of biological research results;

Yu.G. Borisova – collection and processing of the material and writing the text of the article;

R.M. Sultanova – consultations on planning;

S.S. Zlotskii – development of the concept of scientific work, critical revision with the introduction of valuable intellectual content.

The authors declare no conflicts of interest.

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About the authors:

Airat I. Musin, Postgraduate Student, Department of General, Analytical and Applied Chemistry, Ufa State Petroleum Technological University (1, Kosmonavtov ul., Ufa, 450064, Russia). E-mail: musin_1995@list.ru. ResearcherID R-9142-2016, RSCI SPIN-code 9573-4624, https://orcid.org/0000-0002-8662-9680

Yulianna G. Borisova, Cand. Sci. (Chem.), Teacher, Department of General, Analytical and Applied Chemistry, Ufa State Petroleum Technological University (1, Kosmonavtov ul., Ufa, 450064, Russia). E-mail: yulianna_borisova@mail.ru. Scopus Author ID 56526865000, ResearcherID P-9744-2017, RSCI SPIN-code 3777-0375, https://orcid.org/0000-0001-6452-9454

Shahobiddin Sh. Dzhumaev, Cand. Sci.(Chem.), Laboratory Engineer, Department of General, Analytical and Applied Chemistry, Ufa State Petroleum Technological University (1, Kosmonavtov ul., Ufa, 450064, Russia). E-mail: shakhob2993@mail.ru. Scopus Author ID 7801627714, ResearcherID HLH-5542-2023, RSCI SPIN-code 4999-3682, https://orcid.org/0000-0002-1938-1478

Nailya S. Khusnutdinova, Assistant, Department of General Chemistry, Bashkir State Medical University (3, Lenina ul., Ufa, 450008, Russia). E-mail: neilyhusnutdinova@yandex.ru. RSCI SPIN-code 1383-7308, https://orcid.org/0000-0003-0460-8382

Gul'nara Z. Raskil'dina, Dr. Sci. (Chem.), Professor, Department of General, Analytical and Applied Chemistry, Ufa State Petroleum Technological University (1, Kosmonavtov ul., Ufa, 450064, Russia). E-mail: graskildina444@mail.ru. Scopus Author ID 56069888400, ResearcherID F-1619-2017, RSCI SPIN-code 2183-3333, https://orcid.org/0000-0001-9770-5434

Rimma M. Sultanova, Dr. Sci. (Chem.), Professor, Department Department of General, Analytical and Applied Chemistry, Ufa State Petroleum Technological University (1, Kosmonavtov ul., Ufa, 450064, Russia). E-mail: rimmams@yandex.ru. Scopus Author ID 6602738038, RSCI SPIN-code 8208-6060, https://orcid.org/0000-0001-6719-2359

Simon S. Zlotskii, Dr. Sci. (Chem.), Professor, Head of Department of General, Analytical and Applied Chemistry, Ufa State Petroleum Technological University (1, Kosmonavtov ul., Ufa, 450064, Russia). E-mail: nocturne@mail.ru. Scopus Author ID 6701508202, Researcher ID W-6564-2018, RSCI SPIN-code 6529-3323, https://orcid.org/0000-0001-6365-5010

Об авторах:

Мусин Айрат Ильдарович, аспирант кафедры общей, аналитической и прикладной химии, ФГБОУ ВО «Уфимский государственный нефтяной технический университет» (450064, Россия, г. Уфа, ул. Космонавтов, д. 1). E-mail: musin_1995@list.ru. ResearcherID R-9142-2016, SPIN-код РИНЦ 9573-4624, https://orcid.org/0000-0002-8662-9680

Борисова Юлианна Геннадьевна, к.х.н., преподаватель кафедры общей, аналитической и прикладной химии, ФГБОУ ВО «Уфимский государственный нефтяной технический университет» (450064, Россия, г. Уфа, ул. Космонавтов, д. 1). E-mail: yulianna_borisova@mail.ru. Scopus Author ID 56526865000, ResearcherID P-9744-2017, SPIN-код РИНЦ 3777-0375, https://orcid.org/0000-0001-6452-9454

Джумаев Шахобиддин Шамсидинович, к.х.н., инженер-лаборант кафедры общей, аналитической и прикладной химии, ФГБОУ ВО «Уфимский государственный нефтяной технический университет» (450064, Россия, г. Уфа, ул. Космонавтов, д. 1). E-mail: shakhob2993@mail.ru. Scopus Author ID 7801627714, ResearcherID HLH-5542-2023, SPIN-код РИНЦ 4999-3682, https://orcid.org/0000-0002-1938-1478

Хуснутдинова Наиля Сабитовна, ассистент кафедры общей химии, ФГБОУ ВО «Башкирский государственный медицинский университет» (450008, Россия, г. Уфа, ул. Ленина, д. 3). E-mail: neilyhusnutdinova@yandex.ru. SPIN-код РИНЦ 1383-7308, https://orcid.org/0000-0003-0460-8382

Раскильдина Гульнара Зинуровна, д.х.н., профессор кафедры общей, аналитической и прикладной химии, ФГБОУ ВО «Уфимский государственный нефтяной технический университет» (450064, Россия, г. Уфа, ул. Космонавтов, д. 1). E-mail: graskildina444@mail.ru. Scopus Author ID 56069888400, ResearcherID F-1619-2017, SPIN-код РИНЦ 2183-3333, https://orcid.org/0000-0001-9770-5434

Султанова Римма Марсельевна, д.х.н., профессор кафедры общей, аналитической и прикладной химии, ФГБОУ ВО «Уфимский государственный нефтяной технический университет» (450064, Россия, г. Уфа, ул. Космонавтов, д. 1). E-mail: rimmams@yandex.ru. Scopus Author ID 6602738038, SPIN-код РИНЦ 8208-6060, https://orcid.org/0000-0001-6719-2359

Злотский Семен Соломонович, д.х.н., заведующий кафедрой общей, аналитической и прикладной химии ФГБОУ ВО «Уфимский государственный нефтяной технический университет» (450064, Россия, г. Уфа, ул. Космонавтов, д. 1). E-mail: nocturne@mail.ru. Scopus Author ID 6701508202, ResearcherID W-6564-2018, SPIN-код РИНЦ 6529-3323, https://orcid.org/0000-0001-6365-5010

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ANALYTICAL METHODS IN CHEMISTRY AND CHEMICAL TECHNOLOGY

АНАЛИТИЧЕСКИЕ МЕТОДЫ В ХИМИИ И ХИМИЧЕСКОЙ ТЕХНОЛОГИИ

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REVIEW ARTICLE

Chemical sensors based on photonic colloidal crystals

Andrei A. Kozlov✉, Anton S. Aksenov, Vasilii A. Dvoretsky, Vitaly R. Flid

MIREA – Russian Technological University (M.B. Lomonosov Institute of Fine Chemical Technologies), Moscow, 119571 Russia

