

INTRODUCTION TO AN ENGLISH TRANSLATION OF MARKOVNIKOV'S FIRST PAPER DESCRIBING "MARKOVNIKOV'S RULE"

David E. Lewis, Department of Chemistry, University of Wisconsin-Eau Claire, Eau Claire, WI 54702-4004, USA; LewisD@uwec.edu

Translator's Preface (1)

Vladimir Vasil'evich Markovnikov (2)

The first volume of the brand new *Zhurnal Russkogo Fiziko-Khimicheskogo Obshchestva*, published in 1869, contained several key papers, including Mendeleev's first report of his periodic system of the elements (3) and Markovnikov's first publication of his observations on the formation of alkenes and the addition of unsymmetrical electrophilic reagents to unsymmetrical alkenes (4), which is the subject of this translation.

Vladimir Vasil'evich Markovnikov (1838-1904) was born to a member of the lesser nobility near Nizhny-Novgorod, and educated at Kazan University. He entered the university in 1856 as a student in economic science in the Cameral division of the Juridical faculty, and in later years—despite his position as a leader of Russian organic chemistry—he spoke proudly of the fact that he had completed his degree in *economics*. At that time, Cameral students were required to take two years of chemistry; Markovnikov had intended to satisfy this requirement by study in technology, but following the departure of the Professor of Chemical Technology, Modest Yakovlevich Kittary (1825-1880), for Moscow in 1859, he turned to the course in chemistry taught Aleksandr Mikhailovich Butlerov (1828-1886).

At this time, Butlerov had just returned from his *komandirovka* in western Europe and was cogitating

the structural theory of organic chemistry that he had heard in Paris (although he was not yet converted to the views of the structural theorists, Kekulé and Couper). The images in Figure 1 are taken from Markovnikov's lithographed version of his handwritten notes as transcribed by no fewer than three different calligraphers (5). They show that Butlerov had not yet been converted from a Type Theorist to a Structural Theorist.

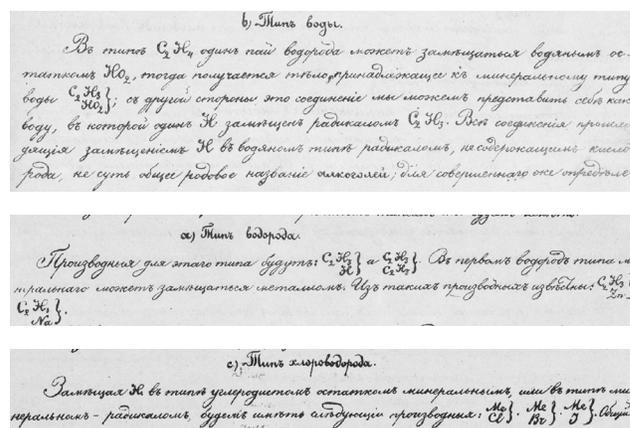


Figure 1. Excerpts from Markovnikov's notes of Butlerov's 1859-1860 course in organic chemistry (5). The headings of the excerpts are, in sequence, "Water Type," "Hydrogen Type," and "Hydrogen Chloride Type."

Butlerov's view remained unaltered when this course ended, in September, 1860. Markovnikov quickly became Butlerov's enthusiastic disciple, and wrote his disserta-

tion for the degree of *kandidat* in economic science on “Aldehydes and their relation to alcohols and ketones” (6). In it, Markovnikov uses Type theory throughout, showing that Butlerov was still a Type Theorist at the end of October, 1860 (otherwise, we would expect him to have shared his new theory with his star student). This 44-page, hand-written dissertation most closely corresponds to what would be an undergraduate honors dissertation at an American or British Commonwealth university and was used to determine if the student was ready for graduate work. It was not, from my reading, the equivalent of a modern Master’s degree as I have asserted on many occasions in the past (7).

