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Historical Article

Vladimir Vasilyevich Markovnikov (1838-1904) – the eminent Russian chemist, author of one of the best known empiric rule in organic chemistry

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Abstract. This is a survey of the literature concerning the empiric rule developed by Vladimir Vasilyevich Markovnikov in 1869 and its various, unauthentic versions, which are available in the organic chemistry textbooks published in the XX and XXI centuries. This survey is supplemented with: 1) information about Markovnikov's chemical research, 2) selected facts of his life.

Keywords. V.V. Markovnikov, organic chemistry, Markovnikov's Rule, unsaturated hydrocarbons, Russia - XIX century.

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WORDING OF THE ORIGINAL MARKOVNIKOV'S RULE

In 1869-1876, Vladimir Vasilyevich Markovnikov (Fig. 1) presented the formulation of his empiric rule in a few articles published in Russia, Germany and France. This rule, known in the chemical literature as *Markovnikov's Rule*, appeared for the first time in the article entitled *Materialy Po Voprosu O Vzaimnom Vliyanii Atomov V Khimicheskikh Soyedineniyakh* (Materials on the Question of the Mutual Influence of Atoms in Chemical Compounds) in the *Uchenyye zapiski Imperatorskogo Kazanskogo universiteta* (Scientific notes of the Imperial Kazan University), that was published in 1869. Markovnikov wrote: «Если к такому пропилену будет присоединяться галоидоводородная кислота, то является вопрос: который из углеродов более способен соединяться с галоидом и который с водородом? Опыт показывает, что *галоид присоединяется к наименее гидрогенизированному углероду, т.е. к такому, который наиболее подвержен влиянию других углеродных паев*» [1,2].

The translation of the Russian text describing the original Markovnikov's rule is the following: "If a hydrohalic acid is added to such a propylene, then the question is: which carbon is more capable of combining with a halogen and which one with hydrogen? Experience shows that the *halide adds to the least hydrogenated carbon, that is, to the one most susceptible to the influence of other carbon units*".

Figure 1. Vladimir Vasilyevich Markovnikov (1838-1904) (Public domain, from reference 3).

In 1870, Markovnikov published an article entitled *Ueber die Abhängigkeit der verschiedenen Vertretbarkeit des Radicalwasserstoffs in den isomeren Buttersäuren* (On the Dependence of the Various Acceptability of the Hydrogen Chloride in the Isomeric Butyric Acids) in the journal *Justus Liebigs Annalen der Chemie*. At the end of this article he presented a German version of his rule as follows: „*...wenn ein unsymmetrisch constituirter Kohlenwasserstoff sich mit einer Haloïdwasserstoffsäure verbindet, so addirt sich das Haloïd an das weniger hydrogenisirte Kohlenstoffatom,* d. h. *zu dem Kohlenstoff, welcher sich mehr unter dem Einflusse anderer Kohlenstoffe befindet* " [4].

The translation of the German text is the following: "When a hydrocarbon with an unsymmetrical structure combines with a halogen hydracids, the halogen adds itself to the less hydrogenated carbon atom, i.e. the carbon which is more influenced by the presence of another carbon".

Markovnikov in this article presented the equations of the addition of hydroiodic acid (HJ) to: propylene (1), 2-methylpropene (2), 1-butene (3), alpha-amylene (1-pentene) (4) and reaction of the addition of hydrochloric acid (HCl) to 3-methyl-1-butene (5) as examples of the application of his rule. In these equations he showed the formulae of both substrates and products of these reactions in the form which was typical at that time. In this article semi-structural formulae were used to illustrate these reactions:

$CH_3CHCH_2 + HJ = CH_3CH(J)CH_3$; (1)
$(CH_3)_2CCH_2 + HJ = (CH_3)_2C(J)CH_3$; (2)
$C_2H_5CHCH_2 + HJ = C_2H_5CH(J)CH_3$; (3)
$C_2H_5CH_2CHCH_2 + HJ = C_2H_5CH_2CH(J)CH_3$; (4)
$(CH_3)_2CHCHCH_2 + HCl = CH_3)_2CHCH(Cl)CH_3$ [4]. (5)

