

## Chapter 2

### Beginnings

#### 2.1 Introduction

At the start of the twentieth century, organic chemistry was not yet 75 years old as a separate and legitimate sub-discipline of the science. Considerable progress had been made in these first seven decades, and the stage was set for the dramatic advances in the science to come in the following century. Most practicing organic chemists are familiar with many of the great German, French and English organic chemists whose work helped the fledgling discipline grow, but few are familiar with the role that Russian organic chemists of the nineteenth and early twentieth century played in the development of the science. And this is in spite of the fact that many of the named rules and reactions that one studies in the first course in organic chemistry are, in fact, of Russian origin. It is the intent of this book to help rectify that deficiency.

#### 2.2 The Early History of Organic Chemistry

As a separate discipline, most organic chemists trace the origins of their science as a separate sub-discipline of chemistry to the serendipitous synthesis of urea by Friedrich Wöhler (1800–1882), reported in 1828 [1]. This had not been the first synthesis of urea, which had actually been accomplished by John Davy (1790–1868), in 1811 [2], and by Wöhler himself in 1824 [3], but Wöhler did something that Davy did not—he recognized that he had *not* prepared the ammonium cyanate he was trying to make. After four years of careful work, he succeeded in identifying the water-soluble non-electrolyte that he had prepared as urea.

Friedrich Wöhler (1800–1882) had entered university at Heidelberg, where he underwent the training required to become an obstetrician. His heart, however, had always belonged to chemistry, and on the advice of Leopold Gmelin (1788–1853),

he forsook medicine and pursued a chemical career instead, moving to Sweden to study with the great Swedish chemist, Jöns Jacob Berzelius (1779–1848). It was in Berzelius' laboratory that he began the study of cyanates that would end with his synthesis of urea. At heart, however, Wöhler remained an inorganic chemist, despite his lifelong friendship and collaboration with Justus Liebig (1803–1873), whom he had met as a young man. Among his accomplishments are the isolation of aluminum, beryllium, and yttrium in metallic form.



Friedrich Wöhler (1800-1882)



Jöns Jacob Berzelius (1779-1848)

Many introductory textbooks of organic chemistry imply that this synthesis of urea—as Wöhler told his mentor, Berzelius, “without the need for a kidney”—spelled the end of vital force theory, only just formalized by Jöns Jacob Berzelius in the second decade of the nineteenth century [4]. Of course, this is not the case. Chemists, like other scientists, are reluctant to abandon the old, familiar theories that form the framework of their science, preferring to modify them until new experimental evidence finally makes the theory totally untenable. Urea, for example, could be argued as being an excretion product, and therefore devoid of its vital force. Thus, it took another three decades, the synthesis of acetic acid from its elements by Hermann Kolbe (1818–1884) in 1845 [5] and the publication of Marcelin Berthelot’s *Chimie organique fondée sur la Synthèse* in 1860 [6] before vital force theory was finally consigned to the scrapheap of organic chemistry. Kolbe’s synthesis was the first in the modern meaning of the language: In the reaction sequence he used, acetic acid was prepared from elemental carbon, sulfur, chlorine, and water, by a carefully designed sequence of reactions. More importantly, none of the starting materials in this sequence was ever associated with having a vital force.

The rapidity with which vital force theory had attracted adherents is partly due to its first major proponent. Jacob Berzelius was, at the time, the most influential chemist in Europe: if he accepted an idea, it was accepted universally, if he did not, it was certain to be consigned to obscurity. Some evidence of his impact can be gauged even today: the terms, catalysis, polymer, allotrope, halogen, and protein, for example, were all suggested by Berzelius. It helped, of course, that he had been responsible (in part, at least) for the training of many of Europe’s leading young chemists. Following his graduation from the Gymnasium, Berzelius studied medicine at the University of Uppsala, graduating with his M.D. in 1804. However, he soon turned his efforts to chemistry. He was one of the first to embrace Dalton’s atomic theory, and spent a considerable part of his early professional life to gaining evidence to support the Law of Definite Proportions; in the course of this work, he developed the first accurate table of atomic weights. He also developed the modern chemist’s short-hand for writing formulas, replacing John Dalton’s pictograms by the modern one- or two-letter symbols for the elements. From his researches with the electricity, he developed the theory that atoms formed certain stable groupings, which he termed, “radicles,” that behaved as a single unit in chemical reactions. He discovered selenium (1818), silicon (1824) and thorium (1829). On the occasion of his marriage, in 1835, Berzelius was created baron by King Charles XIV of Sweden.