✉Corresponding author, e-mail: anar42@yandex.ru

Abstract

Objectives. *The paper analyzes the results of research into the formation of photonic crystal structures from polymer microspheres and the mechanisms of spectral shifts during selective reflection of non-monochromatic incident radiation from them in the visible and infrared light, as well as the use of polymer microspheres as sensors for detecting chemical substances having similar structures.*

Results. *Research carried out at the Ya.K. Syrkin Department of Physical Chemistry in the Institute of Fine Chemical Technologies of the RTU MIREA is presented. Issues related to the detection of substances with similar chemical structure using sensors based on photonic crystals made of polystyrene microspheres 160–300 nm in size, are considered. Spectral shifts of the reflected radiation from the crystal surface are registered in the visible spectrum when substances in the liquid or gas phase are detected by the crystal surface.*

Conclusions. *The method of electrophoretic deposition of colloidal particles in the form of polymeric microspheres on conducting surfaces can be used to create ordered structures over large areas. However, the detection of individual compounds by the optical method is impossible without controlling the kinetics of spectral shifts of reflected radiation from the surface of photonic colloidal crystals. The spectral characteristics of such radiation are directly related to the particle sizes that determine the period of the crystal lattice.*

The diffusion of chemical substances into a photonic crystal, which results in a swelling of the particles forming it and a shift in the spectrum of reflected radiation, is determined by a change in the period of the crystal lattice due to a change in the size of these particles. A kinetic model of swelling polymer microspheres, which describes the diffusion of substances into porous polymer particles, is proposed. An excess amount of substance deposited on the surface of a photonic crystal above the limit is shown to lead to its degradation, which is manifested in the "fading" of the crystal surface and the concomitant disappearance of narrow peaks of reflected radiation.

Keywords: *photonic crystals, colloidal crystals, optical sensors, polymeric microspheres, ordered structures, mathematical modeling*

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ОБЗОРНАЯ СТАТЬЯ

Химические сенсоры на основе фотонных коллоидных кристаллов

А.А. Козлов✉, А.С. Аксенов, В.А. Дворецкий, В.Р. Флид

МИРЭА – Российский технологический университет (Институт тонких химических технологий им. М.В. Ломоносова), Москва, 119571 Россия
✉*Автор для переписки, e-mail: anar42@yandex.ru*

Аннотация

Цели. *Проанализировать результаты исследований формирования фотонно-кристаллических структур из полимерных микросфер, механизмов спектральных сдвигов при селективном отражении от них немонохроматического падающего излучения в видимой и инфракрасной области, а также применения этих структур в качестве сенсоров для детектирования близких по строению химических веществ.*

Результаты. *Представлены разработки авторского коллектива, проводимые на кафедре физической химии им. Я.К. Сыркина Института тонких химических технологий РТУ МИРЭА. Рассмотрены вопросы, связанные с детектированием близких по химическому строению веществ с помощью сенсоров на основе фотонных кристаллов, изготовленных из коллоидных частиц, представляющих собой полимерные микросферы размерами 160–300 нм. Показано, что детектирование происходит в видимой области спектра за счет регистрации спектрального сдвига отраженного излучения от поверхности кристалла при нанесении веществ из жидкой или газовой фазы.*

Выводы. *Установлено, что метод электрофоретического осаждения коллоидных частиц в виде полимерных микросфер на проводящих поверхностях позволяет создать упорядоченные структуры на больших площадях. Детектирование индивидуальных соединений оптическим способом невозможно без контроля кинетики спектральных сдвигов отраженного излучения от поверхности фотонных коллоидных кристаллов. Спектральные характеристики такого излучения напрямую связаны с размерами* *частиц, определяющих период кристаллической решетки. Диффузия химических веществ в фотонный кристалл приводит к набуханию образующих его частиц и смещению спектра отраженного излучения, которое определяется изменением периода кристаллической решетки за счет изменения размеров этих частиц. Предложена модель для описания кинетики процессов набухания полимерных микросфер, описывающая диффузию веществ в пористые полимерные частицы. Показано, что увеличение количества вещества, наносимого на поверхность фотонного кристалла выше предельного, приводит к деградации кристалла, что выражается в «выцветании» его поверхности и проявляется в исчезновении узких пиков отраженного излучения.*

Ключевые слова: *фотонные кристаллы, коллоидные кристаллы, оптические сенсоры, полимерные микросферы, упорядоченные структуры, математическое моделирование*

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INTRODUCTION

Research in the field of photochemistry, conducted at the Department of Physical Chemistry of the M.V. Lomonosov Institute of Fine Chemical Technologies (IFCT), have a long history. In his lectures on physical chemistry during the 1930s–1940s, Ya.K. Syrkin noted the fundamental nature of the interaction of matter and light. He emphasized that light can be regarded as a universal, inertialess chemical reagent, whose use and importance will continuously increase.

In recent decades, the work of the Department of Physical Chemistry in the field of photochemistry has been associated with three main areas of both fundamental and applied nature:

- development of photochemical and photocatalytic methods for waste-free and environmentally friendly storage and conversion of solar energy into thermal energy [1, 2];
- fundamental work on the creation of polymethine dyes, comprising molecular ensembles built from colored organic compounds [3–7];
- development and research of physical and chemical processes based on nanosized ordered structures called photonic colloidal crystals (PCCs). Based on these structures, sensors for the selective detection of various chemical objects can be created [8].

The present review aims to summarize works on the creation of multilayer ordered structures from colloidal polymeric microspheres (PM) of submicron sizes, the description of the processes that occur when various substances are deposited on them, and the development of sensors based on them.

PCCs can become an effective means for developing sensors for express analysis, one of the most important tasks in analytical chemistry [9]. PCCs can be formed from various suspensions having a high-volume fraction of colloidal particles (CP) with the participation of external fields, for example, gravitational or electric [10]. Particles of small size can exhibit Brownian motion, moving randomly until the entire ensemble passes into an ordered state. As a result, CPs (often spherical in shape) form

PCCs in which the particles are arranged in a regular packing to form a two- or three-dimensional array.

