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Vladimir Nikolayevich Ipatieff (1867-1952) – The Eminent Russian-American Chemist of the First Half of the XX Century

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Abstract. Vladimir Nikolayevich Ipatieff (1867–1952) was one of the most prominent chemists of the first half of the 20th century. He studied catalytic processes in organic chemistry. His discoveries include, among others, the explanation of the structure of isoprene, the method of obtaining butadiene from ethanol, dehydrogenation of alcohols to aldehydes and ketones, dehydration of alcohols to alkenes, including ethanol to ethylene, hydrogenation of benzene to cyclohexane, polymerization of ethylene in the presence of various catalysts. Much of his experimental studies were carried out at high pressure in a rotating autoclave, the so-called "Ipatieff bomb". The purpose of this article was to familiarize readers with important events in the life of V. N. Ipatieff and his research activities, in particular with selected results of his experimental studies. In addition, the statements by American and Russian chemists about V. N. Ipatieff and his research were presented.

Keywords. V. N. Ipatieff, Organic chemistry, Catalysis and catalysts, Russia, United States - XX century.

Just as rays of the sun are distributed to all men, rich and poor, good and evil, so also scientific ideas, new discoveries, and inventions serve all humanity.
V. N. Ipatieff (1867-1952) [1]

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THE IMPORTANT EVENTS IN THE IPATIEFF'S LIFE[1]

Vladimir Nikolayevich Ipatieff (Fig. 1) was called a man of the unusual fate, a brilliant experimenter and an outstanding organizer of industrial production. Sixty-eight years have passed since his death, but in that time little has appeared in the literature about this outstanding man. His contribution to catalytic organic synthesis, as well as to major change in the chemical industry, is enormous. Therefore, his name was forewer written in letters in gold in the history of chemistry.

Vladimir N. Ipatieff was born in Moscow on November 9 [according to the Julian calendar (Old Style); Nov. 21, by the Gregorian calendar (New Style), adopted in Russia on February 1, 1918] 1867, the son of Nikolay Alekseevich Ipatiev (1841-1891)[2], an architect from an old and respectable merchant family, and Anna Dmitrievna Ipatieva (née Gliki) (1847-1880)[3].

At the age of 11, after two years of study at the Fifth Classical Gymnasium, he continued his education at the Third Moscow Military Gymnasium. In 1884 he began studying at the 3rd Alexandrovskaya Military School in Moscow. After two years, he transferred to the Mikhaylovskaya Artillery School in St. Petersburg, which he graduated in 1887. For the next two years, he served in the artillery brigade in Serpukhov, near Moscow.

To continue with his education, Ipatieff successfully passed the entrance exams at the St. Petersburg's Mikhaylovskaya Artillery Academy in August 1889. After three years of study, he graduated from the Academy and became a tutor there. From September 1892, he began to give lectures on inorganic and theoretical chemistry. He also perfected his experimental skills in the organic chemistry in the chemical laboratory at the St. Petersburg Imperial University. Lecturer of the organic chemistry, privat-docent, Alexey Evgrafovich Favorsky (1860-1945) offered him help and advice. In May 1895, after working for three years as tutor, he defended his dissertation in chemistry entitled *Deystviye broma na tretichnyye spirty i bromistogo vodoroda na atsetilenovyye i allennovyye uglevodorody v uksusnom rastvore* (Action of Bromine on Tertiary Alcohols and the Action of Hydrogen Bromide on Acetylenic and Allene Hydrocarbons in an Acetic Solution) and was nominated a full-time lecturer of chemistry at the Academy.

A foreign internship in Germany, which Ipatieff began in 1896, was very important to shape him as a scientist. He worked there in the Chemical Laboratory of the Academy of Sciences in Munich (*Das chemische Laboratorium der Akademie der Wissenschaften zu München*) with Adolf von Baeyer (1835-1917). In December 1896, Baeyer and Ipatieff published a paper, "Ueber die Caronsaüre", in which the authors described their

Figure 1. Vladimir Nikolayevich Ipatieff (1867-1952) (Public domain, from reference 20). The image was made in 1914. V. N. Ipatieff is in the uniform of Lieutenant General [13].

[1] Presented facts from Ipatieff's life were collected, basing on the following sources of information from 1905-2017 [2-14,16,17,19]. A brief description of the life and achievements of 38-year-old Ipatieff was found in the Encyclopedic Dictionary, published in 1905 [2]. Very useful turned out to be the book with his scientific biography published in Russian in the early 1990s [3]. Interesting information on his life and scientific activity was also found in scientific literature, both in Russia [4-9] and the USA [10-13]. Many descriptions of Ipatieff's experimental studies were found in his authoritative book published in Russian in 1936 [14]. This book was translated into English in 1937 [15]. A great source of information about the life of Vladimir N. Ipatieff was a two-volume book with his memories from the years 1867-1930, published in Russian in New York in 1945 [16,17]. This book was published in English by Stanford University Press a year later [18]. In the ex-Soviet Union excerpts from this book were published in the journal Khimiya i zhizn' (Chemistry and Life) in 1989 [19].