In 1875, Markovnikov published his rule in French in the journal *Comptes Rendus Hebdomadaires de Séances de l'Academie de Sciences*: «En examinant la plupart des cas, suffisamment étudiés, de l'addition directe, je suis arrivé, il y a quelques années, à la conclusion suivante: *Lorsqu'à un hydrocarbure non saturé, renfermant des atomes de carbone inégalement hydrogénés, s'ajoute un acide haloïdhydrique, l'élément électronégatif se fixe sur le carbone le moins hydrogéné. ...* Cette loi générale semble être adoptée aujourd'hui par la plupart des chimistes» [5].

The English translation of the French version is: "In examining most of the sufficiently studied cases of direct addition, a few years ago I came to the following conclusion: *When to an unsaturated hydrocarbon, containing unequally hydrogenated carbon atoms, a halohydric acid is added, the electronegative element is fixed on the least hydrogenated carbon. ...* This general law seems to be adopted today by most chemists".

French language version of the original Markovnikov's rule is very similar to the Russian one, which was published by Markovnikov in the article entitled *O Zakonakh Obrazovaniya Pryamykh Soyedineniy Nepredel'nymi Organicheskimi Chastitsami* (On the Laws of the Formation of Direct Compounds by Unsaturated Organic Particles) in the journal *Zhurnal Russkogo khimicheskogo obshchestva* in 1876. Markovnikov wrote: «Разбирая большинсво случаев прямого соединения углеводородов, я пришел несколько лет тому назад к заключению, что *при соединении несимметрично построенных углеводородов с галоидоводородными кислотами галоид (электроотрицательный элемент) присоединяется к наименее гидрогенизированному углероду. ...* Это положение применяется ныне, повидимому, большинством химиков» [2,6].

Summing up, one may say that in the cited versions of the original Markovnikov's rule in three languages (Russian, German, and French) we are talking about "the addition of the halogen atom from halohydric acid to the *less hydrogenated carbon atom* of the unsymmetrical molecule of the unsaturated hydrocarbon".

David E. Lewis, professor of chemistry at the Wisconsin-Eau Claire University (U.S.A.) in his book entitled *Early Russian Chemists and Their Legacy* (2012), referring to the article which Markovnikov published in the *Comptes Rendus Hebdomadaires des Séances de l'Acdemie des Sciences* [5] stated that: "he [Markovnikov] had established a solid experimental basis for his rule based on his studies of halohydrin formation and other additions to alkene hydrocarbons" [7].

REFERENCES TO THE MARKOVNIKOV'S ORIGINAL RULE IN THE CHEMICAL LITERATURE

Analysis of the chemical literature from the years 1908 – 2019 shows that some authors referred to the original Markovnikov's rule in their publications.

In 1908, British chemist Alfred Walter Stewart (1888-1947), lecturer on the Stereochemistry at the London University College in his book entitled *Recent Advances in Organic Chemistry* explained an application of this rule emphasized that in reaction of hydrobromic acid addition to 2-methylpropene "$(CH_3)_2C=CH_2$" 2-bromo-2-methylpropane "$(CH_3)_2CBr\text{-}CH_3$" is produced and not 1-bromo-2-methylpropane "$(CH_3)_2CH\text{-}CH_2Br$" [8].

In 1922, the German chemist Richard Stoermer (1870-1940), professor of organic chemistry at the University in Rostock formulated the original Markovnikov's rule and its use in examples of two addition reactions: hydrogen iodide to propylene and hydrogen bromide to 2-methylpropene: "Bei der Addition von Halogenwasserstoff nimmt vorzugsweise das wasserstoffärmere Kohlenstoffatom eines Olefins das Halogenatom auf (In the addition of hydrogen halide, preferably, the hydrogen-poor carbon atom of an olefin absorbs the halogen atom):

$CH_2 : CH \cdot CH_3 + HJ = CH_3 \cdot CHJ \cdot CH_3$; $(CH_3)_2C : CH_2 + HBr = (CH_3)_2CBr \cdot CH_3$" [9].