The presence of periodicity in a PCC structure causes the occurrence of resonance phenomena in them when exposed to radiation; here, it is the characteristic size of the element base (100–500 nm) of the package that leads to the manifestation of such interactions (and, accordingly, structural coloration, i.e., the color of the sample) in the visible light in accordance with the Bragg–Snell law (Fig. 1):

$$m\lambda = 2d_{111}\sqrt{n_{\mathrm{eff}}^2 - n_{\mathrm{air}}^2 \sin^2\theta}\,, \tag{1}$$

$$n_{\mathrm{eff}} = \sqrt{f_{\mathrm{p}} n_{\mathrm{p}}^2 + f_{\mathrm{s}} n_{\mathrm{s}}^2}\,, \tag{2}$$

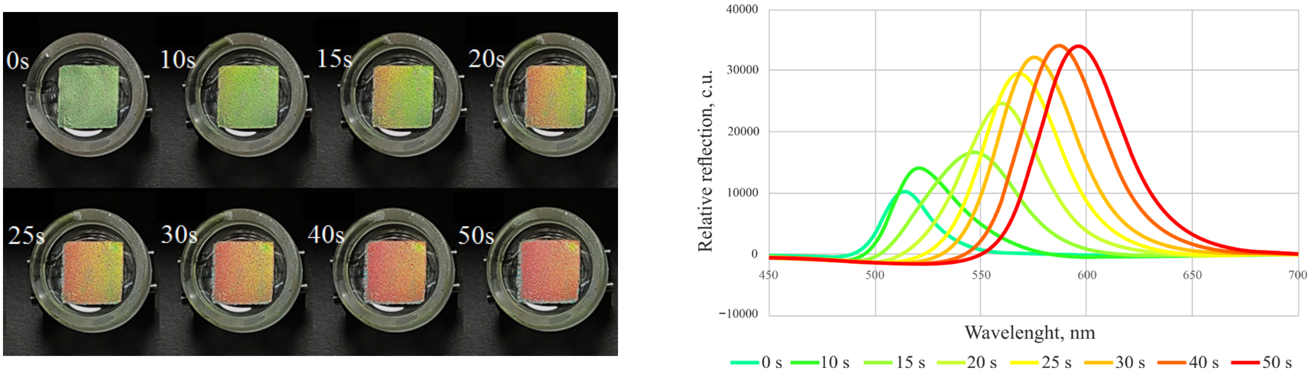
where m is the order of the diffraction maximum; λ is the wavelength of the maximum in the reflected spectrum; d_{111} is the interplanar distance between the (111) crystal planes; n_{eff} is the effective refractive index of the structure; n_{air} is the refractive index of the medium (air) from which light is incident; θ is the angle of incidence; f_{p} is the volume fraction of particles in the PCC; n_{p} is the refractive index of particles in the PCC; f_{s} is the volume fraction of matter (air) in the interparticle space in the PCC; n_{s} is the refractive index of the substance (air) in the interparticle space in the PCC.

The aim of the present work is to analyze the results of studies on the formation of photonic crystal (PC) structures from PMs, the mechanisms of spectral shifts upon selective reflection of non-monochromatic incident radiation from them in the visible and infrared light, and the use of these structures as sensors for detecting chemicals with similar structures.

CHEMICAL SENSORS BASED ON PCC

The analytical signal in PC sensors represents a shift in the maximum of the spectrally selective reflection band, which is recorded as a hypsochromic or bathochromic shift, as well as a change in the reflection intensity (hyper- or hypochromic effect). Spectrophotometers for specular and diffuse reflections are used to obtain a spectrum with high resolution. An illustrative example of such a bathochromic shift is the shift of the reflected radiation peak when *n*-octane is deposited on a PC made of polystyrene microspheres (Fig. 2). Similar dependencies are also observed in the study of other hydrocarbons, for example, toluene [11].

Fig. 1. Photographs of photonic colloidal crystals (PCCs) from polystyrene microspheres of different diameters: (1) 180 nm, (2) 200 nm, (3) 220 nm, (4) 230 nm, (5) 240 nm, (6) 260 nm.



(a) (b)

Fig. 2. Shift of the selectively reflected radiation from the surface of a photonic crystal during treatment with *n*-octane (a) and the corresponding normalized reflection spectra (b) in dynamics.

Using aromatic and aliphatic hydrocarbon vapors, the kinetic dependencies of the peak shifts from the PCC surface are also determined under the influence of volatile organic compounds on them during the course of the experiments [12]. PC-based sensors represent crystalline colloidal arrays of submicron polystyrene particles embedded in a polydimethylsiloxane matrix by the self-assembly method [13, 14]. In the case of applying a drop of a substance (for example, *p*-xylene) directly to the crystal surface, gradient color changes are observed. In the experiments, the reflection band of the PCC sensor was also found to broaden with an increase in the applied sample volume above a certain limit, resulting in a visual whitening of the crystal. This effect makes it impossible to register the spectral shift of light reflection. With prolonged exposure to substances, especially liquid samples of aromatic hydrocarbons, degradation of the treated area of the sensor occurs due to softening and adhesion of polystyrene particles [15], which leads to a visual clouding of the PC array and degeneration of the maxima in the spectra (Fig. 3).

When using PCC-based sensors, it is the registration of a low vapor concentration of volatile organic compounds in dynamics (online) that is of the greatest interest, since in this case there is no significant degradation due to the dissolution of polymer particles.

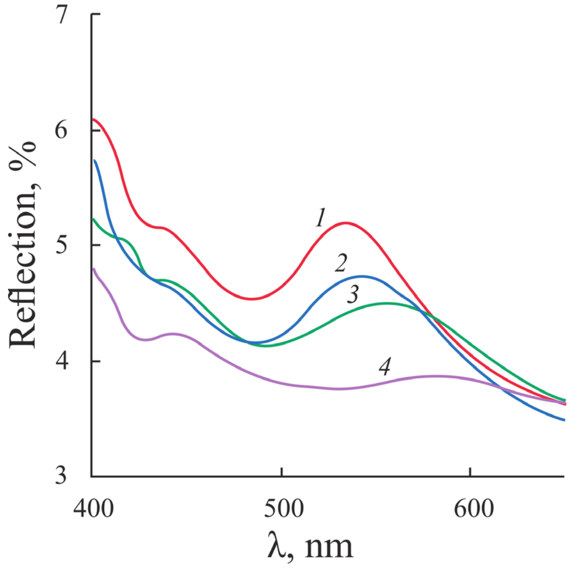


Fig. 3. Effect of liquid *p*-xylene on the photonic crystal sensor; three areas of change in the diffuse reflection spectrum along the radius of the treated spot: (1) untreated area; (2) and (3) affected areas; (4) degraded area in the center of the spot [11].