[2] In 1890, he became seriously ill due to asthma and arteriosclerosis. A year later, he died at the age of 50 [16].

[3] She died of tuberculosis at the age of thirty-three [16].

study on the structure of the caronic acid (3,3-dimethylcyclopropane-1,2-dicarboxylic acid; $C_7H_{10}O_4$) [21]. On March 1, 1897, he completed his an internship abroad. Travelling from Munich to Paris, he stayed 2 days in Strasbourg, where he attended a lecture of the German chemist-organic Wilhelm Rudolph Fittig (1835-1910). In Paris, he for three months worked in the *Laboratoire Central des Poudres et Salpêtre* (Central Laboratory of Gun Powder and Saltpeter) with chemist Paul Vieille (1854-1934), discoverer of the smokeless gunpowder, and physicist Emile Sarrau (1837-1904). On the end of June 1897, on his way from Paris to Russia, he stayed in Germany – first in Frankfurt am Main, where he visited factory manufacturing carbolic acid [phenol], next in Ludwigshafen, where he visited factory producing dyes and soda. Then, he reached Russia via Berlin. After a 3-week rest in Moscow, he went to St. Petersburg.

In 1898, Ipatieff submitted his professor's dissertation to the Academy, entitled *Allenovyye uglevodorody, reaktsiya khloristogo nitrozila i dvuoksi azota na organichaskiye soyedineniya, soderzhashchiye dvoynuyu svaz', i sintez izoprena* (Allene Hydrocarbons, the Reaction of Nitrosyl Chloride and Nitrogen Dioxide on Organic Compounds with Double Bond, and the Synthesis of Isoprene) and paper under the title *Prigotovleniye i vzryvchatyye svoystva trinitrokrezola i trinitronaftalina* (Preparation and Explosive Properties of Trinitro-cresol and Trinitro-naphthalene). At the end of February 1899, after successful public defense of the dissertation, he was unanimously awared the title of Professor of Chemistry and Explosives at the Academy. In 1902, he was appointed Professor Ordinary at the Academy. In the same year, Physico-Mathematical Faculty at the St. Petersburg Imperial University invited Ipatieff as the privat docent to lecture thermochemistry. Since that time, he maintained constant contact with the University up to 1916. From 1906, he was given obligatory lectures of the general chemistry for physicists, mathematicians, and astronomers.

In the thirds decade of March 1908, Ipatieff defended his dissertation for the Doctor of Chemistry degree at the St. Petersburg Imperial University entitled *Kataliticheskiye reaktsii pri vysokikh temperaturakh i davleniyakh* (Catalytic Reactions at High Temperatures and Pressures).

V. N. Ipatieff was elected the supervisor of the chemical laboratory at the St. Petersburg's Mikhaylovskaya Artillery Academy in 1909. His helper was a full-time lecturer, chemist Nikolay Mikhalovich Vittorf (1869-1929).

Ipatieff's military career did not interfere with his scientific life. In 1910, he was promoted to the rank of major general of the *Russkoy Imperatorskoy Armii* (Russian Imperial Army). At the age of forty-seven in 1914, he had obtained the rank of lieutenant general.

During World War I, from February 1915, Ipatieff served as a head of the Commission for Preparation of Explosives, which controlled almost the entire Russian chemical industry until the end of the war, among others, the production of potassium nitrate, dinitronaphthalene, benzene, toluene, sulfuric acid, nitric acid, and picric acid from benzene. In 1916, he was named chairman of the Chemical Committee of the Chief Artillery Administration, which was formed mainly due to the use of poison gas by the Germans on the Eastern Front in May 1915. Thanks to the activities of the Chemical Committee and included in its composition the Commission for the Preparation of Asphyxiating Gases, the production of liquid chlorine, phosgene, chloropicrin and sulfuryl chloride from liquid sulfur dioxide was started.

After the October Revolution in 1917, Ipatieff began to cooperate with the Bolsheviks. He was appointed chairman of both the Chemical Committee and the Technical Department of the Military Economic Council of the People's Commissariat for Military Affairs. In June 1918, he was relieved from these positions. In the years 1921-1926, he served as chairman of the General Chemical Directorate of the Supreme Council of the National Economy. At the beginning of 1927, he was relieved of all posts in state structures. He returned from Moscow to Leningrad [name of the city of St. Petersburg in 1924-1991], where he founded and directed the Institute of High Pressures.

On October 23-26, 1927, Ipatieff took part in the jubilee celebrations organized in Paris on the occasion of the 100th anniversary of the birth of the French chemist Marcellin Berthelot (1827-1907). The ceremony was attended by scientists from 60 countries around the world, including Richard Willstätter (1872-1942), who was honoured by the award of the Nobel Prize for Chemistry in 1915, Heinrich Wieland (1877-1957), Fritz Haber (1868-1934), who was awarded the Nobel Prize for Chemistry in 1918, Wilhelm Schlenk (1879-1943), and Walther Nernst (1864-1941), who was the winner of the 1920 Nobel Prize in Chemistry. There he first met with 73-year-old Paul Sabatier, who received the Nobel Prize in Chemistry in 1912. Their meeting took place in a pleasant and friendly atmosphere.