Some chemists referred to the German version of the Markovnikov's rule, for instance Julius Berend Cohen (1859-1935), professor of organic chemistry at the University of Leeds, in his book entitled *Organic Chemistry for Advanced Students* published in 1919 [10], Gurnos Jones from the University College of North Staffordshire in England in his article published in the *Journal of Chemical Education* in 1961 [11], Robert C. Kerber, professor at the Department of Chemistry at the State University of New York in the article published in the *Foundations of Chemistry* in 2002 [12] and Peter Hughes from the Westminster School in London in his article published in the *Journal of Chemical Education* in 2006 [13].

Other authors, for instance the Russian chemists Irina P. Beletskaya and Valentine G. Nenajdenko, professors at the Department of Chemistry at the Lomonosov Moscow State University, presented a translation of the Russian version of Markovnikov's rule into English [14].

In the ex-Soviet Union, the organic chemist Alfred Feliksovich Plate (1906-1984) wrote about the original Markovnikov's rule in the book entitled *Kniga dlya chteniya organicheskoy khimii. Posobiiye dlya uchashchikhsya* (A Book for Reading in Organic Chemistry. Student Handbook) in the chapter devoted to Vladimir Vasilyevich Markovnikov. The book was edited by Pranas Florionovich Buckus and published in 1975 [15]. The historian of chemistry Yuri Ivanovich Soloviev (born in 1924) cited the rule in the book entitled *Istoriya khimii: Razvitiye khimii s drevneyshikh vremen do kontsa XIX v.* (History of Chemistry: The Development of Chemistry from Ancient Times to the End of the XIX Century) [16].

VARIOUS UNAUTHENTIC VERSIONS OF MARKOVNIKOV'S RULE IN THE CHEMICAL LITERATURE

The American chemist John Tierney, professor of chemistry at the Pennsylvania State University (U.S.A.), in his article entitled *Markownikoff's Rule: What Did He Say and When Did He Say It?* published in the *Journal of Chemical Education* thirty-one years ago, wrote that in 11 analyzed American organic chemistry textbooks, published between 1962 and 1987, he found three different versions of this rule [17].

Version (A) goes as follows: "When a hydrogen halide adds to an unsymmetric alkene the addition occurs such that the halogen attaches itself to the carbon atom of the alkene bearing the least number of hydrogen atoms".

The consecutive version (B)[1] is the following: "When a hydrogen halide adds to an unsymmetric alkene the addition occurs such that the halogen attaches itself to the carbon atom of the alkene bearing the greater number of carbon atoms".

The third version (C) was found by Tierney in 7 textbooks. He thinks that its wording "though not incorrect, is only obtained by inference from the original statement written in German …". The rule in version

[1] Author of this article found slightly different wording of (B) version of Markovnikov's rule in the book wrote by John McMurry entitled *Fundamentals of Organic Chemistry*: "In the addition of HX to an alkene, the H attaches to the carbon with fewer alkyl substituents and the X to the carbon with more alkyl substituents" [18].

C goes as follows: "When a hydrogen halide adds to an unsymmetric alkene the addition occurs such that the hydrogen of the hydrogen halide attaches itself to the carbon atom of the alkene bearing the most number of hydrogens".

The chemist Harold Hart (born in 1922), professor at the Michigan State University (U.S.A.), in the VIII edition of his textbook entitled *Organic Chemistry. A Short Course*, published in 1991 presented the rule in the following version*: When an unsymmetric reagent adds to unsymmetric alkene, the electropositive part of the reagent bonds to the carbon of the double bond that has the greater number of hydrogen atoms attached to it"* [19]. In the footnote related to this rule Hart stressed that "actually, Markovnikov stated the rule a little differently" and also that the wording included in his textbook "is easier to remember and apply". Then he invite the readers to read the paper written by Tierney [17] to obtain more information "on what he [Markovnikov] actually said" [19].

