

1860-1861: MAGIC YEARS IN THE DEVELOPMENT OF THE STRUCTURAL THEORY OF ORGANIC CHEMISTRY (1)

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Introduction

The logical way to start this talk is by briefly looking at a chronology of organic structures. The first contribution in this area was the observation by Friedrich Wöhler (1800-1882, Figure 1) and Justus Liebig (1803-1873, Figure 1), that a substructure $C_{14}H_5O_2$ (C=6, O=8) survived unchanged through a large number of transformations of oil of bitter almonds (Bittermandelöl). They called this group benzoyl (2) and published it in a series of papers in contemporary outlets in both German (3) and French (4). The reactions used by Wöhler and Liebig to support their theory are gathered in Figure 2.

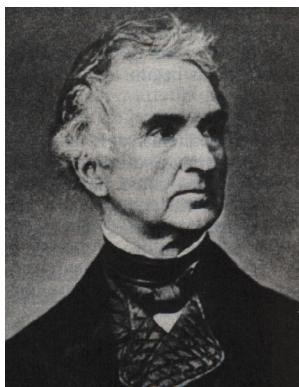


Figure 1. (l-r): Friedrich Wöhler (1800-1882), Justus (von) Liebig (1803-1873) and Jöns Jacob Berzelius (1779-1848). Public domain images downloaded from Wikipedia.

It is ironic that just two years later, Wöhler wrote to his former mentor, Jöns Jacob Berzelius (1779-1848, Figure 1), “Organic chemistry just now is enough to drive one mad. It gives me the impression of a primeval forest full of the most remarkable things, a monstrous

and boundless thicket, with no way of escape, into which one may well dread to enter” (5)—right after he himself had done exactly that.

Substitution Theory

Between 1832 and 1839, Jean-Baptiste André Dumas (1800-1884, Figure 3), Charles Frédéric Gerhardt (1816-1856, Figure 3), and Auguste Laurent (1807-

1853, Figure 3) had taken the complex radicals of Liebig and Wöhler and built the first “modern” theory of organic chemistry, Substitution Theory (6). This theory arose from the observations of Dumas, in

particular, that substituting certain hydrogen atoms of an organic compound with chlorine, for example, did not dramatically affect its physical or chemical properties: the difference between trichloroacetic acid and acetic acid was one of degree, not basic reactivity. Its proposers did not explicitly specify that it applied solely to organic com-

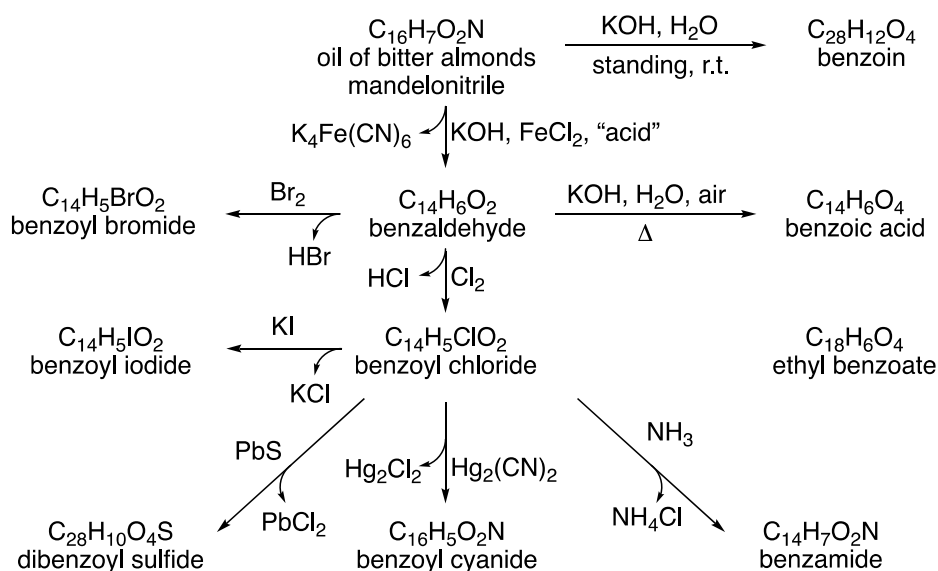


Figure 2. Transformations used by Wöhler and Liebig in their studies in the benzoyl series [C=6, O=8, S=16].

pounds, so this new theory was not without opposition. Wöhler wrote a parody of it (7), under the pseudonym S. C. H. Windler, where he described the complete replacement of all atoms in manganous acetate by chlorine without any change in the properties of the material: *reductio ad absurdum*.