## 2.3 The Western European Schools

The three decades following Wöhler’s serendipitous discovery of the conversion of ammonium cyanate to urea were dominated by contributions from France and, more especially, Germany. The demise of vital force theory coincided to some degree with the rise of the great German and French schools under Liebig, Wöhler, Kolbe, Robert Bunsen (1811–1899), and Emil Erlenmeyer (1825–1909) in Germany, and Adolphe

Wurtz (1817–1884) in Paris. Somewhat later, the English schools established by August Wilhelm von Hofmann (1818–1892) and Alexander William Williamson (1824–1904) rose to a level of prominence to join their continental counterparts. During this period, the concepts of radicals, types, and substitution all came into their own, until they were supplanted in 1858 by the structural theory of organic chemistry [7]. During this time period, progress in organic chemistry was hampered by the lack of a uniform set of atomic weights, with many chemists rigidly adhering to the equivalent weights of elements ( $C = 6$ ,  $O = 8$ ). This practice led to the necessity of using “double atoms,” often written with a barred symbol, in order to write acceptable formulae for organic compounds. The values for the atomic weights of the elements were finally settled by the Italian chemist, Stanislao Cannizzaro (1826–1910), at the Karlsruhe conference of 1860; the preceding decades had seen a gradual separation of meaning for the terms, “molecule,” and “atom.” The concept of valence, which was critical for the development of the structural theory of organic chemistry, was proposed by English chemist, (later Sir) Edward Frankland (1825–1899), in 1852, following his studies with the dialkylzincs.

The underpinning of each of these theories was due to observations by a series of organic chemists. The fruitful collaboration between Liebig and Wöhler resulted in the seminal study of benzoyl compounds that led to the concept of the polyatomic radical [8]. Liebig further clarified his definition of a radical in 1837, where he stated [9]:

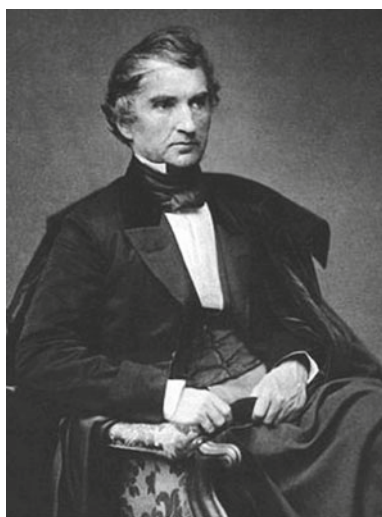
We call cyanogen a radical (1) because it is a non-varying constituent in a series of compounds, (2) because in these latter it can be replaced by other simple substances, and (3) because in its compounds with a simple substance, the latter can be turned out and replaced by equivalents of other simple substances.



Adolph Wilhelm Hermann Kolbe (1818-1884)



Sir Edward Frankland (1825-1899)



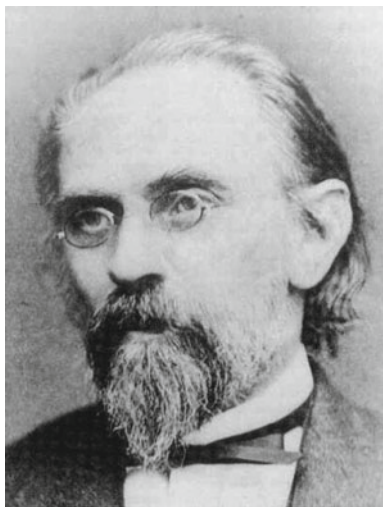
Justus von Liebig (1803-1873)



Charles Adolphe Wurtz (1817-1884)



Robert Wilhelm Eberhard Bunsen  
(1811-1899)



Richard August Carl Emil Erlenmeyer  
(1825-1909)



August Wilhelm von Hofmann  
(1818-1892)



Alexander William Williamson  
(1824-1904)

## 2.4 The Origins of Russian Science

The year 1725 marks a watershed in the development of science in Russia. In that year, Peter the Great established the Russian Academy of Sciences, and appointed some of the most distinguished western European scientists as the first Academicians. For the next seventeen years, until 1742, all appointments to the Academy were from western Europe, but in 1742 that situation changed with the appointment of Mikhail Vasil'evich Lomonosov (Михаил Васильевич Ломоносов, 1711–1765) as an Adjutant Member of the Academy. Lomonosov was elected a Full Member of the Academy three years later.