In 1929, the political situation in the Soviet Union worsened. The campaign against specialists has begun. Many people were arrested in Moscow and Leningrad by the G.P.U. (State Political Administration), among them those, who worked with Ipatieff for years. He, com-

ing back from the International Engineering Congress in Tokyo, was agitated by the execution of five military engineers-technologists. All were his very smart students at the Academy, who since the very beginning of the October Revolution worked on the bringing factories manufacturing military equipment to work. Moreover, physicochemist Yevgenii Ivanovich Shpitalsky (1879-1931) was arrested. Later, in 1945, Ipatieff wrote in his memoirs: "My mood became especially alarming, because Ye. I. was my great friend, knew all the details of my life and during an interrogation, purely incidentally, he could report some facts, that would allow to bring me to interrogation, and subsequently to be arrest" [17].

In early June 1930, Ipatieff was appointed as one of the ten delegates to the International Energy Congress in Belin called *The Second World Power Conference*. He replaced one of the professors of electricity who was arrested. On June 12, 1930, he and his wife Varvara Dmitrievna (1869-1952) crossed the Soviet Union (USSR) border in Negorloe[4]. Their matured children – Anna Vladimirovna and son Vladimir Vladimirovich stayed in USSR[5]. The oldest of their two other sons, Dimitri (1893-1914) was already dead. He was killed near Vilnius during the World War I. Their next son Nicolay after the October Revolution left Russia with participants of the White Movement called *Belogvardeytsi* (White Guardsmen) and has lived in Belgium since 1919[6] [22]. Ipatieff's half-brother chemist Lev Aleksandrovich Chugaev[7] (1873-1922) was already dead, and his younger brother, engineer Nikolay Nikolayevich Ipatiev (1869-1938), from 1921 he stayed in Prague (Czechoslovakia, now the Czech Republic)[8].

At the Berlin conference, which took place on June 16-26, 1930, Vladimir N. Ipatieff met many eminent chemists from different countries all over the world. One of them was an American chemist Gustav Egloff (1886-1955) from Universal Oil Products Company (UOP) in Chicago [12]. He told Engloff that he interested in visiting UOP laboratories in the USA. In September, 1930, he and his wife arrived in New York City, thanks to Egloff's help in obtaining a visas from the American Consul. After his visit to Research Laboratories of the UOP in Riverside (Illinois), and talk with the president of UOP – Hiram J. Halle (1867-1944), he agreed to take a post of the Director of Chemical Research. As he was bound by a 3-year contract with German *Bayerische Stickstoffwerke* (Bavarian Nitrogen), he agreed with Halle that 6 months he will stay in Germany and remaining 6 months in the United States. Then, Ipatieffs returned to Berlin. In May, 1931, both spouses came to the USA again. In addition to working as a research director at UOP Research Laboratories, he also became a lecturer on catalysis in organic chemistry at Northwestern University.

The political situation in the USSR, after leaving the country by Ipatieff, did not improve. In 1934, his close associate organic chemist Grigory Alekseevich Razuvayev (1895–1989) was arrested. A former his student, a geochemist Nikolay Alexandrovich Orlov (1895-1937) was also arrested. In January 1935, many well-known people from the party and government were convicted and soon shot, including Lev Borisovich Kamenev (1883-1936) and Grigory Yevseyevich Zinoviev (1883-1936), with whom he has previously collaborated.

From the last month of the third quarter of 1936, correspondence was conducted between the permanent secretary of the Academy of Sciences of the U.S.S.R, academician Nikolay Petrovich Gorbunov (1892–1938) and Ipatieff about the need to return the scientist to the USSR. The translation of an excerpt of Gorbunov's letter of September 17, 1936, to Ipatieff into English is as follows: "… For about six years now you have been outside the borders of the USSR and are not taking any part in the practical work of socialist construction. You are a citizen of the USSR, a major scientist, a full member of the Academy of Sciences, our country needs you. Therefore, on behalf of the Presidium of the Academy of Sciences, I ask for your direct, clear and frank answer to the following question - do you consider yourself obligated to work fully for your homeland - the Soviet Union, for to enhance his power and prosperity … . If you answer the question posed to you in the affirmative, then you should soon return to the USSR for scientific work. …" [9]. Here is an excerpt from a Ipatieff reply to Gorbunov, translated from Russian into English (letter of 1 December, 1936). "… I must say, firstly, that I

[4] While wives were usually not allowed to travel abroad with their husbands, Ipatieff received his wife's passport in just three days, stating that he would be a delegate only if his spouse can accompany him because she needs treatment abroad. Until they left Russia, he didn't tell his wife that he did not expect to return to the country [13].