Nevertheless, the logic behind the theory is clear when one compares the effects of the same substitution in a pair of inorganic compounds and a pair of organic compounds (Table 1). Replacing an electropositive element (e.g., hydrogen) by an electronegative element (e.g., chlorine) leads to a dramatic change in physical and/or chemical properties, as we see when the hydrogen in sodium

hydride is replaced by chlorine: the highly reactive, strongly basic, sodium hydride, which reacts violently with water instead of simply dissolving, becomes the

benign, very weakly basic sodium chloride. If, instead, we replace the electropositive element in sodium chloride with chlorine, the product is chlorine gas—producing a substance that is clearly obviously not the same or even remotely similar. It is worth noting that

to chemists of this era, hydrogen was always electropositive.

On the other hand, when a chlorine atom replaces one of the methyl hydrogens of acetic acid, the chloroacetic acid obtained has physical and chemical properties only slightly different from the acetic acid used to start with; the same effect is observed when the

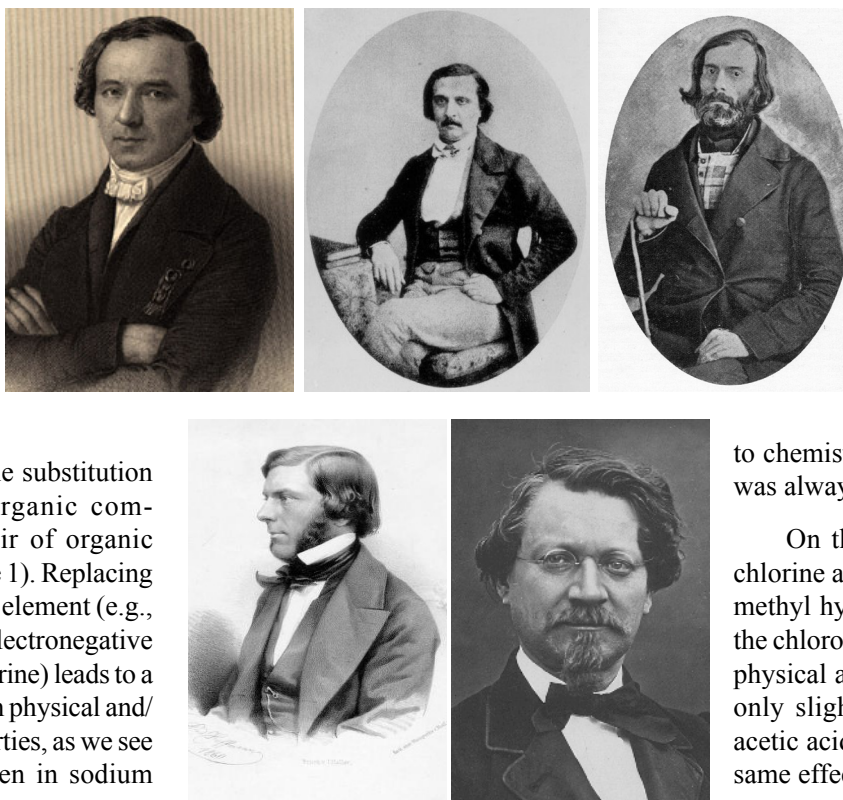


Figure 3. Top row (l-r): Jean-Baptiste André Dumas (1800-1884), Charles Frédéric Gerhardt (1816-1856), and Auguste Laurent (1807-1853). Bottom row (l-r): Alexander William Williamson (1824-1904) and August Wilhelm Hofmann (1818-1892). Public domain images downloaded from Wikipedia.

Table 1. Comparison of Substitution Theory for Organic and Inorganic Compounds.

Inorganic Compounds	Organic Compounds
Replacing an electropositive element (e.g., hydrogen) by an electronegative element (e.g., chlorine) leads to a dramatic change in physical and/or chemical properties.	Replacing an electropositive element (e.g., hydrogen) by an electronegative element (e.g., chlorine) leads to only a small change in physical and/or chemical properties.
Comparing NaH and NaCl, the replacement of hydrogen by chlorine in the ionic sodium hydride dramatically changes the chemical character of the compound from a strong base (H ⁻) to a very weak base (Cl ⁻)	Comparing CH ₃ CO ₂ H and CCl ₃ CO ₂ H, the replacement of the methyl hydrogens in acetic acid by chlorine gives a carboxylic acid that exhibits chemical and physical properties very similar to those of acetic acid

substitution is reversed. The properties of acetic acid and its chlorinated derivatives are summarized in Table 2.