FORMATION OF THE PCC

Colloidal polystyrene particles that make up PCC with a narrow size distribution are obtained by emulsion polymerization in the presence of an anionic surfactant [16] (Fig. 4).

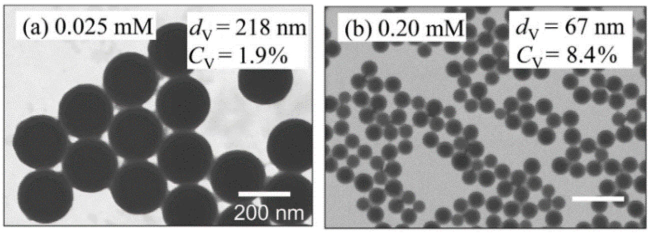


Fig. 4. Transmission electron microscopy images of polymer nanoparticles prepared by emulsion polymerization of styrene in the sodium octadecyl sulfate solutions with concentrations of (a) 0.025 mM and (b) 0.2 mM. The concentrations of styrene and ammonium persulfate were 0.3 M and 20 mM, respectively. Each scale bar shows 200 nm [16].

These particles arrange ordered arrays in the form of colloidal crystalline structures. Such arrays can be obtained in different ways. Although methods based on solvent evaporation [17–19], crystallization in a matrix [20], and sedimentation [21] are most widely used, films of the highest quality are mainly formed by vertical deposition [22, 23]. However, the low rate of film formation (in some techniques requiring from several weeks to months to form a sample) still remains one of the barriers hindering the entry of PC to markets.

One of the possible solutions to the problem is the deposition of colloidal crystalline coatings by electrophoretic deposition (EPD). The essence of the technologically-advanced EPD process, which is used in many areas of industry, lies in the migration of PCs in a liquid under the influence of an electric field; that is, using electrophoresis, followed by deposition on an electrode (Fig. 5).

By studying the EPD process using reflectance spectrophotometry in the visible wavelength range, a number of stages that accompany the formation of ordered colloidal arrays can be identified (Fig. 6) [24].

There are four such stages in colloidal crystallization (Fig. 7).

At the first stage, a concentrated disordered colloidal suspension acquires an ordered structure of a loosely packed colloidal crystal due to the Alder phase transition, after which a Bragg diffraction peak and structural color appear. At the second stage following the evaporation of the solvent, the

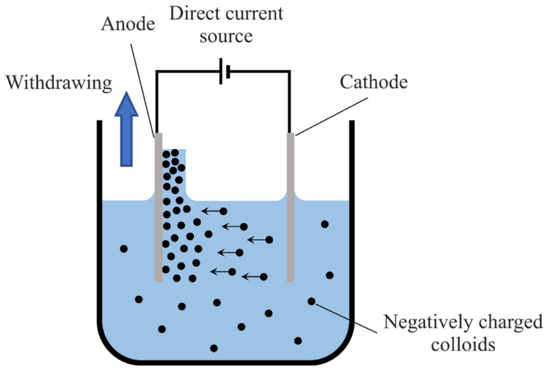
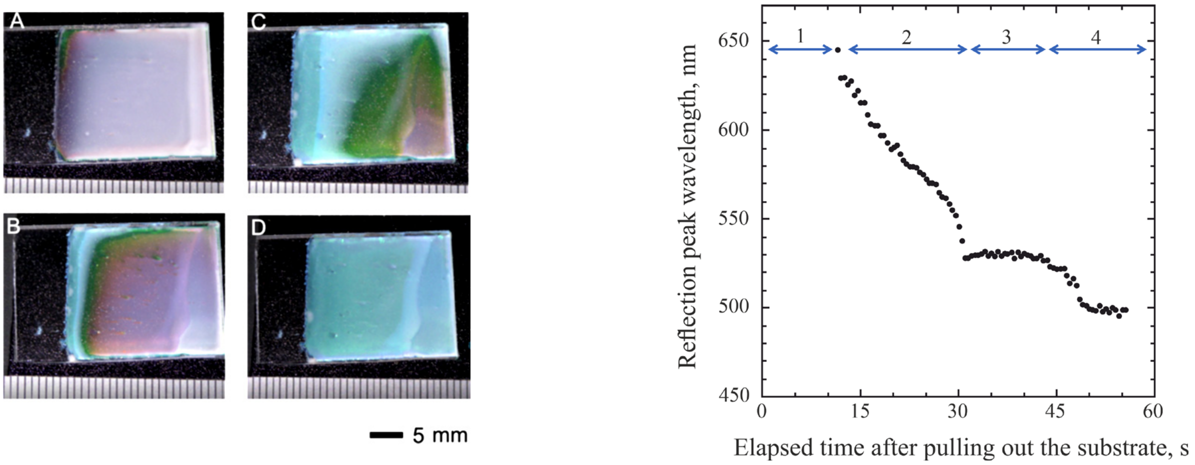


Fig. 5. Scheme of electrophoretic deposition (EPD) of negatively charged particles [17].

maximum of the selectively reflected radiation shifts to the short-wavelength region due to a decrease in the distance between the particles of a loosely packed colloidal crystal. This peak shift continues until a close-packed colloidal crystal lattice is formed. The evaporation of liquid film covering the PCC, which occurs at the third stage, does not change the position of the diffraction peak for some time. However, the complete drying of the colloidal crystalline film at the fourth stage leads to a hypsochromic shift in the structural color of the film (Fig. 7) as the solvent evaporates from the interparticle spaces of the PCC. Such a change in color is associated with a change in the effective refractive index of the medium (1).



(a) (b)

Fig. 6. (a) Photographs of various colloidal crystallization stages (A) 11.5 s, (B) 25 s, (C) 35 s, (D) 55 s. (b) Position of the maximum of the spectrally selective reflection as the dispersion medium evaporates [24].