### 2.4.1 *Lomonosov and the Early Academy of Sciences*

A true renaissance man and an obvious genius, Lomonosov not only contributed to the development of science in Russia, but he made major contributions to Russian language and poetry. With his patron, the Count Ivan Ivanovich Shuvalov (Иван Иванович Шувалов, 1727–1797),<sup>1</sup> he founded Moscow University (now Lomonosov Moscow State University).

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<sup>1</sup> Shuvalov was a leader of the enlightenment in Russia following the death of Peter the Great. A favorite (and lover) of Empress Elizaveta Petrovna (r. 1741–1762), he was the first Russian Minister of Education, and was instrumental in establishing Moscow University, of which he became the first Curator. He was a strong patron of the arts, and Russia's first theater and its first Academy of Arts were established at his initiative; he served as President of the Academy of Arts from 1857–1862. The Gymnasias at St. Petersburg and Kazan' were also the results of his efforts.



In many ways, Lomonosov was a man ahead of his time. He was a courtier, a poet, and a scientist of the first rank [10]. Three decades before Lavoisier wrote his treatise against phlogiston [11], Lomonosov came to the conclusion that the theory of phlogiston was incorrect, and showed, in an unpublished memoir in 1756, that the oxidation of a metal in a hermetically sealed container leads to no change in mass [12]. In 1673, Robert Boyle had carried out the same experiment, calcining lead in a sealed retort. However, he had opened the vessel in which the metal was fired before weighing it, and found that the weight of the calcination product exceeded the weight of the original metal. From this observation, he concluded that “corpuscles of fire” had passed through the glass of the retort and were absorbed (fixed) by the metal [13]. Lomonosov’s observations that there was, in fact, no increase in weight until air was admitted to the vessel, led to his proposal of a form of the Law of Conservation of Matter [14]:

Every change that takes place in nature occurs in such a way that if something is added to something else, the same is subtracted from another body. Thus matter added to one body is lost by another. The number of hours I sleep is subtracted from the time I am awake, and so on. Since this is a universal law of nature, it also governs the rules of motion: a body which jolts another body to move loses as much of its motion as it imparts to the one it started moving.



Михаил Васильевич Ломоносов  
(1727-1797)  
(Mikhail Vasil'evich Lomonosov)

During the harsh winter of 1759, he and Academician I. A. Braun were the first to observe the freezing of mercury and to describe the properties of the solid metal. Lomonosov made contributions to the theory of heat (which he believed to be associated with motion); as a result of these studies, he promulgated his “universal

law,” a law of conservation of matter and energy [15], and the wave theory of light, and he first alluded to the principle that would later be known as the conservation of matter.

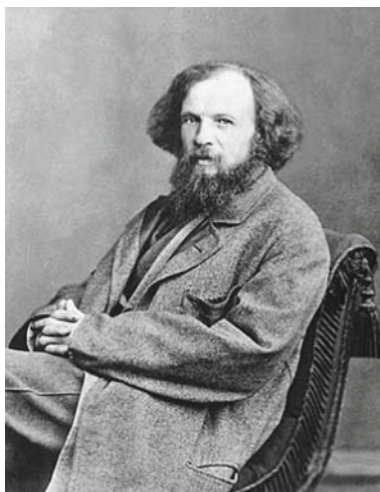
The rise of chemistry in Russia, and of organic chemistry later, required an infrastructure that was not present in 1725, when Peter the Great founded the Academy of Sciences in St. Petersburg. Due to the lack of qualified Russians, Peter populated his new Academy with eminent foreign scientists. Over the next quarter century, much of the progress in chemistry in Russia was due to an influx of (especially German) chemists from abroad, as Peter’s successors opened Russia to foreign scientists. However, by the middle of the century, that had begun to change. By that time, Lomonosov, the first Russian Academician, had risen to a position of some power in the Academy, and he was constantly at loggerheads with the leaders of the German faction in the Academy, who saw his rise as a threat to their continued dominance of the Academy.

### ***2.4.2 Russification of Russian Chemistry***

In the mid 1830s, there was a general movement towards nationalism throughout Europe, and Russia was no exception to this trend. The nationalist movement in Russia was embraced by Tsar Nicholas I, whose reign had begun in 1825 with what is known as the Decembrist revolt. This failed revolt had the long-term effect that Nicholas and his advisors had a distrust of foreigners, whom they suspected of planning to foment revolution (unreasonable, perhaps, but not baseless, given the political turmoil in western Europe at the time). Consequently, around 1835, a movement towards Russification of the universities in Russia began in earnest. As part of this process, severe limits were placed on any activity that might be described as “freethinking,” and there was an attempt to forestall the entry of foreign (read, “revolutionary”) educators into Russia. However, Nicholas’ attempt to promote Russification by establishing a purely Russian “Professional Institute” failed to meet the need for qualified teachers. This meant that Russian students still needed to go abroad to western Europe to complete their technical education; students abroad—especially at progressive institutions such as Giessen—were closely monitored by the Tsar’s secret police.