Type Theory

The successor to Substitution Theory was Type Theory, which was proposed in 1839 by Dumas (8). It was subsequently extended by Alexander William Williamson (Figure 3), who described the “water” types (9), and August Wilhelm Hofmann (Figure 3), who described “ammonia” types (10, 11). Then, in 1853, Gerhardt published what has come to be known as “New Type Theory” (12).

The general features of Type Theory are summarized in Figure 4, where the formulas are based on the equivalent weights C=6 and O=8. Organic compounds could be viewed as being derived from the characteristic hydride by replacement of the hydrogen atoms by radical groups. Four basic Types were proposed: the hydrogen type (HH), the hydrochloric acid type (HCl), the ammonia type (NH₃), and the water type (H₂O₂ [H₂O]). Subsequently, Kekulé added the “marsh gas type,” (C₂H₄ [CH₄]) (13). These Types made it possible to standardize organic chemistry, based on the functional groups characterized by each type. When we examine Type Theory, it is difficult not to perceive in it, an embryonic precursor to the theory of functional groups.

The year 1857 was pivotal in the development of the Structural Theory of Organic Chemistry. In that year, August Kekulé (1829-1896, Figure 5) was formulating his theory of organic structure in Heidelberg—and converting his fellow Privatdocent, Emil Erlenmeyer (1825-1909, Figure 5) to his views at the same time. In Paris, discussions in the laboratory of Adolphe Wurtz

Table 2. Comparison of Properties of Acetic Acid and its Chlorinated Derivatives

Acid	m.p. (°C)	b.p. (°C)	D ₄ ²⁰ (g mL ⁻¹)	n _D	pK _a
CH ₃ CO ₂ H	16-17	118-119	1.049	1.371	4.756
ClCH ₂ CO ₂ H	63	189.3	1.58	1.4351 (55 °C)	2.86
Cl ₂ CHCO ₂ H	9-11	194	1.5643 (20 °C)	1.466	1.35
Cl ₃ CO ₂ H	57-58	196-197	1.62 (20 °C)	1.62	0.66

$\begin{array}{c} \text{H} \\ \\ \text{H} \end{array}$ hydrogen type	$\begin{array}{c} \text{C}_2\text{H}_3 \\ \\ \text{H} \end{array}$ methane	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{H} \end{array}$ ethane	$\begin{array}{c} \text{C}_2\text{H}_3 \\ \\ \text{Na} \end{array}$ methylsodium	
	modern: CH ₃	C ₂ H ₅	CH ₃ Na	
$\begin{array}{c} \text{H} \\ \\ \text{Cl} \end{array}$ hydrochloric acid type	$\begin{array}{c} \text{C}_2\text{H}_3 \\ \\ \text{Cl} \end{array}$ methyl chloride	$\begin{array}{c} \text{C}_2\text{H}_2\text{Cl} \\ \\ \text{Cl} \end{array}$ methylene chloride	$\begin{array}{c} \text{C}_2\text{H}_3\text{O}_2 \\ \\ \text{Cl} \end{array}$ acetyl chloride	
	modern: CH ₃ Cl	CH ₂ Cl ₂	CH ₃ COCl	
$\begin{array}{c} \text{H} \\ \\ \text{HO} \end{array} \text{O}$ water type	$\begin{array}{c} \text{C}_2\text{H}_3 \\ \\ \text{HO} \end{array} \text{O}$ methanol	$\begin{array}{c} \text{C}_2\text{H}_3 \\ \\ \text{C}_2\text{H}_3\text{O} \end{array} \text{O}$ dimethyl ether	$\begin{array}{c} \text{C}_2\text{H}_3\text{O}_2 \\ \\ \text{C}_2\text{H}_3\text{O} \end{array} \text{O}$ methyl acetate	
	modern: H ₃ C-O	H ₃ C-O	CH ₃ CO ₂ -O	
$\begin{array}{c} \text{H} \\ \\ \text{H} \end{array} \text{N}$ ammonia type	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{H} \end{array} \text{N}$ ethylamine	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{C}_2\text{H}_5 \\ \\ \text{H} \end{array} \text{N}$ diethylamine	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{C}_2\text{H}_5 \\ \\ \text{C}_2\text{H}_5 \\ \\ \text{H} \end{array} \text{N}$ triethylamine	$\begin{array}{c} \text{C}_2\text{H}_3\text{O}_2 \\ \\ \text{H} \end{array} \text{N}$ acetamide
	modern: C ₂ H ₅ -N-H	C ₂ H ₅ -N-C ₂ H ₅	C ₂ H ₅ -N-C ₂ H ₅ -C ₂ H ₅	CH ₃ CO-N-H
$\begin{array}{c} \text{H} \\ \\ \text{H} \\ \\ \text{H} \end{array} \text{C}$ marsh gas type	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{H} \\ \\ \text{H} \end{array} \text{C}$ propane	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{C}_2\text{H}_5 \\ \\ \text{H} \\ \\ \text{H} \end{array} \text{C}$ pentane	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{C}_2\text{H}_5 \\ \\ \text{C}_2\text{H}_5 \\ \\ \text{H} \end{array} \text{C}$ 3-ethylpentane	$\begin{array}{c} \text{C}_2\text{H}_3\text{O}_2 \\ \\ \text{H} \\ \\ \text{H} \end{array} \text{C}$ acetone
	modern: H-C-H	C ₂ H ₅ -C-H	C ₂ H ₅ -C-H	CH ₃ CO-C-H