[5] Professor and Doctor of Science, Vladimir Vladimirovich Ipatiev (1897-1955), like his father, was a chemist. He managed the laboratory of the Leningrad Scientific-Research Institute dealing in the processing of crude oil and the production of synthetic liquid fuel. He also lectured at the Forestry Academy and the Leningrad State University [4].

[6] In 1935, Nikolay [Nicolas (d') Ipatieff] died in Africa testing a treatment he had invented for yellow fever. At that time, he worked in the Belgian Congo as the government inspector Industry and Commerce [22].

[7] The father of Lev Aleksandrovich was the teacher Alexander Fomich Chugaev. His mother was Ipatieff's mum, Anna Dmitrievna. Vladimir N. Ipatieff did find out that Lev A. Chugaev is his half-brother in 1907 [16].

[8] On July 17, 1918, in his house in Yekaterinburg the Bolsheviks killed Tsar Nicholas II and his family [17].

can in no way agree with the fact that I do not take any part in the scientific work that has taken place in the USSR over these six years. … It is enough to indicate that … I wrote a book, which, in addition to summarizing my old studies, contains very valuable new material that will be used to great advantage in the USSR. … In addition, I sent all my new studies to Russian chemical journals at the same time as sending their translations to American journals. … It is undeniable that every scientist works not only for his country, but for all mankind. I love my homeland and, making new discoveries, I always thought and think now that all this belongs to her and she will be proud of my work. … I ask you to declare to the Presidium of the Academy of Sciences that I'm not giving up my hope of coming to the USSR, but now the circumstances are such that I actually can't do this. ..." [9].

On December 29, 1936, Ipatieff was deprived the title of the Member of the Academy of Science Of the USSR. In its justification was written, among other, "Refusing to return to work at the Academy of Science, decidedly preferring work in the foreign commercial company, V. N. Ipatiev grossly violates the basic duty of every citizen of the Soviet Union – to work for the good of his homeland" [23]. Ipatieff was expelled from the Academy by sixty-three votes in favor, no one against, and six abstentions [24]. On January 3, 1937, Presidium of the Central Executive Committee USSR in the decision signed by Mikhail Ivanovich Kalinin (1875-1946) and Ivan Alekseyevich Akulov (1888-1939) decided to "deprive Vladimir Nikolayevich Ipatiev of citizenship of the USSR, because he refused to fulfill his duty to his homeland and forbid to cross the borders of the Soviet Union" [25][9].

Vladimir N. Ipatieff did not wait long for American citizenship. On March 11, 1937, he became United States citizen. His wife received such citizenship one month later. On the day of the 70th birthday of Ipatieff, Chicago Section of the American Chemical Society (ACS) organized ceremonious meeting, in which he gave the lecture entitled "Catalysis - chemistry of the future". He in this occasion received greetings from the scientists of 30 countries all over the world, for instance German chemist Friedrich Bergius (1884-1949), American chemist-organic Mozes Gomberg (1866-1947) and Estonian chemist Gustav Tammann (1861-1938).

On December 18, 1939, Ipatieff underwent a serious throat surgery, after which he spoke in a hoarse whisper. His doctor forbade him any public speech. However, this problem did not exist too long, and after a few months after surgery, he was again able to speak at meetings.

Particularly interesting were the celebrations that took place on November 14-20, 1942, on the occasion of Ipatieff's 75th birthday, 50 years of his scientific activity and the Golden Anniversary (50 years of his marriage). In the organized ceremonious meetings, warm greetings he received from Gustav Egloff and representatives of the chemical institutions from various American States. Greeting sent also American chemists: Linus Pauling (1901-1994), Paul Emmet (1900-1985), and Kasimir Fajans (1887-1975).

Between May 28 and June 6, 1951, Ipatieff attended the *Third World Petroleum Congress* in the Hague (the Netherlands). In July 1952, he celebrated the 60th Anniversary of his wedding. There were no any meetings on the occasion of his 85th birthday because he categorically opposed their organization by Northwestern University. He died a few month later, at 07:00, in Saturday on November 29, 1952, and was buried in the Saint Vladimirs Russian Orthodox Cementary in Jackson, Ocean County (New Jersey). Ten days later (on December 9) died his wife Varvara Dimitrievna.

IPATIEFF'S RESEARCH ACTIVITIES. DESCRIPTION OF SELECTED RESULTS OF EXPERIMENTAL STUDIES

The list of Ipatieff's published works includes 399 papers. There are the articles published in Russia and the Soviet Union, among other in the journals *Zhurnal Russkogo fiziko-khimicheskogo obshchestva* (Journal of the Russian Physical-Chemical Society) and *Doklady Akademii Nauk SSSR* (Proceedings of the Academy of Sciences of the U.S.S.R), and many papers published in German, French and American journals [13,26].

