INTRODUCTION TO AN ENGLISH TRANSLATION (ABRIDGED) OF KIZHNER'S PIONEERING PAPERS ON DEOXYGENATION

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Translators' Preface (1)

Just over a century ago, in 1911, the two papers that are the subject of this abridged translation (2) appeared in the *Zhurnal Russkago Fiziko-Khimicheskago Obshchestva.* The first describes the reactions of the hydrazones (generically called alkylidenehydrazines in the papers) from saturated ketones with potassium hydroxide to give the corresponding saturated hydrocarbon. The second describes the reaction of the hydrazones of aldehydes and unsaturated ketones with potassium hydroxide to give hydrocarbons. These two papers established the basic requirements for the reduction of carbonyl compounds through base-promoted decomposition of the hydrazones. Eighteen months later, Ludwig Wolff published his version of the same reaction, by heating semicarbazones with sodium ethoxide to give the corresponding hydrocarbons (3).

Nikolai Matveevich Kizhner (1867-1935) led one of the most eventful lives of any organic chemist of Russia during the late Imperial and early Soviet periods of Russian history. A student of Markovnikov at Moscow, he was recruited to Tomsk, in Siberia, as the inaugural Professor of Organic Chemistry at the Imperial Tomsk Technological Institute (now Tomsk Polytechnic University) immediately following his graduation into the Dr. Chem. degree. The most comprehensive biographies of Kizhner (4) are almost all in Russian; materials in English include a brief biographical sketch (4d), a somewhat longer biography (4e), and a paper analyzing Kizhner's career in Tomsk (4f).

Kizhner worked at Tomsk for the first fourteen years of the twentieth century, building a first-rate laboratory, and discovering the two reactions that carry his name. After just three years at Tomsk, he fell victim to "gangrene of the limbs," which eventually necessitated the amputation of both legs below the knee. He discovered both of the reactions for which he is known after he had lost both lower legs and was confined to a wheelchair. His progressive political activities proved to be dangerous in a conservative city like Tomsk; he was exiled from the city and the steppes region of Siberia early in 1906, by orders of the Governor-General of western Siberia. His reinstatement over a year later on the orders of the Minister of Education did not meet with universal approval, and in 1912 he resigned his position, albeit under duress.

His return to Moscow, where he spent the rest of his life, began in 1914 with an appointment to the Shanyavskii People's University. This was quickly followed by the October Revolution and the establishment of the Soviet state in 1917, with the accompanying seismic shift in research priorities from basic to applied research topics. For Kizhner, this meant his transfer in 1919 to become the Director of the Aniline Trust Institute (a relatively thankless and monotonous task), where he built the Soviet dye industry, eventually becoming an Honorary Member of the Soviet Academy of Sciences. Like many Russian organic chemists at the time, his creativity and productivity was curtailed during the Soviet era, as a result of his efforts becoming focused on industrial problems instead of basic scientific questions to meet the mandates of the new Soviet economic system.

Nevertheless, he continued to carry out original research, in addition to studying the problems in applied chemistry demanded by the Soviet economic plan.

The historical importance of these papers, neither of which has ever appeared in English, lies in their report of an unprecedented reaction, for which Ludwig Wolff initially received the accolades, even though his publication (3) appeared some eighteen months later. Because a small minority of native speakers of western European languages can read Russian, these papers have not been as accessible to readers as those in French or German. The two papers also provide excellent examples of the practice of organic synthesis in early twentieth-century Russia by a superb (and prolific) practitioner of the art.

Kizhner was a meticulous experimenter, so his work provides a window into the practice of organic synthesis in the era before chromatography and modern spectroscopy. These two papers are especially instructive in how structural information was gleaned from measurements of physical constants. Combustion analysis for carbon and hydrogen, and the Dumas method for determining nitrogen (5), were the cornerstones of characterization of new compounds. In the absence of chromatography, mixtures were separated by fractional crystallization for solids, and by both fractional distillation and by steam distillation for liquids. All boiling points were reported using calibrated thermometers, and with the pressure specified, thus allowing them to be corrected to normal boiling points. The refractive index and density of compounds were important parameters of molecular structure and composition by virtue of their combination into the molecular refractivity (*A*, but *R* was used by Kizhner) of the compound. This fascinating constant was much used by Kizhner in his work. It is a measure of the total polarizability of a mole of the substance. The definition currently used is

$$R = \frac{\left(n^2 - 1\right)}{\left(n^2 + 2\right)} \frac{M}{\rho};$$

it has the advantage that it is almost independent of the density, temperature and aggregation state of the compound, and that it can be predicted on the basis of simple addition of the of contributions from bonds, atoms or groups (CH, CH_2, CH_3, CO, etc.) within the molecule. The value may also be approximated by

$$A = \frac{M}{\rho} \frac{n^2 - 1}{3}$$

(6). The usefulness of this constant lay in the fact that the value of the molar refractivity could be calculated, and that measured values that diverged significantly from the calculated values were suspect, and could be used as evidence that a proposed structure was wrong.