Figure 4. The four original Types to 1853, and then, below the double lines, after Kekulé's addition of the “marsh gas type” in 1857.

(1818-1886, Figure 5) were often devoted to papers on the structures of organic compounds (14), as were the meetings of the fledgling Société chimique de Paris. Archibald Scott Couper (1831-1892, Figure 5) was among the early members of this society; he was admitted to membership in January 1858.



Figure 5. (l-r): Charles Adolphe Wurtz (1818-1886), Friedrich August Kekulé (1829-1896), Archibald Scott Couper (1831-1892), Richard August Carl Emil Erlenmeyer (1825-1909) Public domain images downloaded from Wikipedia.

The Emergence of Structural Theory

Kekulé first proposed his “marsh gas type” in the course of reporting his conclusions concerning the tetravalency of carbon in 1857. At the same time, Type theory itself had begun to unravel, and the structure of compounds had become possibly the most intriguing question in organic chemistry. The problem with Type theory emerged when a molecule could be assigned to multiple different types—e.g., ethane could be viewed as ethyl hydride, $\text{H}-\text{C}_2\text{H}_5$, belonging to the hydrogen type, or as methyl methylide, CH_3-CH_3 , belonging to the marsh gas type. Obviously, a better (i.e. more general) theory was needed. That theory was the Structural Theory of Organic Chemistry.

Before the new theory could emerge, however, the confluence of three intellectual concepts was necessary: 1) just what constitutes an atom, as opposed to an equivalent of an atom, had to be settled, especially for what we now call polyvalent elements; 2) the tetravalent carbon atom had to be conceived; and 3) the idea of catenation had to be conceived.

The question of atomicity had been nagging chemists for a number of years (15) and would not really be settled until the Karlsruhe Conference of 1860. In 1858, there were two sets of atomic weights and symbols for carbon and oxygen: Kolbe used the older equivalent weights, $\text{C}=6$ and $\text{O}=8$, which required doubling the number of these atoms in formulas [giving the formula $\text{C}_2\text{H}_3\text{C}_2(\text{O}_2)\text{OOH}$ for acetic acid], while Kekulé used the newer values, indicated by “barred” symbols ($\bar{\text{C}} = 12$, $\bar{\text{O}} = 16$). Kekulé had proposed in a footnote to his 1857 paper, already referred to (13), that carbon is always tetravalent. The concept of catenation was proposed by both Kekulé (16) and Couper (17) as the key component of their independent versions of the Structural Theory of Organic Chemistry in 1858.

At that time, Kekulé was a docent at Heidelberg, which allowed him to publish his work immediately. (As a member of the faculty, he did not require approval to submit his manuscript.) Couper, on the other hand, was a student in Wurtz’ laboratory, and had no similar freedom to publish—obtaining Wurtz’s approval would have been imperative. Moreover, Wurtz was not yet a member of the Académie des Sciences, so he could not present the paper before the Académie without a sponsor. This meant that Kekulé’s paper appeared first, allowing him to claim priority for the theory thenceforth. Couper blamed Wurtz for the delay in the publication of his paper, and immoderately and impolitely (but not necessarily unjustly) scolded his mentor for delaying publication. The relationship between the two men rapidly soured, and shortly thereafter Wurtz summarily dismissed Couper from his laboratory (18). The eminent historian of chemistry, Alan J. Roche, suggested to this author that “immoderate” may well be an understatement given the level of offensiveness required to bring the normally placid Wurtz to such a rage (19). Within two years, Couper’s scientific career had been ended by a nervous breakdown.