Ipatieff's first work was published in 1892 and concerned the chemical investigation of the structure of steel. In the following years, he focused his research in the field of organic chemistry. In two articles from 1897 he described his method of the synthesis of isoprene (2-methyl-1,3-butadiene) and as the first among chemists, correctly explained the diene nature of its structure [5,27,28]. Information about isoprene synthesis by Ipatieff appeared, among other, in the book written by Thomas Percy Hilditch (1886-1965) – British chemist – in 1911 [29], and in 1913 in the book written by another British chemist Benjamin Dawson Porritt (1884-1940) [30].

[9] Ipatieff's daughter, Anna Vladimirovna (1894-1958) persistently fought for the restoration of the good name of her parents. In 1957, she turned to Kliment Efremovich Voroshilov (1881–1969) for posthumous rehabilitation of her father. In 1990, citizenship and membership in the USSR Academy of Sciences was posthumously restored to Vladimir N. Ipatieff [4].

The studies of catalytic processes in organic chemistry was started by Ipatieff in 1901, independently and simultaneously with French chemist Paul Sabatier (1854-1941) [1,16]. He did a lot of safe laboratory experiments using a rotating autoclave, so-called "Ipatieff bomb", which he designed to conduct studies under pressure of several hundred atmospheres. Such apparatuses, for the first time, were made in 1904 according to the drawings of Ipatieff in a private mechanical workshop by the mechanic *Mal'mstrem* (Malmstrom), and then were made at a mechanical plant in St. Petersburg, which belonged to Richard Langensiepen (1847-1920) [14].

V. N. Ipatieff used various catalysts in his experimental studies. He and his co-workers carried out many different catalytic reactions, among others, the reactions of dehydrogenation, dehydration, hydrogenation, alkylation, destructive hydrogenation, condensation, destructive alkylation, polymerization, selective demethylation, and isomerization. The examples given below relate to experimental studies carried out in 1901-1951.

Based on studies of both dehydration and dehydrogenation of alcohols, carried out in high temperatures under ordinary pressure, Ipatieff stated that depending on the material of the tube in which alcohol was decomposed, he received various products [31]. Dehydration of ethanol to ethylene was his first experimental study carried out in the laboratory of the St. Petersburg's Mikhaylovskaya Artillery Academy in 1901. In this study, he passed vapors of the ethanol through a graphite tube inserted into an iron tube at 600°C. Confirmation of obtaining ethylene in this reaction was that the resulting gas reacted with bromine to form ethylene dibromide (1,2-dibromoethane) [14]. In another study, he passed vapors of the ethanol through a glass tube containing pieces of graphite mass also at 600°C, and the ethanol quickly decomposed into ethylene and water. Propyl alcohol in the same way was dehydrated into propylene [32]. When the vapors of a primary aliphatic alcohol, for instance ethanol, passed through a platinum tube inserted into a wide iron tube, at 780°C the alcohol decomposed and the main reaction product was acetaldehyde [14]. He also found that secondary alcohols dehydrogenate in an iron tubes to ketones [33], and tertiary to olefins [14].

Vladimir N. Ipatieff discovered a new method for the conversion of ethanol to divinyl (1,3-butadiene), during which hydrogen was formed. When passing the vapors of this alcohol at high temperature and ordinary pressure over powdered aluminum as a catalyst, the following reaction take place:
$CH_3 - CH_2OH + CH_3 - CH_2OH = 2H_2O + CH_2 = CH - CH = CH_2 + H_2$ [14,34].

Using a rotating bomb, Ipatieff studied the reduction of benzene by hydrogen under high pressure. He, working with 25 grams of benzene and 2 grams of black nickel oxide (nickel (III) oxide) at 250°C under a hydrogen pressure of 180-186 atmospheres[10](18.238500 to 18.846450 MPa), hydrogenated benzene to hexahydrobenzene (cyclohexane) for one and a half hours [14,35].

The hydrogenation of the citral (3,7-dimethyloctа-2,6-dienal) was carried out by Ipatieff at 110°C in the presence of palladium. He found that under a hydrogen pressure of 110 atmospheres (11.145750 MPa), pure decanol (3,7-Dimethyl-1-octanol) could be obtained in four hours [14]. The simultaneous used of nickel oxide and alumina, in another experimental study, allowed him to obtain isocamphane ($C_{10}H_{18}$) from borneol ($C_{10}H_{17}OH$) within 10-12 hours at 215-220°C under a hydrogen pressure of 110 atmospheres (11.145750 MPa). He also mixed 30 grams of camphor ($C_{10}H_{16}O$) with 3 grams of nickel oxide and 1.5 grams of alumina. The hydrogenation of camphor into isocamphane was achieved in 24 hours at 200°C under a hydrogen pressure [14].

For the first time, V. N. Ipatieff and Finish chemist O. Rutala polymerized ethylene in the presence of dry zinc chloride as a catalyst at 275°C under pressure 70 atmospheres (7.092750 MPa). According to the gas product analysis, paraffins (61%), olefins (36%) and hydrogen (3%) were present. The results of study also showed that the liquid reaction product contained pentane and hexane, and some alkenes (hexylene, hepylene, octylene and nonylene) [14,36].