Nevertheless, by now he was clearly committed to a career in chemistry rather than a career in economics. Immediately following his graduation with the degree of *kandidat*, Markovnikov became Butlerov’s assistant; two years later, he was assigned to teach the course in analytical chemistry. In order to enter the chemistry professoriate, the degree of *Magistr Khimii* (M. Khim.) was required; this degree was the equivalent of a modern Ph.D. In order to obtain this degree, Markovnikov needed to be admitted to the degree program in the Physical-Mathematics Faculty. However, since his *kandidat* degree was in the Juridical Faculty, he could not become a graduate student in the Physical-Mathematical Faculty. It required Butlerov’s intervention and strong recommendation for Markovnikov to be permitted to pursue the M. Khim. (just as Butlerov would later have to do for Aleksandr Mikhailovich Zaitsev). In 1863, Markovnikov had passed all the required examinations, and in 1865 he presented and successfully defended his M. Khim. dissertation, “On the Isomerism of Organic Compounds” (8).

Upon his graduation, Markovnikov was immediately promoted to Extraordinary Professor of Chemistry and shortly thereafter he was awarded a two-year *komandirovka*, which he spent mainly in Germany, in the laboratory of Hermann Kolbe. In Kolbe’s laboratory, Markovnikov was allowed much more freedom than the other *Praktikanten* because he already held an advanced degree. Here he began working on the consequences of structural theory, and he became a strong advocate for acknowledging his mentor’s (Butlerov’s) claims for credit as one of the developers of structural theory (9, 10).

In Berlin, early in his *komandirovka*, he had been asked a very simple question by Graebe: “Why is the chlorine in acetyl chloride different from the chlorine in ethyl chloride?” This set in motion his thoughts on the mutual influences of atoms in a molecule that became

the subject of his *Doktor Khimii* dissertation (11), and led to the publication of this paper in the inaugural volume of the *Zhurnal*.

The Translation

Many of the problems associated with the translation of pre-Soviet Russian into English have been addressed in the translators’ preface to our translations of Kizhner’s pioneering papers on the base-promoted decomposition of hydrazones to give hydrocarbons (12), and the reader is referred to that paper. It is worthwhile repeating the caveat that a literal (or close to literal) translation of the Russian original will result in very stilted English prose. Many Russian authors tend to write exceptionally long sentences, so it is not unusual to find that a whole paragraph may consist of a single sentence. In contrast to Markovnikov’s *M. Khim.* and *Dr. Khim.* dissertations, where the writing certainly fits this pattern, the writing in this short paper is not full of such over-long sentences. Nevertheless, where necessary, I have permitted myself the small luxury of breaking overly-long Russian sentences into shorter English ones. In making these stylistic changes, I have sought to preserve the author’s meaning, while making the English readable. It is my hope that I have accomplished this goal in the translation that follows.

Markovnikov’s Russian is not always straightforward and free of idioms, and his quest for clarity of ideas sometimes leads to exactly the opposite outcome, often making it necessary to deduce the meaning of the archaic idioms and terms from the chemistry before translating the paper into good idiomatic English. The single reference in the original paper (to Markovnikov’s *Dr. Khim.* dissertation, 11) has been relocated to the end of the translation in conformity with *Bulletin* practice.

As with any translation, there are places where a literal translation of the original into English leads to ambiguity. In those places, I have chosen to preserve, as best as I could, Markovnikov’s intended meaning, rather than adhering slavishly to a verbatim translation. I trust that the reader will forgive these minor adjustments.

References and Notes

1. The transliteration from the Cyrillic alphabet presents a recurring problem for western writers, translators and publishers referring to Russian authors and articles. The exact transliteration used will depend on the writer, and on the language into which the article or name is translated/transliterated. In this paper, I have adhered to