Kekulé’s version of Structural Theory was the more conservative of the two, and was much more widely accepted by the chemistry community. It retained many of the concepts of Type Theory familiar to chemists, so the (generally conservative) chemistry community felt more comfortable with it and found it easier to accept than the

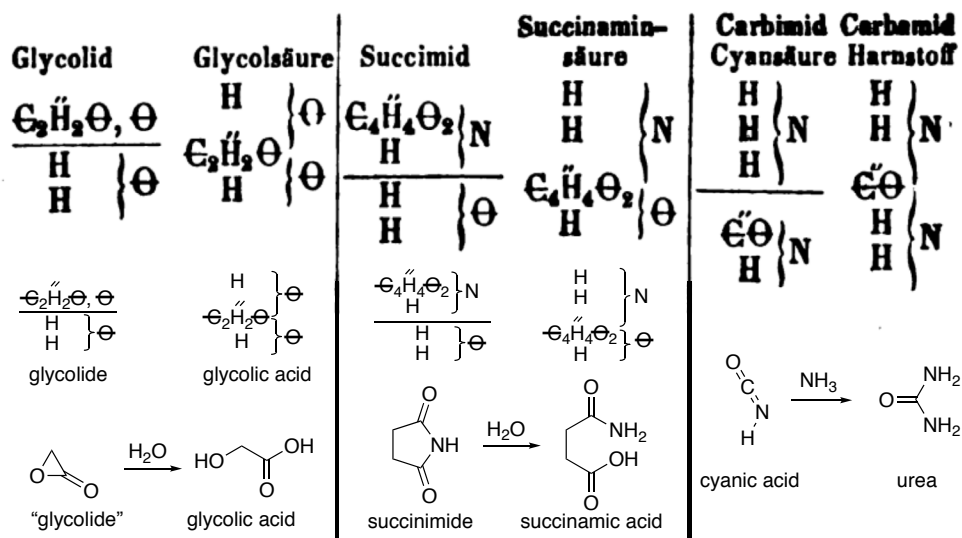


Figure 6. Kekulé's versions of the hydrolyses of glycolide and succinimide, and the ammonolysis of isocyanic acid. In these formulas, C=12 and O=16 (Ref. 16, p 139).

more radical versions of the theory. Even in his *Lehrbuch* (20), which was published in a series of fascicles over the ensuing decade, Kekulé still retained many of the trappings of Type Theory throughout. (It is fascinating to speculate, also, that this may have been done with an eye towards sales of the book.)

In Figure 6, Kekulé's originals and modern structural formulas for the hydrolysis of glycolide, the partial hydrolysis of succinimide and the ammonolysis of isocyanic acid are shown. In Kekulé's formalism, the reactants are stacked vertically, so we see water in the lower row in the hydrolysis reactions and the ammonia in the top row for the ammonolysis. It is worth noting that Kekulé's formula for glycolide is $\text{C}_2\text{H}_2\text{O}_2$, i.e., the empirical formula rather than the molecular formula; it actually corresponds to the α -lactone.

Couper's version of Structural Theory went much further than Kekulé's. Where Kekulé had retained many of the characteristics of Type Theory, Couper advocated that it be discarded completely, and that the new theory be built *ab initio*. This is what he did, but for many chemists—including Butlerov (later to become Structural Theory's most ardent champion)—this was a step too far (21). Couper's theory made many organic chemists uncomfortable, as Butlerov's objections show. Butlerov clearly disagrees with Couper's statement that theory is the purpose of scientific investigations:

•Butlerov saw the foundation of new chemical *Laws* as the purpose of science.

•Butlerov saw a theory as a series of analogies in behavior from which laws could be deduced.

•Butlerov discounted any theory that went beyond what could be deduced from experimental observations—he accepted *deductive* reasoning, but was less trustful of *inductive* reasoning.

•Butlerov still saw no reason to abandon Gerhardt's Types, despite their occasional minor disagreements with observation.