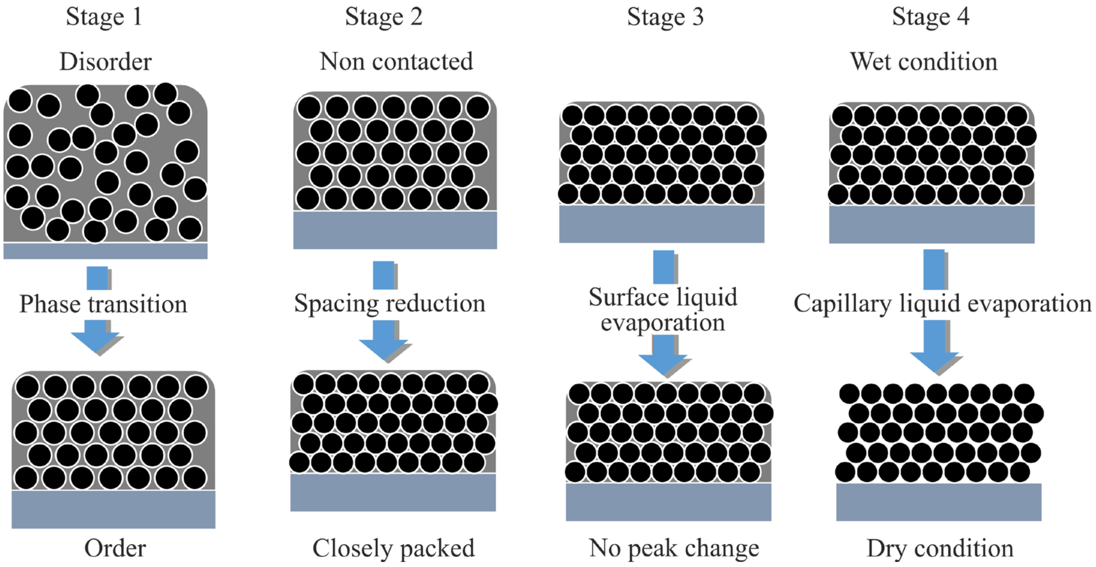


Fig. 7. Schemes of EPD stages [24].

KINETIC STUDY OF THE CP SWELLING PROCESSES IN PCC

The main disadvantage in the interaction of detectable substances with the PC surface is the lack of data on their kinetics due to the small sizes of CPs (<1 μm). As a rule, the observation of ordered structures and their changes when substances are applied to them is carried out using scanning electron microscopy or atomic force microscopy. However, such methods cannot be used in visualizing the kinetics of the interaction of chemicals with PCC to determine the relationship between the spectral responses of reflected radiation and changes in the morphology of CP, i.e., PM, affecting the optical properties of the entire package.

The behavior of PCCs when exposed to various chemicals strongly depends on the properties of the CPs that form them, such as the size distribution of particles, the presence of surfactants, and a number of other factors that affect their surface properties. This affects the rate of diffusion processes that result in a swelling of colloidal microspheres in PCCs and changes in their sizes (parameter *d* in Eq. (1)), which, in turn, affects the rate of change in the reflection spectrum from the PCC surface. Therefore, the study of the individual CP swelling dynamics is an extremely important task for analyzing the behavior of FAs under the action of chemicals.

The porous medium of CP has a very complex structure, which can be considered in fractal terms. Due to the geometry of the pores and their distribution over the volume, the diffusing substance performs complex movements when migrating through the pore channels. In this case, diffusion in a porous medium can be expected to be similar to anomalous diffusion occurring in the motion of elementary particles under the action of various force fields [25].

Thus, to study the kinetic processes of spectral shifts in PCCs, it is necessary to study the diffusion processes of substances in CPs, which are accompanied by their swelling. The methods of scanning electron microscopy and atomic force microscopy cannot be used to study the dynamics of processes in PCC; this is particularly true of the particle swelling processes under the action of deposited substances in real time. However, optical observation methods in the visible wavelength range can be used to eliminate this disadvantage. As model objects, CPs are selected for observation from the same material as particles for PCC in the visible light (submicron sizes), but with significantly larger diameters in order to visualize the dynamics of CP swelling.

In this case, the observation tool is an optical microscope [26]. In the experiments, CPs with an average diameter of 213 μm were used. When various substances are applied to such particles, the latter swell with visual changes in their size over time (Fig. 8). Such model experiments can be used to compare the kinetics of changes in the spectra [11] with the dynamics of swelling of microspheres and relate these kinetics with changes in wavelengths according to Eqs. (1) and (2). Differences in the sizes of the CPs for PCs determine the differences in the bands of the photonic band gap for PCCs of submicron and submillimeter particles. For submicron particles with sizes up to 300 nm, the photonic band gap is in the visible light, while, for particles larger than 100 μm, the gap occurs in the frequency band below 1 THz. Here, the optical properties of PCCs in terms of the spectral selectivity of radiation reflected from the surface are retained for both cases [27]. Therefore, submillimeter particles can be selected as objects for modeling the dynamics of changing the period of a PC as a diffraction grating.

To obtain images of CP during the swelling process, a setup is used, consisting of an optical microscope with various magnification factors, as well as a video camera connected to a computer for receiving and recording images from it.

All experimental time dependencies of the microsphere diameters with the introduction of various substances (aromatic hydrocarbons) into them have a similar shape (Figs. 9 and 10).

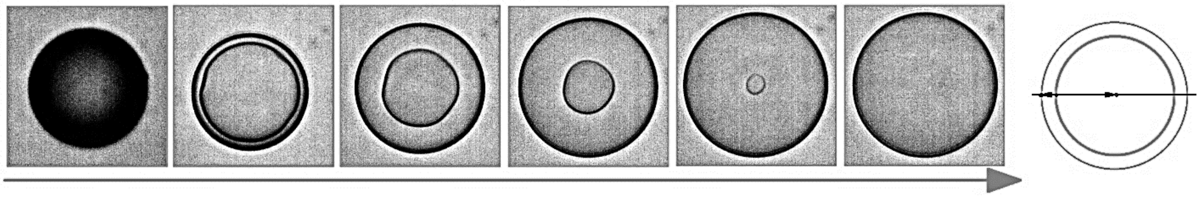


Fig. 8. Photos of the swelling process of colloidal particles from polystyrene $d = 213$ μm in a solvent.

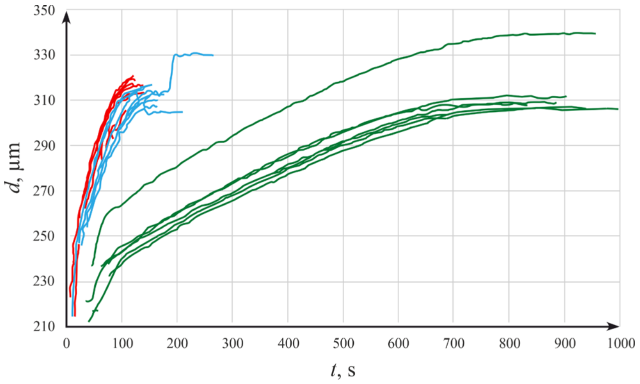


Fig. 9. Time changes in the diameters of polystyrene microspheres $d = 213 \pm 6$ µm upon swelling in benzene (red), toluene (blue), and o-xylene (green).