The study on the catalytic synthesis of methane from carbon and hydrogen Ipatieff carried out in the presence of catalyst consisting of nickel and alumina at 500-519°C and under hydrogen pressure of 35 to 60 atmospheres (3.546375 to 6.079500 MPa) [14,37].

For hydrogenation of anethole (1-methoxy-4-(1-prop-1-en-1-yl)benzene), Ipatieff used nickel as a catalyst. This compound was reduced to dihydroanethole (1-methoxy-4-propylbenzene) at 95°C under a hydrogen pressure of 50 atmospheres (5.066250 MPa) within 4 hours [14,38].

For the first time V. N. Ipatieff and his associates carried out alkylation of phenol in the presence of alumina. The phenol was heated with methyl alcohol and alumina in a Ipatieff rotating bomb at 440°C. It was found that at a pressure of up to 200 atmospheres (20.265000 MPa), o-cresol ($CH_3C_6H_4OH$) as a the main product of this reaction was obtained within 24 hours. Neither m-cresol nor p-cresol was found in reaction products [14,39].

[10] In the article the conversions have been made from atmospheres to MPa as a derivated unit of SI.

As the result of experimental study V. N. Ipatieff and N. Kljukvin were successful in solving the problem of destructive hydrogenation of naphthalene in a rotating autoclave. They, working with 3 grams of catalyst (50% NiO, 50% Al_2O_3) and 40-60 grams of naphthalene at 450-480° under a hydrogen pressure of 60 atmospheres (6.079500 MPa), succeeded in hydrogenating naphtalene in 25 hours. The main reaction product was hydrogen. Small amounts of methane and carbon dioxide were also obtained [14,40].

Vladimir N. Ipatieff and his associates proposed a new method for obtaining xanthene ($CH_2[C_6H_4]_2O$) in a catalytic condensation reaction. This compound was obtained by heating o-cresol ($CH_3C_6H_4OH$) and phenol (C_6H_5OH) in the presence of alumina as a catalyst at 440-450°C under the high pressure [14,41].

V. N. Ipatief and V. I. Komarewsky conducted research that enabled the destructive alkylation of benzene. They used 81.1 grams of benzene and 8 grams of aluminum chloride saturated with hydrogen chloride. The reaction proceeded in a rotating bomb at 125°C within 24 hours [14,42]. The main reaction products were ethylbenzene ($C_6H_5C_2H_5$) and diphenyl ($C_6H_5C_6H_5$). "The formation of these two compounds makes probable the following scheme of the reaction: (a) two parts of benzene combine to form [under the influence of aluminum chloride] diphenyl, liberating hydrogen; (b) a destructive hydrogenation of the benzene occurs during which benzene decomposes, and the *decomposed fragments are hydrogenated* to form ethylene; (c) ethylene *alkylates* the unchanged benzene to form ethylbenzene" [42].

For the first time polymerization of ethylene under pressure of 48.39 atmospheres (4.903325 MPa) at 330°C in the presence of 90% phosphoric acid as a catalyst was studied by V. N. Ipatieff and Herman Pines (1902-1996). Olefins, paraffins, naphthenes and aromatic hydrocarbons were found among the reaction products obtained within eight hours [43].

Studies of the catalytic dehydrogenation of gaseous of paraffins in the presence chromium oxide on alumina as a highly selective catalyst at 500-750°C have been carried out by V. N. Ipatieff and Aristid V. Grosse (1903-1985). It was found that the conversion of paraffins to the corresponding olefins proceeded with a yield of 90-95%. The ethane was converted into ethylene, the propane into propylene, and isobutane (2-methylpropane) into isobutylene (2-methylpropene). A mixture consisting of α-butylene (1-butene), cis-β-butylene (cis-2-butene) and trans-β-butylene (trans-2-butene) was obtained from n-butane [44].

The research of V. N. Ipatieff and Robert L. Burwell, Jr. (1912-2003) has led to the preparation of various ethers. As a result of the passage of an equimolar mixture of benzyl alcohol and methanol over seventy five cubic centimeters of "solid phosphoric acid" in the form of pellets (5 x 7 mm) used as a catalyst at 350°C under pressure of 50 atmospheres (5.066250 MPa), benzyl methyl ether (methoxymethylbenzene) was obtained. They also showed that "solid phosphoric acid" catalyze at 336°C under pressure of 60 atmospheres (6.079500 MPa), the reaction between methanol and ethanol. The product of this reaction was ethyl methyl ether (methoxyethane) [45].

Vladimir N. Ipatieff with Vladimir Haensel (1914-2002) developed the catalytic method of selective demethylation. This method was used to obtain triptane (2,2,3-trimethylbutane), a hydrocarbon with antiknock properties. Triptane began to be used as an aviation gasoline component. Thanks to it, the performance of aircraft engine has improved significantly [46].