•Butlerov noted that double decomposition reactions (the basis of Gerhardt's theory) did not provide any information about the internal structure of substances. He did not doubt that this might become possible, but he did not concede that Couper's theory was the answer.

As is evident from Figure 7, Couper's structures were much closer to modern structural formulas, and it was not long before Butlerov himself would come to prefer them.

The differences between the two versions of the theory are illustrated by the two structural formulas in Figure 8. In Kekulé's structure of succinamic acid, for example, the backbone of the molecule is not visible, and the molecule is drawn as a "mixed" type. The part of the molecule contained in the box is written as a divalent group in the formula. In Couper's structural formula of tartaric acid, in the other hand, the backbone of the

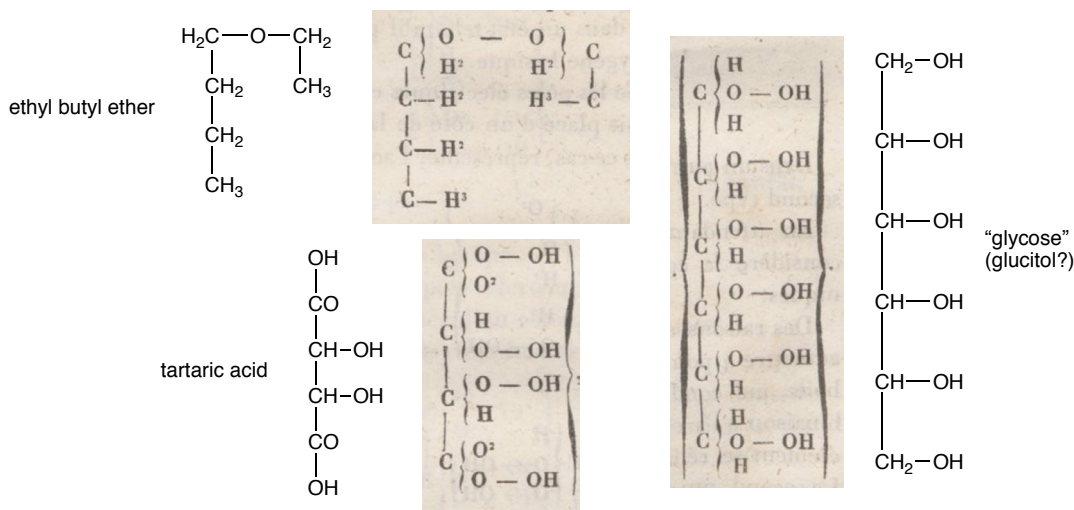


Figure 7. Couper's structural formulas. For these formulae, C=12 and O=8. (Ref. 17b).

molecule is shown explicitly, and the formula much more closely resembles the modern representation.

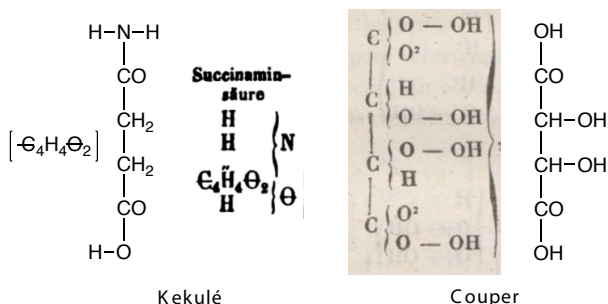


Figure 8. Comparing the structural formulas of the Kekulé and Couper versions of Structural Theory

There was also a third bloc of chemists, to whom neither version of Structural Theory was acceptable. Hermann Kolbe, who abjured the new theory in favor of his own concept of Rational Constitution, led the opposition to both new theories (22). This resistance to new ideas was typical of Kolbe. He had an inherent distrust of new theoretical ideas that he perceived not to have a firm basis in experiment, but rather from the application of deductive and inductive logic. His 1874 response to van't Hoff's postulate of the tetrahedral carbon atom is illustrative of this (23).

Butlerov

One of the major protagonists of this presentation, the Russian chemist Aleksandr Mikhailovich Butlerov (Бутлеров, Александр Михайлович, 1828-1886, Figure 9) (24) was born to the minor Russian nobility and was educated at Kazan University in Russia. As a student at

Kazan, Butlerov had been strongly influenced by Nikolai Nikolaevich Zinin (Зинин, Николай Николаевич, 1812-1880, Figure 9); Zinin had become an adherent of the unitary theory of Gerhardt while on *komandirovka* (official study leave) in western Europe in 1837. Thus, although he had begun his study of chemistry under Karl Karlovich Klaus (Клаус, Карл Карлович, 1796-1864, Figure 9), who was a strong adherent of Berzelius' dualistic theory, Butlerov soon gravitated to Zinin with his more modern perspectives. When Zinin left for to the St. Petersburg Medical-Surgical Academy, instead of returning to study under Klaus, Butlerov reverted to his first love, entomology, and wrote his *kandidat* dissertation on the diurnal butterflies of the Volga region (25).