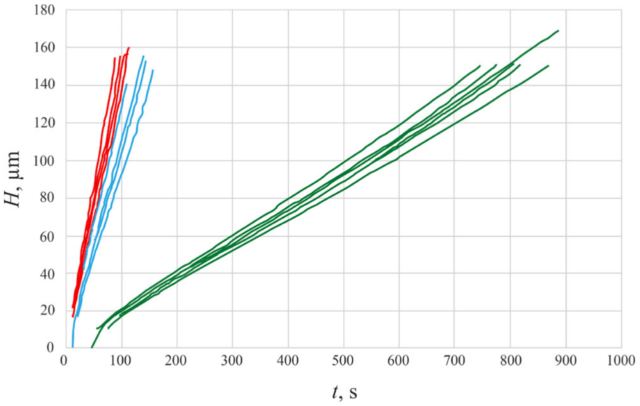


Fig. 10. Time changes in the thickness of the swollen layer (H) of polystyrene microspheres with $d = 213 \pm 6$ µm upon swelling in benzene (red), toluene (blue), and *o*-xylene (green).

SIMULATION OF THE KINETICS FOR CP SWELLING

The curves in Fig. 9 represent a family of sigmoidal curves, indicating anomalous processes occurring during the diffusion of organic nonpolar solvents into colloidal microspheres [15, 28]. At the same time, mathematical models for non-stationary modes of diffusion in media containing pores require a special solution of a set of differential equations [25, 29].

The experimental dependencies of the PM size changes due to diffusion of solvents on time (Fig. 9) are converted into the PM size rate υ_{V_i} (3):

$$\upsilon_{V_i} = \frac{V_{i+1} - V_i}{t_{i+1} - t_i}, \tag{3}$$

where V_i is the PM volume at time t_i.

This dependence υ_{V_i} can be used to determine changes in the PM size rate. The graph of the function υ_{V_i} for a microsphere with an initial size of 213 µm during the diffusion of paraxylene into it is shown in Fig. 11.

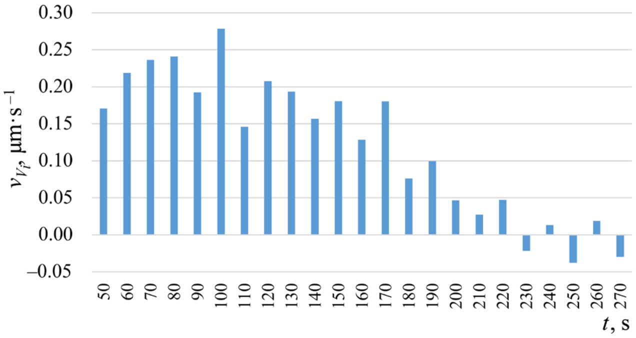


Fig. 11. Graph of the swelling rate υ_{V_i} of a polystyrene microsphere with the initial size of 213 µm during *p*-xylene diffusion.

In this case, diffusion into porous structures is characterized by strong interactions of the diffusing substance with PM, as well as unpredictable and anomalous transport processes in time, which generally deviate from the corresponding standard laws [30]. This approach in the analysis of the kinetics of diffusion processes can be represented in the form of fractional differential equations, whose solutions are apparently better adapted for such problems. At the same time, the replacement of the local time derivative with a fractional operator in the diffusion equation well describes the anomalous transport processes in porous media. For axisymmetric objects, spatial solutions in such models can have a dimension equal to one.

If the mass flux of the diffusing substance is proportional to the fractional derivative of the concentration c with respect to the spatial coordinate r [31], then the spatial derivative in the classical Fick diffusion equation should be accompanied by the additional inclusion of temporal nonlocality effects by introducing a fractional derivative with respect to time t. The non-local character of the change in the mass flow over time has been confirmed by numerous theoretical and experimental studies [30, 32, 33].

In this case, for the mass flux J_c [30] (4):

$$J_c = D_f \partial_t^{1-\gamma}\left(\frac{\partial^{\beta} c}{\partial x^{\beta}}\right), \ \gamma > 0, \ \beta < 1, \tag{4}$$

where D_f is the effective diffusion coefficient (subscript f means the distinguished spatial direction of diffusion); x is the diffuse flux; γ and β indicate the order of time and spatial fractional derivatives; respectively.

If in Eq. (4) the effective diffusion coefficient D_f is represented as a function of the spatial coordinate r, then the diffusion equation $\partial c/\partial t = -\partial/\partial r\,(J_c)$ in a porous medium can be rewritten as follows (5):

$$\frac{\partial c}{\partial t}=\frac{D_f}{r^{d_f-1}}\frac{\partial}{\partial r}\left(r^{d_f-1-\theta}\frac{\partial c}{\partial r}\right), \qquad (5)$$

where d_f is the fractal size; θ is the anomalous diffusion index (the fractional derivative of the concentration with respect to the spatial coordinate).

The solution of Eq. (5) agrees well with the results of exact diffusion calculations performed by the fractal method using Sierpiński triangles [34].

The solution of differential Eqs. (4) and (5) is a combination of gamma functions [35], involving the choice of the corresponding parameters D_f, β, γ and initial conditions. If we represent the solution of Eq. (5) in the form of the lower incomplete gamma function (6):

$$\gamma(m,x)=\int_0^x \alpha^{m-1}e^{-\alpha}d\alpha, \qquad (6)$$

where α and m are the integration parameters, and x is the upper limit of the γ-function, then the integrand is the product of the exponential and the other exponential functions that determine the rate of change in the concentration of the diffusing substance inside the PM.

Assuming a linear nature of the relationship between the rate of mass transfer of a substance and the change in volume V of the CP during their swelling $\partial c/\partial t = K\,\partial V/\partial t$, we can write the integrand function (6) $\left(\frac{t}{t_0}\right)^m e^{-k\left(\frac{t}{t_0}\right)}$ in the form (7) with the coefficients k and m as parameters that determine the rate of volume change υ_V CP:

$$\upsilon_V = KV_0\exp\left[-k\left(\frac{t}{t_0}\right)\right]\cdot\left(\frac{t}{t_0}\right)^m = KV_0\exp(-k\alpha)\alpha^m, \qquad (7)$$

where V_0 is the initial volume of CP; K is the coefficient of proportionality; $\alpha = t/t_0$; t is the current time; t_0 is the saturation time of the CP with the diffusing substance. The parameters m and k were selected by superimposing function (5) on the experimental graphs shown in Fig. 9.

Function (7) has an extremum at point (8):

$$\frac{d\upsilon_V}{d\alpha}\Big|_{\alpha=\alpha_c}=0. \qquad (8)$$

Then, using Eq. (9), we can derive the time of maximum swelling rate of PM t_c (10):

$$-k\alpha+m=0;\ \frac{t_c}{t_0}=\frac{m}{k}, \qquad (9)$$

$$t_c=t_0\frac{m}{k}. \qquad (10)$$

Figure 12 shows a theoretical approximation of the rate of change in the size of the PM.