The results of experimental studies conducted by Herman Pines, William A. Huntsman, and V. N. Ipatieff showed that alkylation is accompanied by isomerization. For instance, by reacting of 1.2 mole of benzene (C_6H_6) with 0.1 mole of ethylcyclopropane ($C_3H_5C_2H_5$) in the presence of 0.5 mole hydrogen fluoride as a catalyst, at 0-5°C, were obtained the mixture which consisted of about 63% of 2-phenylpentane [$CH_3CH(C_6H_5)C_3H_7$] and 37% of 3-phenylpentane [$C_2H_5CH(C_6H_5)C_2H_5$] [47]. They also showed that the product from the reaction 0.114 mole of 3-pentanol ($CH_3CH_2CHOHCH_2CH_3$) with 1.0 mole of benzene and 1.0 mole of hydrogen fluoride in the same temperature consisted of 56% 2-phenylpentane and 44% 3-phenylpentane [48].

STATEMENTS BY AMERICAN AND RUSSIAN CHEMISTS ABOUT VLADIMIR N. IPATIEFF AND HIS SCIENTIFIC RESEARCH

In 1942-2018, some chemists and historians of chemistry in both the United States and Russia have spoken very positive about Ipatieff and his scientific research. In their eyes, he was not only creator, excellent experimenter, and organizer, but also the great patriot. Below, these statements are quoted.

Frank Clifford Whitmore (1887-1947), professor at the School of Chemistry and Physics of the Pennsylvania State College said in 1942: "Russia has produced three outstanding chemists among its many great ones. These are Lomosoff, Mendeleev, and Ipatieff. Ipatieff has had a far greater influence on world chemistry than his two famous countrymen. He is a chemist who was a pioneer 50 years ago and is still pioneering today" [11].

Ward V. Evans (1880-1957), former chairman of the Department of Chemistry of Northwestern University, on the ocassion of the Ipatieff's eightieth birthday said in 1947: "OCASIONALLY a great research worker is born. Occasionally the world produces a great teacher. Occasionally a great humanitarian appears in the race. Very rarely, almost in defiance of the law of probability, are all these personalities embodied in a single individual. When to this unusual combination is added yet another, the gallantry to endure unheardof hardship and suffering and to rise above it with head unbowed and eyes bright, to carry out at 80 years some of the greatest researches of a lifetime, you have an idea of the man you meet in this Russian scientist whom we now proudly claim as a fellow American—Vladimir N. Ipatieff" [49].

Jacob Joseph Bikerman (1898-1978), head of the Adhesives Laboratory of the Massachusetts Institute of Technology (1956-1964) wrote: "If he were born in America instead of Russia, he probably would become the president of a billiondollar corporation. He emigrated to the United States when he was about 60, learned English at this age, and showed (in the Universal Oil Company) that he was more than a match for American-born rivals. … The first great success was achieved by Ipatiev relatively late because he was trained to be an army officer and, as a chemist, was a self-made man. This success was in the field of heterogeneous catalysis. Other scientists studied and utilized this technique at moderate temperatures and at the atmospheric pressure" [50].

In the 1991 book historian of chemistry Vladimir Ivanovich Kuznetsov (1915-2005) wrote, that Ipatieff was "the originator of the catalysis theory in the high temperatures and pressures, which became scientific basis of the industrial organic synthesis", and also that during the World War I, he was "the organizer of the sulfuric acid and benzene industries in Russia" [8].

The authors of the brochure commemorating the research carried out the "UOP Riverside research and development laboratory" wrote that Ipatieff "was one of only three industrial chemists to receive the prestigious Willard Gibbs Medal of the Chicago Section of the ACS since the award's inception in 1911. Because he played a leading role in the development of UOP's polymerization, alkylation, and isomerization processes, Ipatieff made a major contribution to the development of the high-octane aviation fuel that helped the Allies win World War II" [51].

In the 2017 publication Andrey G. Morachevskiy, professor of St. Petersburg Polytechnic University of Peter the Great wrote: "He laid the groundwork of the innovated heterogenic catalysis in the organic chemistry, he was an excellent experimenter and industrial production organizer. The General-Liutenant, academician, he managed the whole military-chemical industry in Russian in the difficult years of the World War I" [52].

Herman Pines, who was the "student, friend, and the executor of V. N. Ipatieff's will" said in 1967: "You, Russians, cannot even comprehend who Vladimir Ipatieff was. Every hour of his life here, in the United States, every step in his research, he dedicated it all to Russia. His limitless love for his motherland, which I have never seen in any of the emigrants, was the soil on which grew the outstanding results of his scientific work …" [53].

In 2018 publication Christopher P. Nicholas, principal scientist at Honeywell UOP wrote: "Vladimir Ipatieff contributed numerous concepts to catalysis including high pressure, dispersion of metals on supports, and the use of promoters. He also discovered many catalysts and reactions, several of which are still in use today, some 80 years later. His efforts continue to inspire the catalysis community in many ways, including through the Ipatieff Prize administered by the ACS, processes offered by industry, and the teaching of students at Northwestern University" [54].