- my previous practice of transliterating the Cyrillic using the BGN/PCGN romanization system for Russian as the most intuitive for English speakers. In this system, the name of the subject chemist becomes Markovnikov. In German, Markovnikov's name is transliterated as "Markownikoff," and this spelling was also seconded to English until the last quarter of the twentieth century. In French papers, Markovnikov's name was transliterated as "Markownikoff."
- Obituaries of Markovnikov are available in several languages. (a) Russian: I. A. Kablukov, "Vladimir Vasil'evich Markovnikov (biograficheskaya svedeniya i kratkii ocherk nauchnykh rabot) [Vladimir Vasil'evich Markovnikov (biographical information and a brief essay on his scientific work)]," *Zh. Russ. Fiz.-Khim. O-va.*, **1905**, *37*, 247-303. (b) German: H. Decker, "Wladimir Wasiliewitsch Markownikoff," *Ber. dtsh. chem. Ges.*, **1905**, *38*, 4249-4259. (c) English: E. J. Mills, "Wladimir Wasiljewitsch Markownikoff," *J. Chem. Soc.*, **1905**, *87*, 597-600. For other English-language biographies, see (d) H. M. Leicester, "Vladimir Vasil'evich Markovnikov," *J. Chem. Educ.*, **1941**, *18*, 53-57. (e) G. V. Bykov, "Markovnikov, Vladimir Vasilevich," *Complete Dictionary of Scientific Biography*, 2008. (f) D. E. Lewis, *Early Russian Organic Chemists and Their Legacy*, Springer Verlag, Heidelberg, 2012, pp 64-69.
 - D. Mendeleev, "Sootnoshenie svoistv s atomnym vesom elementov [The correlation of properties with the atomic weights of the elements]," *Zh. Russ. Fiz.-Khim. O-va.*, **1869**, *1*, 60-77.
 - V. Markovnikov, "K voprosu o vzaimnom vliyanii atomov v khimicheskikh soedineniyakh [On the question of the mutual influence of atoms in chemical compounds]," *Zh. Russ. Fiz.-Khim. O-va.*, **1869**, *1*, 242-247.
 - This is clear from the lecture notes of his course in organic chemistry taken by Markovnikov during the 1859-1860 academic year. *Organicheskaya khimiya, sostavlenaya po lektsiyam ord. prof. A. M. Butlerova stud. VI. Morkovnikovym [Organic chemistry compiled from the lectures of Ord. Prof. A. M. Butlerov by student V. Morkovnikov]*, Lit. A. Petersen at Kazan, 1859-1860 (166 pp). (Department of manuscripts and rare books of the N. I. Lobachevskii Science Library, Kazan Federal University.) Throughout these notes, Butlerov is a firm Type Theorist. The notes were published by Markovnikov at his own expense.
 - V. Markovnikov, "O al'degidakh i ikh otnosheniyakh k alkogol'am i ketonam [On aldehydes and their relationship to alcohols and ketones], Kand. Diss., Kazan, 1860.
 - For example, Ref. 2(f), p 34.
 - V. Markovnikov, "Ob izomerii organicheskikh soedinenii [On the isomerism of organic compounds]," M. Khim. Diss., Kazan, 1865.
 - H. M. Leicester, "Kekulé, Butlerov, Markovnikov: Controversies on Chemical Structure from 1860 to 1868," in R. F. Gold, Ed., *Kekulé Centennial, Adv. Chem.*, **1966**, *66*, 13-23.
 - D. E. Lewis, "Static to Dynamic: The Transformation from Chemical Structure to Reaction Regiochemistry," *Angew. Chem. Int. Ed.*, **2018**, *57*, accepted for publication.
 - V. Markovnikov, "Material'ny po voprosu o vzaimnom bliyanii atomov v khimicheskikh soedineniyakh [Materials on the mutual influence of atoms in chemical compounds]," Dr. Khim. Diss., Kazan, 1869, p 86. By convention, this was also published under the same title as a contribution to *Scientific Notes of Kazan University*, 1869.
 - V. Suntsov, D. E. Lewis, "Introduction to an English translation of Kizhner's pioneering papers on deoxygenation," *Bull. Hist. Chem.* **2015**, *40*(2), 61-64.

About the Author

David E. Lewis, a former Chair of HIST, is Professor of Chemistry at the University of Wisconsin-Eau Claire. He is a synthetic organic chemist with interests in asymmetric synthesis and the synthesis of new probes for fluorescence microscopy, and is the author of *Advanced Organic Chemistry* (Oxford University Press, 2016). He is also a historian of organic chemistry with particular emphasis on the development of organic chemistry in Russia. His works in English have been translated into Russian, and he is the author of *Early Russian Organic Chemists and Their Legacy* (SpringerBriefs in the History of Chemistry, 2012). He is the recipient of the 2018 HIST award.