An analysis of the available literature shows that the Markovnikov's rule in (C) version is present also in the American textbook of the organic chemistry published in the years 2012-2015 [20,21], as well as in the Polish textbook [22], in the Russian chemical literature [23,24] and the German book [25].

INFORMATION ABOUT MARKOVNIKOV'S CHEMICAL RESEARCH

The list of works published by V. V. Markovnikov in 1860-1904 includes 318 papers. The majority of these are the articles presenting the results of his experimental works, published in *Zhurnal Russkogo khimicheskogo obshchestva* in Russia, as well as in German and French journals. Here his original articles devoted to the problems of the chemical structure of the organic compounds, chemistry of the petroleum, and alicyclic compounds [26,27] can be found.

The results of the 43 experimental research conducted by Vladimir V. Markovnikov were published in German in the following journals: 1) *Justus Liebigs Annalen der Chemie* (14 articles in 1870-1904); 2) *Journal* für Praktische Chemie (7 articles in 1892-1899); 3) *Berichte der deutschen chemischen Gesellschaft* (22 article in 1873-1902) [28,29].

A few Markovnikov's articles were published in French in *Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences* and *Bulletin de la Société chimique de Paris* [2,26].

SELECTED FACTS FROM V. V. MARKOVNIKOV'S LIFE[2]

Vladimir Vasilyevich Markovnikov was born December 10 (22) 1838 in the village of Chernoreche, near Nizhny Novogorod. After high school graduation at the Aleksandrovskii Institute in Nizhny Novogorod, he entered the Imperial University of Kazan in 1856.

Markovnikov was the first and most talented student of Aleksandr Mikhaylovich Butlerov (1828-1886). Being a third-year student, Markovnikov started participating in the chemical laboratory activities and attended Butlerov's lectures. These experiences impressed him very much and defined his future career.

In 1860, defended his *kandidat* dissertation entitled *Aldegidy i ikh otnosheniya k alkogolyam i ketonam* (Aldehydes and Their Relationship to Alcohols and Ketones). Since November 11th 1860, Markovnikov started working at the Kazan Imperial University as laboratory technician in the chemical laboratory, and later as assistant.

In 1862, Markovnikov was lecturer of inorganic and analytical chemistry at the university, because of Butlerov's illness. In 1863, he passed the master's examination. Two years later, he defended his master's dissertation entitled *Ob izomerii organicheskikh soyedineniy* (About the Isomerism of Organic Compounds). Then, he left Russia and went to Germany for a two-year *komandirovka* (official mission abroad). First, Markovnikov moved to Heidelberg and attended the lectures given by the chemist Hermann Kopp (1817-1892), the physicist Gustav Kirchoff (1824-1887), and chemist Emil Erlenmeyer (1825-1909). He worked in Erlenmeyer's laboratory. Then, he moved to the University in Berlin, where he carried out a research in Adolf von Baeyer's (1835-1917) laboratory. Finally, he left Berlin and went to Leipzig, where he settled down for a long period. At the Leipzig University he attended the lectures of the chemist Adolph Wilhelm Kolbe (1818-1884) and worked in his laboratory.

In 1867, Markovnikov's *komandirovka* was prolonged for half a year. He spent this time visiting several western chemical industries. For the same reason he attended the World Exhibition in Paris in August 1867. Once back in Russia, Markovnikov worked at Kazan Imperial University in 1867-1873. In 1868, he was one of the founders of the Russian Chemical Society.

In spring 1869, Markovnikov defended his doctoral dissertation entitled *Materialy po voprosu o vzaimnom vliyanii atomov v khimicheskikh soyedineniyakh* (Materials on the Question of the Mutual Influence of Atoms in

[2] Presented facts from Markovnikov's life were collected, basing on the following publications [7, 14, 26, 29, 30, 31, 32].

Chemical Compounds). In May 1869, he was nominated Extraordinary Professor (Associate Professor). In March 1870, he was promoted to Ordinary (Full) Professor. In 1871-1873, Markovnikov worked at the Imperial Novorossiysk University in Odessa as Professor of Chemistry; between 1873 and 1904, he was professor at the Imperial Moscow University. In 1901, Markovnikov celebrated 40 years of his research and didactic work.