After Butlerov had graduated as *kandidat*, the University administration chose to retain him for the professoriate—not as an entomologist, but as a chemist—and he was appointed as Assistant to Klaus in 1850. In 1851, he submitted his successful dissertation (26) to Kazan University for the degree of *Magistr Khimii* (*M. Khim.*) and was promoted to Adjunct (Assistant Professor) in Chemistry by a 21-3 vote of the University Council. In 1852, he submitted a dissertation for the degree of *Doktor Khimii* (*Dr. Khim.*). At the time, the Chair of Chemistry was vacant following Klaus' move to Dorpat, so Modest Yakovlevich Kittary (Киттары, Модест Яковлевич, 1825-1880, Figure 9), the Professor of Technology, and Aleksandr Stepanovich Savel'ev (Савельев, Александр Степанович, 1820-1860, Figure 9), the Professor of Physics, were appointed to examine the dissertation. Savel'ev returned a vote of "not acceptable" (24g), so the degree was not awarded.



Figure 9. Top row (l-r): Aleksandr Mikhailovich Butlerov (1818-1886), Nikolai Nikolaevich Zinin (1812-1880). Middle row: Karl Karlovich Klaus (1796-1864). Bottom row (l-r): Modest Yakovlevich Kittary (1825-1880), Aleksandr Stepanovich Savel'ev (1820-1860). Public domain images courtesy of the Butlerov Museum of the Kazan Chemistry School (Butlerov, Zinin, Klaus, Kittary) and downloaded from Wikipedia (Savel'ev).

In May, 1853, Butlerov submitted his re-written dissertation (27) and his *M. Khim.* diploma to Moscow University for the degree of *Dr. Khim.* and in March 1854 he was awarded the degree. Neither his *M. Khim.* nor his *Dr. Khim.* dissertation has ever been published as a stand-alone volume, although both were published in German in the *Bulletin de la Classe physico-mathématique de l'Académie impériale des Sciences de St.-Petersbourg* (26b, 27b), and are contained as Russian translations

in Butlerov's selected works (*Sochinenie*) (26c, 27c). Neither dissertation, at least as revealed by the papers in the *Bulletin*, presages the brilliant chemist who emerged just a few years later. Nevertheless, six months later, he was promoted to Extraordinary Professor on a 23-1 vote, and this was followed in March 1857 by his promotion to Ordinary Professor by a 20-1 vote. In June the same year, his *komandirovka* "to attend lectures in Germany, Switzerland, Italy, France and England during one year" was approved (28). As had Zinin before him, Butlerov managed to turn a strictly lecture-hall experience into a research experience, an event that proved critical in the development of the Kazan Chemistry School.

Butlerov's *komandirovka* could hardly have come at a more opportune time. The organic chemistry community, in particular, was obsessed with the "hot topic" of atomicity and of just what constituted the structure of a compound. During his trip, Butlerov met twice with August Kekulé at Heidelberg, as well as with Erlenmeyer, who was one of the first to adopt Kekulé's perspectives on the structure of organic compounds. During his six months in the Paris laboratory of Adolphe Wurtz, the Société Chimique de Paris was founded; Couper and Butlerov both became members. As alluded to above, the structure of organic compounds was a frequent topic for discussions in the laboratory and at meetings of the Société, so Butlerov witnessed the early development of a structural theory of organic chemistry first-hand. He would certainly have been aware of Couper's stance on the question.

By the beginning of 1859, the battle lines were fairly clear (Figure 10): Kolbe remained unyielding in his opposition to Structural Theory, whereas its two major protagonists were Couper, who advocated the complete replacement of Type Theory, and Kekulé who advocated retaining certain aspects of it. Wurtz was not an adherent of Structural Theory, but neither was he as obstinately opposed to it as Kolbe; he held a position rather between those of Kekulé and Kolbe. In January 1858, Butlerov had read a paper before the Société in which he espoused ideas similar to those of Kekulé, Kolbe and Wurtz. Unfortunately, this paper has not survived, except as referred to in the minutes of the Société (14). It may, however, provide a rationale for his 1859 criticism (21) of Couper's theory in the *Annalen der Chemie und Pharmacie*.