Thus, the extraction of data on an individual substance can be carried out by differences in the swelling time of the CP, corresponding to the rate of diffusion of these substances in the PM and manifesting itself in different rates of spectral shifts of the reflected radiation from the surface of the PCC.

DEGRADATION OF REFLECTED RADIATION FROM PCC

In the section on chemical sensors based on PCC, it was shown that the reflection band of the PCC sensor broadens when the sample volume

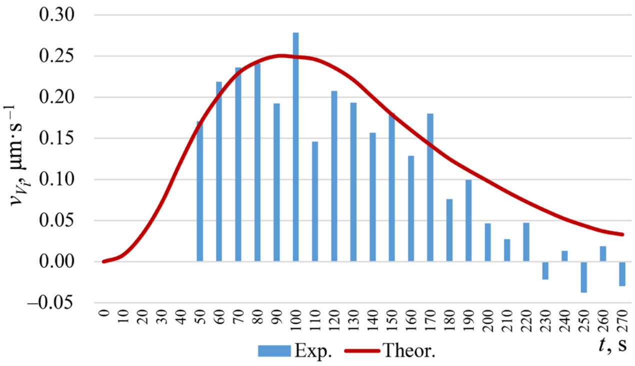


Fig. 12. Experimental graph and theoretical curve of the swelling rate of PM with a diameter of 213 ± 6 μm within p-xylene: $k = 6$; $m = 2.6$; $t_0 = 220$ s; $t_c = 95.3$ s.

applied to the crystal exceeds a certain limit, resulting in a loss of ability on the part of the crystal to selectively reflect non-monochromatic light from its surface. This occurs due to the processes of degradation of the structure of the PC during repeated application of samples of chemical substances to it. In [15], processes are described that lead to a change in the properties of CPs that form PCCs; this, in turn, changes the intensity of radiation reflected from the surface of the crystal as a whole. For example, Fig. 13 shows two electron micrographs of PCCs from polystyrene microspheres of submicron sizes (~240 nm) both before applying the substance and after the PCCs lose their optical properties.

A comparison of sections of electronic images (Fig. 13) reveals more blurred edges of individual CPs in the right image than in the left one. Such blurring indicates the smoothness of the microsphere surface following diffusion of the substance penetrating into them. To visualize the kinetics of these processes, polystyrene microspheres 213 ± 6 μm in size were chosen as model CPs. Following treatment of microspheres with a substance (toluene), an increase in the size of microspheres occurs due to the straightening of macromolecules when a substance is introduced into them and the concomitant change in the structure of internal pores.

The study [36] showed that uniaxial deformation of polymer films with a thin layer of hard coating deposited on them is accompanied by the appearance of a regular microrelief on it, followed by its destruction. In this case, the microrelief is always oriented along the tension axis of the polymer chains and located perpendicular to the cracks in the damaged coating. As is known, when rubber-like polymers are stretched, their volume hardly changes. Instead, significant lateral compression occurs, causing the coating to deform in a direction perpendicular to the tensile axis of the polymer. As a result of compression, the hard coating loses its stability, leading to the appearance of a microrelief.

The images of swelling and contraction of polystyrene microspheres following the introduction of the analyte (toluene) are shown below in Figs. 14.

Due to inelastic deformation following evaporation of the substance, the surfaces of the polystyrene microspheres are compressed to produce additional roughness (Fig. 15). This causes greater scattering of the incident radiation on the PCC surface, which introduces additional noise into the reflected radiation.

Thus, the degradation of PCC under the action of substances can be divided into the following stages:

- swelling of CP with formation of dense packing;
- an increase in the friability of the CP surface under the action of a substance, increasing the scattering of the incident radiation and reducing the spectralefficiency of the Bragg reflection from the PCC surface;

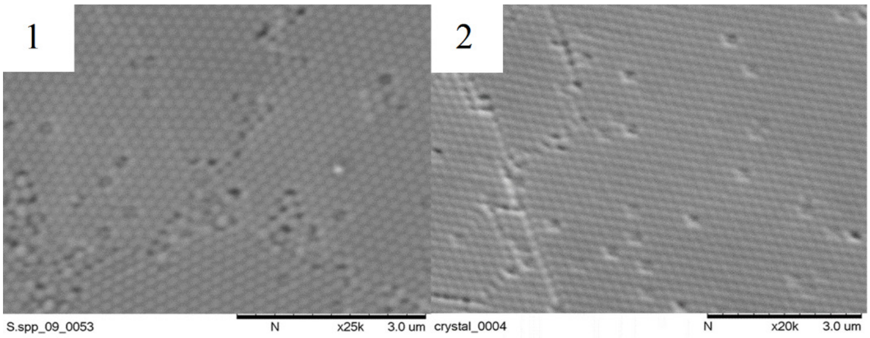


Fig. 13. Scanning electron microscope images of PCCs: (1) before the application of the analyte, (2) after the degradation of PCCs [15].

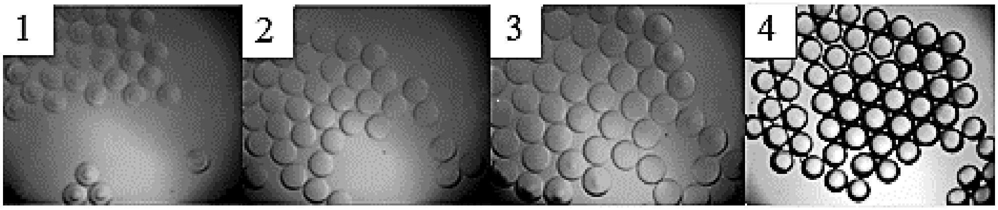


Fig. 14. Images (1) and (2) represent swelling of PCC from polystyrene CPs; (3) and (4) show compression following evaporation of the substance (toluene) from the PCC [15].

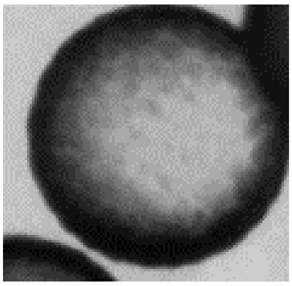


Fig. 15. Loose surface of the microsphere following the evaporation of toluene from its volume [15].

- the friability of CP is accompanied by a decrease in their hardness, which leads to the “pressing” of microspheres into each other (Fig. 16). This reduces the depth of slits in the formed reflective diffraction grating during the interaction of coherent reflected waves from the PCC surface.