In 1904, in the last days of Markovnikov's life the chemist Ivan Alexandrovich Kablukov (1857-1942) wrote "On his return from Petersburg on Christmas he felt bad and doctors forbade him to leave home. On January 13, he was better and even expected to leave home, despite doctors' prohibitions, to go to the chemical laboratory, but at six o'clock in the evening a stroke deprived him consciousness. V. V. Markovnikov died on the 29th January [11 February]" [33].

CONCLUSION

In 1869, V. V. Markovnikov designed one of the most known empirical rules in organic chemistry, named after him *Markovnikov's Rule*. The original wording of this rule in Russian, French, and German is the "addition of the *halogen atom* from the halidic acid to the *least hydrogenated carbon atom* of the unsymmetrical molecule of unsaturated hydrocarbon". It is worth stressing that actually Markovnikov's rule with such a phrase (*original Markovnikov's rule)* appears only in some textbooks and organic chemistry books, published among other in U.S.A. and Russia. A very widespread version in the chemical literature is the unoriginal version (C), called also Markovnikov's rule by the authors of organic chemistry textbooks and books and chemical dictionaries, despite the fact that its wording completely differs from the original.

Another field of interest, which brought Markovnikov fame in the world of chemistry was his research of the Caucasian petroleum. Together with the chemist Vladimir Nikolayevich Ogloblin, his laboratory assistant in the chemical laboratory at the Imperial Moscow University [34], Markovnikov wrote an article entitled *Issledovaniye Kavkazskoy Nefti* (Study of the Caucasian Petroleum), which was published in the *Zhurnal Russkogo khmicheskogo obshchestva* in 1883 [35]. In this article, Markovnikov and Ogloblin described the properties of several organic compounds isolated from the petroleum, which they named "naphtens" [cycloalkanes]. These are the following: octonaphten [cyclooctane] (C_8H_{16}), nonaphten [cyclononane] (C_9H_{18}), decanaphten [cyclodecane] ($C_{10}H_{20}$), undecanaphten [cycloundecane] ($C_{11}H_{22}$), dodecanaphten [cyclododecane] ($C_{12}H_{24}$), tetradecanaphten [cyclotetradecane] ($C_{14}H_{28}$), and pentadecanaphten [cyclopentadecane] ($C_{15}H_{30}$).

In 1895, Markovnikov described hexanaphtene [cyclohexane] (C_6H_{12}), a new naphten isolated by him from the petroleum, in the article entitled *Ueber das Vorkommen des Hexanaphtens in kaukasicher Naphta* (On the Occurrence of the Hexanaphtens in Caucasian Naphtha) published in *Berichte der deutschen chemischen Gesellschaft* [36,37]. Two years later, in the article entitled *Ueber einige neue Bestandtheile der kaukasichen Naphta* (About Some New Constituents of the Caucasian Naphta), published by the same journal, he informed the readers about the isolation of pentamethylene [cyclopentane] (C_5H_{10}) from petroleum [38].

The Russian literary historian Eufrosina Dvoichenko-Markov (1901-1980) in her article entitled *The American Philosophical Society and Early Russian-American Relations*, published in *Proceedings of the American Philosophical Society* in 1950, wrote, quoting words uttered by the Russian-American organic chemist Vladimir Nikolaevich Ipatieff (1867-1952) that Markovnikov's name "has become known to almost every American chemist working in the petroleum industry" [39,40].

On February 15, 1901, the American Philosophical Society at Philadelphia elected Markovnikov its member in recognition of his merits. On May 30, 1901, Markovnikov sent to the secretary of this Society−Arthur W. Goodspeed (1860-1943)−a letter of thanks for his election: "Sir, I beg you to transmit my profound thanks to the American Philosophical Society at Philadelphia for the honor, which was done me by the election as a Member of that Society. Accept the distinguished salutations of Your obedient servant Vl. Morcownikoff" [40]. On May 8, 1901, Markovnikov became also a member of the American Academy of Arts and Sciences [41].

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