The Translations

Russian presents an interesting challenge to the translator in several ways. There is, of course, the difference in alphabet: Russian uses the Cyrillic alphabet. This difference is somewhat exacerbated because the papers translated here were written before the Russian Revolution of 1917. In 1918, four letters of the alphabet that occur in the original documents (Table 1) were eliminated from Russian orthography during the period when the spelling of Russian was simplified and consolidated; these letters were eliminated due to their compete homophony with those that were retained.

Table 1. Letters eliminated from the pre-Revolutionary Russian alphabet in 1918

Letters eliminated in 1918	Modern Russian equivalents
І і	И и
Ѳ ѳ	Ф ф
Ѣ ѣ	Е е
Ѵ ѵ	И и

In addition, other spelling simplifications were instituted at the same time for much the same reason: complete hompohony with existing letter combinations. Thus, words ending in “аго” before 1918 now carry the ending “-ого” instead (the pronunciation of both is identical); likewise, the consonantal combination, “зс” was replaced by the combination “сс,” as illustrated in the words изслѣдованiе and исследование (investigation)—again, the pronunciation of both spellings is actually identical.

The next major complication for the translator is that the verb “to be” is almost never used in the present tense, which means that many sentences have no explicit main verb. Moreover, there are neither direct nor indirect articles in Russian, which means that it is the job of the translator to supply them as appropriate. The next, and perhaps most significant, challenge to the translator is the fact that since all words except prepositions are either declined or conjugated, word order is of relatively less importance in the sentence. In some ways, this makes translating Russian rather like translating Latin: the endings of the words specify their function in the sentence, so the exact order of words in the sentence has less impact. But, at the same time, word order *does* matter: it is often found that the most important idea in the sentence comes either at the beginning of the sentence, or at the end; how this emphasis is handled in the English translation is frequently one of the most difficult jobs for the translator.

As with any translation, a literal (or close to literal) translation of the original would result in very stilted English prose. In part, this comes from the propensity of Russian authors to write exceptionally long sentences. In fact, it is not unusual to find that a whole paragraph may consist of a single sentence—Kizhner's writing certainly fits this pattern. This situation is clearly untenable in English, so we have permitted ourselves the small luxury of breaking overly-long Russian sentences into smaller English ones. There are also a number of paragraphs in these papers that are composed of single, short sentences, where the ideas are so closely connected that translating them as separate paragraphs in English is effectively ungrammatical. These sentences we have consolidated into single paragraphs, as would be required by good English prose. In making these stylistic changes, we have sought to preserve the author's meaning, while making the English readable. We hope that we have accomplished this goal in the translations that follow.

Fortunately, Kizhner's Russian is fairly straightforward and free of idioms, making the two papers relatively easy to read and translate into good idiomatic English. As an added bonus for the translator, at least, the archaic names for some compounds add an interesting patina to the first translations of the original documents (for example, potassium ferricyanide is the "bloody red salt," and potassium permanganate is "chameleon"). In this translation, archaic and European usages have been changed to modern American usage (e.g. 21°,48 is rendered as 21.48°), but Kizhner's characterization of the hydrazones as alkylidenehydrazines has been retained. The name, "camphane" has also been retained in place of the more modern "bornane."

The references and notes have been re-numbered sequentially, and gathered at the end of the translations in conformity with *Bulletin* practice; they have been cast in their modern forms, but the original version of each citation has been preserved as well. The reproduction of the original drawings directly from the original papers by scanning or other methods gave poor results, and therefore the original drawings have been re-drawn using modern drawing programs, while preserving an appearance as close to the original as possible.

As with any translation, there are places where a literal translation of the original into English leads to ambiguity. In those places, we have chosen to preserve, as best we could, Kizhner's intended meaning, rather than adhering slavishly to a verbatim translation. This translation is the work of a native speaker of Russian, Mr. Suntsov, who is a recent graduate with a B.S. in biology and chemistry, while he was an undergraduate student at UW-Eau Claire. He prepared a relatively modern translation of Kizhner's original papers, and Dr. Lewis, who is a native English speaker, edited the translation to restore some of the chemical subtleties that would not be common knowledge to an undergraduate student in biology. Any deficiencies in this translation should be attributed to Dr. Lewis.