CONCLUSION

Vladimir Nikolayevich Ipatiff was one of the eminent chemist of the first half of the XX century. He played a huge role in the development of catalysis, first in Russia and then in the United States. He was a pioneer in the study of catalytic reactions at high temperatures and pressures in organic chemistry. The results of his many experimental studies have been published in scientific journals in several countries around the world. He, as an inventor or co-inventor, acquired 174 U.S. Patents.

V. N. Ipatieff became a corresponding member of the Imperial St. Petersburg Academy of Sciences on November 29, 1914. He was elected an academician on January 9, 1916. At that time only two chemists Pavel (Paul) Ivanovich Walden (1863-1957) and Nikolay Semenovich Kurnakov (1860-1941) shared this distiction with him.

Vladimir N. Ipatieff became member of the Göttingen Academy of Sciences in 1922. In 1930, he was elected an honorary member of the *Deutsche Chemische Gesellschaft* (German Chemical Society) [10]. The Russian Institute of Science in Belgrade (former Yugoslavia) elected him an honorary member in 1938. On April 26, 1939, he became a member of the National Academy of Science of the United States of America. He was elect-

ed Doctor *honoris causa* of the universities of Munich (1927), of Strasbourg (1928), of Northwestern (1938), and of Sofia (1939) [6,13].

On the American website *Medill Reports Chicago* in the article entitled *NU symposium of honors chemist Vladimir Nikolayevich Ipatieff who helped win World War II* by Lakshmi Chandrasekaran [55] is an information about symposium devoted to Ipatieff's 150th Anniversary, which took place on September 7, 2017. It was organized by *The Center for Catalysis and Surface Science* (CCSS) and the Institute *of Sustainability and Energy* (ISEN) at Northwestern University [56]. Chandrasekaran's article also contains the photograph of Wolfgang Sachtler (1924-2017), CCSS director in 1985-1994, Robert L. Burwell, Jr., and Herman Pines, standing in the front of a big, hanging on the wall on the second floor of the catalysis building, beautiful, color Ipatieff's portrait. On his chest is visible the insignia of Commander of the Legion of Honour (*Commandeur de la Légion d'Honneur).* This is one of the highest honours of the French Republic, which the French Government awarded him in 1916 in recognition of all his work during World War I [10,57].

The Russian Physical-Chemical Society awarded Ipatieff with the Minor Butlerov Prize in 1896. The Ivanov Prize of the Imperial St. Petersburg Academy of Sciences was awarded to him in 1906; in 1920, the Major Butlerow Prize, and in 1927, the Lenin Prize, granted by the Soviet Government for his work on catalysis and high pressure. In 1928, at the Congress of Industrial Chemistry in Strasbourg, he was honored the Berthelot Medal awarded by *La Société de Chimie Industrielle* (The Industrial Chemistry Society) in Paris [10,13,17].

The High Pressure and Catalytic Laboratory at the Department of Chemistry of Northwestern University, estabilished in 1940, was named in honor of Ipatieff [58]. In the same year, he was honored with the Willard Gibbs award, which is granted to the: "eminent chemists, who through years of application and devotion, have brought to the world developments that enable everyone to live more comfortably and to understand this world better" [59]. In 1942, he was awarded with the Honor Scroll award "presented annually by the Chicago chapter of the American Institute of Chemists for distinguished service to the science and profession of chemistry" [60].

The Russian Academy of Sciences on the occasion of the 150th anniversary of Ipatieff 's birth organized two exhibitions in 2017-2018. The first exhibition on-line organized by St. Petersburg Branch of the Russian Academy of Sciences Archive besides an information about the most important events in Ipatieff's life contains photocopies of his and the members of his family personal documents [4]. The second exhibition contained his selected works, which were ranked, among other, in the following categories: general catalysis, alcohols dehydrogenation, alcohols degradation, hydrogenation, and general chemistry. Moreover, chemistry handbook written by Ipatieff in 1902-1909 were shown: *Kurs neorganicheskoy khimii* (A Course of Inorganic Chemistry, 1902), *Kurs organicheskoy khimii* (A Course of Organic Chemistry, 1903), *Rukovodstvo dlya prakticheskich zanyatiy po khimii* (A Guide for Practical Training in Chemistry, 1905), and *Kratkiy kurs khimii* (A Short Course in Chemistry, 1909). Photographic part of the exhibition is available in the Web, still. It contains among other Ipatieff's photographs made in various periods of his life and photocopies of the title pages of the books written by him [61].

The name of this remarkable Russian-American chemist is loudly heard in the chemists milieu in both United States and Russia. There are two awards associated with his name. First "Ipatieff' Prize", is sponsored by the Ipatieff Trust Fund. It is awarded by the American Chemical Society every three years, since 1947, for "the outstanding chemical experimental work in the field of catalysis or high pressure, carried out by an individual of any nationality, who is not over 40 years of age" [62]. Second prize, *Premiya imeni V. N. Ipat'yeva* (The Prize named after V. N. Ipatiev) is awarded by the Russian Academy of Sciences every three years, since 1994. Russian chemists receive this award "for outstanding work in the field of technical chemistry" [63].

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