Up to this time, Chemistry Departments had been staffed by a preponderance of foreign (usually German) Professors, partly because of a lack of suitably qualified Russian candidates, but also partly because of a perceived inferiority in those Russian candidates. As the Russification process gained momentum, more and more well-trained young Russian scientists began to be appointed to Chairs of Chemistry at Russian universities, and science began to lose its “foreign” trappings. But one should not infer from this that Russification proceeded smoothly or uniformly. It did not. In fact, the Academy of Science remained solidly in foreign hands, and responded to Russification only slowly (much more slowly than the universities), so that the most prestigious positions were still occupied by non-

Russians. Of course, this situation could not last, and as the nineteenth century progressed, a gradual split appeared in the Russian Academy of Sciences, with members in the “Russian” party, and other members in the “German” party. This split came to a head in 1880, when Dmitrii Ivanovich Mendeleev (Дмитрий Иванович Менделеев, 1834–1907) was denied the chair in technology of the Academy of Sciences in St. Petersburg by a single vote [16]. Two years later, the position went to Fyodor Fyodorovich Beil’shtein (Фёдор Фёдорович Бейльштейн, Friedrich Konrad Beilstein, 1838–1906) who was viewed by the Russian party as a German, despite having been born in St. Petersburg, and having taken the unusual step of being naturalized a Russian citizen [17]. Nevertheless, by the turn of the twentieth century, chemistry in Russia was truly Russian, with that generation of organic chemists being able to point to significant contributions by earlier generations of their countrymen.



Дмитрий Иванович Менделеев (1834–1907)  
(Dmitrii Ivanovich Mendeleev)



Фёдор Фёдорович Бейльштейн (1838–1906)  
(Friedrich Konrad [Fyodr Fyodorovich] Beilstein)

One of the major problems that one encounters when studying the history of organic chemistry in Russia comes from the politicization of science and the history of science during the Soviet era. One particularly illuminating example of this concerns the structural theory of organic chemistry, and the part played in its development by Aleksandr Mikhailovich Butlerov (Александр Михайлович Бутлеров, 1828–1886). In 1861, Butlerov had made a presentation at the Chemistry Section of the 36th Congress of German Physicians and Scientists. His presentation “Einiges über die chemische Structur der Körper,” was published in the *Zeitschrift für Chemie und Pharmacie* [18]. In that paper, Butlerov introduced the term, “chemical structure,” and made the point that each compound had one, and only one, structure.

In the west, Butlerov’s contributions were largely overlooked until the last quarter of the twentieth century. In the Soviet Union, however, his contributions were exaggerated to the point that he was, at times, viewed as the founder of the science of organic chemistry. His contributions were most blatantly politicized during the controversy about the theory of resonance in the Soviet Union in the early 1950s, when what should have been a scientific argument degenerated from science into what amounted to jingoism. As described by Hargittai [19]:

The critics of the theory of resonance contrasted Butlerov’s true Russian values with the cosmopolitan views of those who had bowed slavishly to Western values, etc. The proponents of the theory of resonance had to exercise humiliating self-criticism and lost their jobs [9].<sup>2</sup> The minutes of a meeting in Moscow on June 11–14, 1951, were published in a

440-page hardbound volume [10].<sup>3</sup> Four hundred and fifty chemists, physicists, and philosophers attended the meeting, including the top chemists from all over the Soviet Union. There was a report on “The status of chemical structure theory in organic chemistry” compiled by a special commission of the Chemistry Division of the Soviet Academy of Sciences. It was followed by forty-three oral contributions. The report consisted of eight chapters and the first was titled “Butlerov’s teachings and their role in the development of chemistry.”