References and Notes

1. 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, we have adhered to our 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 Kizhner.
2. We have availed ourselves of the opportunity to place the complete text of both papers in Supplemental material accompanying the translations. This has allowed us to minimize the amount of repetitive characterization data in the experiments, while retaining the narrative of the experiments. For the Supplemental material, go to the journal's website, www.scs.uiuc.edu/~mainzv/HIST/bulletin/index.php.
3. L. Wolff, "Methode zum Ersatz des Sauerstoffatoms der Ketone und Aldehyde durch Wasserstoff," *Justus Liebigs Ann. Chem.*, **1912**, *394*, 86-108.
4. There are relatively few biographies of Kizhner available, and almost all are in Russian. Most are focused on his scientific accomplishments and contain relatively little personal information: (a) S. S. Nametkin, *N. M. Kizhner. Issledovaniya v Oblasti Organicheskoi Khimii [N. M. Kizhner. Investigations in the Field of Organic Chemistry]*, Akad. Nauk SSSR, Moscow, 1937. (b) T. V. Boratova and E. A. Zaitseva, "Nikolai Matveevich Kizhner," *Khimiya*, **1996**, *39*, 2. For a biographical sketch

containing more personal details during his Tomsk period, see: (c) V. D. Yushkovskii, "IV. Iz istorii Tomskogo Politekhnicheskogo Universiteta. Protivostoyanie Tomsk v sud'be professora Kizhnera [From the history of Tomsk Polytechnic University. Confrontation in the fate of Professor Kizhner at Tomsk]," *Izv. Tomskogo Pol-ka. Uni-ta.,* **2002**, *305*, 208-221. (d) D. E. Lewis, *Early Russian Organic Chemists and Their Legacy*, Springer, Heidelberg, 2012, pp 105-106. (e) D. E. Lewis, "Disability, Despotism, Deoxygenation—From Exile to Academy Member: Nikolai Matveevich Kizhner (1867-1935)," *Angew. Chem. Int. Ed.*, **2013**, *52*, 11704-11712. (f) V. Suntsov and D. E. Lewis, "A Century of Base-promoted Decomposition of Hydrazones: the Early Career of Nikolai Metveevich Kizhner (1867-1935)," *Bull. Hist. Chem.*, **2014**, *39*, 43-52.

5. A more modern variant involved replacing the oxygen gas with a mixture of copper oxide and calcium carbonate and lowering the oxidation temperature to 550°C to slow down the combustion process and thus avoid loss of volatile materials and nitrogen: F. Shea and C. E. Watts, "Dumas Method for Organic Nitrogen," *Ind. Eng. Chem. Anal. Ed.*, **1939**, *11*, 333-334.

6. M. Born and E. Wolf, *Principles of Optics*, 4th ed., Pergamon Press, Oxford, 1970, pp 88-90.

About the Authors

Vladislav Suntsov was born in Russia and moved to the United States in 2007. He graduated from the University of Wisconsin-Eau Claire in May 2013, with a major in biology and a minor in chemistry. He carried out research in organic synthesis and the history of chemistry with Dr. David E. Lewis during his senior year. He is currently a medical student at Arizona College of Osteopathic Medicine. He is beginning his clinical studies at the Chicago campus.

David E. Lewis is Professor of Chemistry at the University of Wisconsin-Eau Claire and a former Chair of HIST. A frequent contributor to the *Bulletin*, he is most recently author of *Advanced Organic Chemistry* (Oxford University Press, 2016) and a forthcoming Russian translation of his collected papers in the history of chemistry (Kazan University Press).

PRIMARY DOCUMENTS

25. THE CATALYTIC DECOMPOSITION OF ALKYLIDENEHYDRAZINES AS A METHOD FOR THE PREPARATION OF HYDROCARBONS (ABRIDGED)

N. Kizhner
Zhurnal Russkago Fiziko-Khimicheskago Obshchestva, **1911**, *43*, 582-595.
Translated by Vladislav Suntsov and David E. Lewis

Supplemental Material

Introduction

The oxidation of primary hydrazines of the aliphatic and cyclic series, our studies have shown, yields the same products as oxidation of primary aromatic hydrazines. Just as in the last case, the identity of the oxidation products depends on the conditions under which the oxidation takes place.

During oxidation in an alkaline medium, the hydrazine group is substituted by hydrogen; the reaction proceeds so smoothly that it can be used as a method for producing hydrocarbons. During oxidation in an