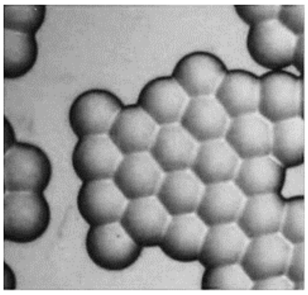


Fig. 16. The “pressed in” structure of the PCC, after the dose of the analyte is exceeded maximum [15].

CONCLUSIONS

Developments undertaking by the authorial team of researchers in recent years, carried out at the Ya.K. Syrkin Department of Physical Chemistry of the IFCT of the RTU MIREA, have been presented. Issues related to the detection of substances with similar chemical structure using CP-based sensors made from CP are considered. The particles are PMs 160–300 nm in size. Detection occurs in the visible wavelengths due to the registration of the spectral shift of the reflected radiation from the surface of the crystal when substances are deposited from the liquid or gas phase. Such crystals can be obtained by the EPD method: by migration of CPs in a liquid under the action of an electric field, followed by their deposition on an electrode. Special additional coatings are used to protect the PCCs obtained from the negative influence of the external environment.

In order to separate substances that are close in chemical structure, it is necessary to use the differences in the kinetics of spectral shifts of reflected radiation from the of photonic colloidal structure surfaces, which is directly related to the diffusion of substances in the CPs that form them. The kinetics of spectral shifts in PCCs are related to processes of diffusion of substances in CPs, which are accompanied by their swelling. For studying the properties of PCs formed from submicron particles, scanning electron microscopy and atomic force microscopy methods are mainly used. However, these approaches cannot be used to study the dynamics of processes in a PCC, in particular, the processes of swelling of particles under the action of a substance in real time. However, by using optical observation methods in the visible wavelength range, this disadvantage can be eliminated.

To visualize the dynamics of CP swelling processes, CPs made of the same material as the particles for PCC in the visible range, but having much larger diameters (213 μm), were chosen as model objects. In this case, the instrument of observation is an optical microscope. When substances are applied to such particles, the latter swell with visual observation of changes in their size with time.

Experimental curves of the polymer particle swelling during the diffusion of chemical substances in them reveal information about the kinetics of these processes. At the same time, the complex structure of the particles themselves significantly complicates the description of these processes. empirically selected coefficients, permits a description with sufficient agreement of the kinetics of diffusion processes of nonpolar organic substances into such polymer particles. The peak position of the swelling rate curve in time forms a basis for identifying substances of the same class, as well as distinguishing between substances that are similar in chemical structure and deposited on a PC. In this case, the repeated application of such substances to PCs leads to a degradation of their optical characteristics caused by changes in the morphological properties of such ordered structures. Such changes are due to the looseness of the surface of CPs during their swelling under the action of substances diffusing in them, which is accompanied by a change in the morphology of the entire crystal as a whole, reducing the spectral efficiency of Bragg reflection from its surface. A decrease in the hardness of the CP leads to a visual clouding of the PC and a degeneracy of the maxima in the reflection spectra. In this case,the use of such structures as sensors of chemical substances is no longer possible.

Further development of similar sensors involves increasing their sensitivity and selectivity, as well as reducing the response time to the injected substance. An important additional task in the development of engineering systems using such devices involves an increase the number of cycles of PC-based sensors.

Authors' contribution

All authors equally contributed to the research work.

The authors declare no conflicts of interest.

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About the authors:

Andrei A. Kozlov, Cand. Sci. (Eng.), Associate Professor, Ya.K. Syrkin Department of Physical Chemistry, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (86, Vernadskogo pr., Moscow, 119571, Russia). E-mail: anar42@yandex.ru. Scopus Author ID 57197377562, RSCI SPIN-code 1050-4508, https://orcid.org/0009-0002-2410-6216

Anton S. Aksenov, Postgraduate Student, Ya.K. Syrkin Department of Physical Chemistry, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (86, Vernadskogo pr., Moscow, 119571, Russia). E-mail: aksen_a@mail.ru. Scopus Author ID 57488662700, https://orcid.org/0009-0002-0610-5906

Vasilii A. Dvoretsky, Master Student, Ya.K. Syrkin Department of Physical Chemistry, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (86, Vernadskogo pr., Moscow, 119571, Russia). E-mail: vasya.dvoretsky@yandex.ru, https://orcid.org/0000-0001-8558-8859

Vitaly R. Flid, Dr. Sci. (Chem.), Professor, Head of the Ya.K. Syrkin Department of Physical Chemistry, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (86, Vernadskogo pr., Moscow, 119571, Russia). E-mail: vitaly-flid@yandex.ru. Scopus Author ID 6602997346, ResearcherID H-1781-2017, RSCI SPIN-code 8790-3380, https://orcid.org/0000-0001-6559-5648

Об авторах:

Козлов Андрей Аркадьевич, к.т.н., доцент кафедры физической химии им. Я.К. Сыркина Института тонких химических технологий им. М.В. Ломоносова ФГБОУ ВО «МИРЭА – Российский технологический университет» (119571, Россия, Москва, пр-т Вернадского, д. 86). E-mail: anar42@yandex.ru. Scopus Author ID 57197377562, SPIN-код РИНЦ 1050-4508, https://orcid.org/0009-0002-2410-6216

Аксенов Антон Сергеевич, аспирант, кафедра физической химии им. Я.К. Сыркина Института тонких химических технологий им. М.В. Ломоносова ФГБОУ ВО «МИРЭА – Российский технологический университет» (119571, Россия, Москва, пр-т Вернадского, д. 86). E-mail: aksen_a@mail.ru. Scopus Author ID 57488662700, https://orcid.org/0009-0002-0610-5906

Дворецкий Василий Анатольевич, магистр, кафедра физической химии им. Я.К. Сыркина Института тонких химических технологий им. М.В. Ломоносова ФГБОУ ВО «МИРЭА – Российский технологический университет» (119571, Россия, Москва, пр-т Вернадского, д. 86). E-mail: vasya.dvoretsky@yandex.ru, https://orcid.org/0000-0001-8558-8859

Флид Виталий Рафаилович, д.х.н., профессор, заведующий кафедрой физической химии им. Я.К. Сыркина Института тонких химических технологий им. М.В. Ломоносова, ФГБОУ ВО «МИРЭА – Российский технологический университет» (119571, Россия, Москва, пр-т Вернадского, д. 86). E-mail: vitaly-flid@yandex.ru. Scopus Author ID 6602997346, ResearcherID H-1781-2017, SPIN-код РИНЦ 8790-3380, https://orcid.org/0000-0001-6559-5648

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