Александр Михайлович Бутлеров (1828-1886)  
(Aleksandr Mikhailovich Butlerov)

This need to preserve the pre-eminence of the Russian chemist over western chemists often led to Soviet historians claiming credit for Russian chemists for discoveries where the actual discovery was not, in fact, made by the Russian. What they missed, which is important, is that there are instances where the original idea was not due to the Russian chemist, but the clarification that improved its utility—often a much more important contribution—was. This was certainly the case with Butlerov, whose status as a giant among Russian organic chemists of the nineteenth century needs no artificial enhancement by claims of accomplishments beyond what he actually did. Nevertheless, despite the promulgation of dubious claims of priority, the seminal contributions of Russian organic chemists to the

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<sup>2</sup> Hargittai I (2000) The great Soviet resonance controversy. In Hargittai M (ed) *Candid Science: Conversations with Famous Chemists*. Imperial College Press, London, pp 8–13.

<sup>3</sup> *Sostoyanie teorii khimicheskogo stroeniya v organicheskoi khimii* (The state of affairs of the theory of chemical structure in organic chemistry). Publishing House of the Soviet Academy of Sciences, Moscow, 1952.

development of the discipline cannot be gainsaid. In the chapters that follow, I hope to show just how large a debt modern organic chemists owe to these early Russian pioneers of their science

## 2.5 Progress Through an Academic Career in Nineteenth-Century Russia

As part of his reforms associated with the establishment of the Academy of Sciences, Peter had envisioned a university associated with the Academy, and a Gymnasium associated with the university. Although Peter died before he could put this plan into action, his successors eventually did just that. The founding of Moscow University was accompanied by founding of two Gymnasias that were directly associated with it: at St. Petersburg, and in the eastern city of Kazan' (Казань), which was to flower into a major center for Russian organic chemistry. The secondary school system in Russia through the time of Nikolai I was heavily stratified, with entry requirements based, in part, at least, on the social class of the student. Serfs and household servants could aspire to an elementary education at parish and district schools, but the Gymnasium was reserved for the children of nobles or officials. The children of priests could obtain their education free at the seminaries, and many did, although the fraction who actually then entered the priesthood was small. The universities, in contrast, were open to all free persons above sixteen years of age who could pass the entrance requirements. Barriers to the education of serfs did not fall appreciably until the Emancipation decrees of Aleksandr II.

Following their graduation from the Gymnasium, students would enter the University by taking entrance examinations (of which Latin was an important component), and then entering an appropriate faculty. The first degree obtained by a student was the *diplom*, which approximates the modern baccalaureate degree. Following the *diplom*, students seeking an academic career would undertake additional advanced study, and would complete a research project on which they would write a dissertation for the degree of *kandidat*. In the nineteenth century, the *kandidat* was approximately at the level of a modern master's degree; today it is the full equivalent of the Ph.D. Completion of the *kandidat* qualified the student for entry-level positions in the university, almost always as Laboratory Assistants attached to the Chair (*kafedra*) of Chemistry.

The next step up the academic career ladder required a more advanced degree, the *Magistr Khimii* (M. Chem.), which was obtained by undertaking a research project, and writing up the results in a dissertation. By the end of the nineteenth century, not only was the dissertation assessed by a committee of examiners, but the candidate was also required to give a public oral presentation on the subject of the dissertation, and to pass an oral examination on the subject of the dissertation. Unlike the *kandidat* dissertation, there was a realistic expectation that the M. Chem. dissertation would contain work at the publishable level, and relatively few individuals obtained the degree without having the work in their dissertations

also appear in the scientific literature. Obtaining the degree of M. Chem. permitted the student to obtain an entry-level faculty appointment, typically at the rank of Adjunct (Assistant Professor), and students could progress from there to the rank of *Extraordinarius* (Associate Professor) without further qualification.

The highest-ranked position in a Russian University was the Professor, who occupied a Chair (*kafedra*) in a discipline. The number of such chairs available at the university was fixed, which meant that the number of professors was also fixed. In order to occupy a *kafedra* in chemistry, the degree of *Doktor Khimii* (Dr. Chem.) was required. This degree approximates the higher earned doctorates (e.g. the Doctor of Science) awarded by British Commonwealth universities, or the *habilitation* in the German system. In order to qualify for the degree, an individual was required to apply for permission to present for the degree. On obtaining permission to become a candidate for the degree, the individual would present a dissertation based on his original research; in most cases, the dissertation contained material that had already been published in peer-reviewed journals. In addition, the candidate was required to sit examinations in all areas of chemistry, and to make a public oral presentation on the dissertation. Only on passing all the examinations, having the public presentation assessed as satisfactory, and having the committee of examiners find the dissertation of sufficiently high standard, did the candidate receive the degree. The degree of Dr. Chem. is still the highest earned degree in chemistry conferred by Russian universities [20].

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