Butlerov returned to Kazan in 1859 to take up the chair of Chemistry left vacant by the departure of Kittary for Moscow. At the same time, he continued his research begun in Paris, and also continued to ponder the details of the new theories. While he was teaching

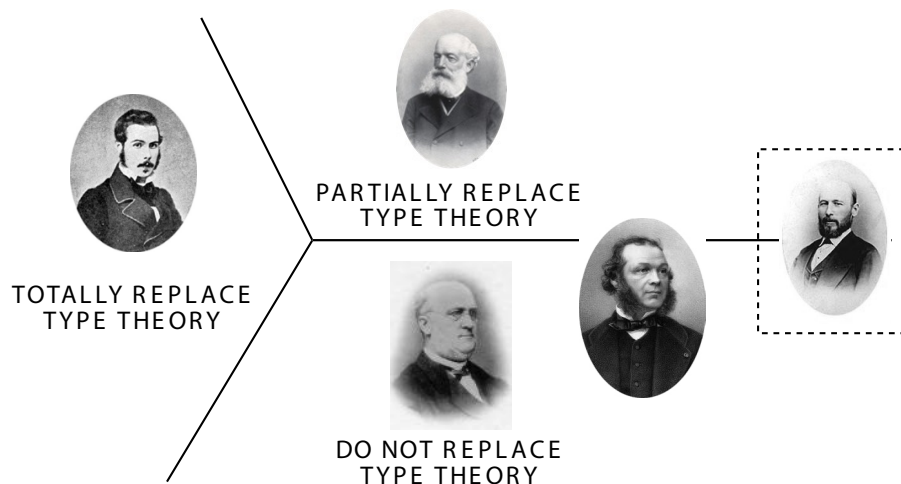


Figure 10. The attitudes of the major figures towards Structural Theory in 1859

organic chemistry in 1859, he held the views contained in his “Bemerkungen” paper, and taught a course based on equivalent weights and Type Theory. This is clear from the notes (29) taken by his student, Vladimir Vasil’evich

Markovnikov (1838-1904) (Figure 11, top row). By 1862, he had completely reversed his position on the merits of Structural Theory, and now taught a course based on modern atomic weights and his version of the theory,

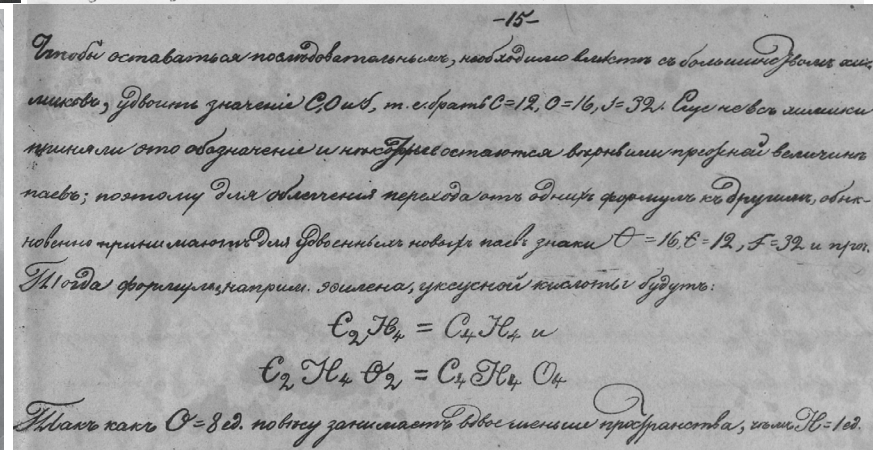
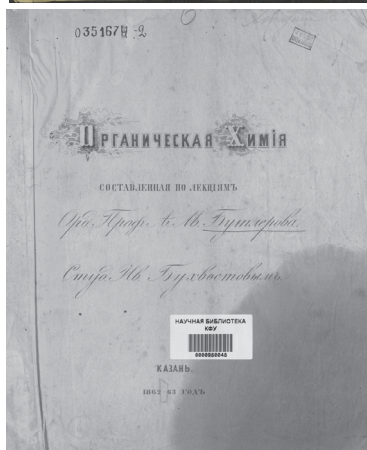
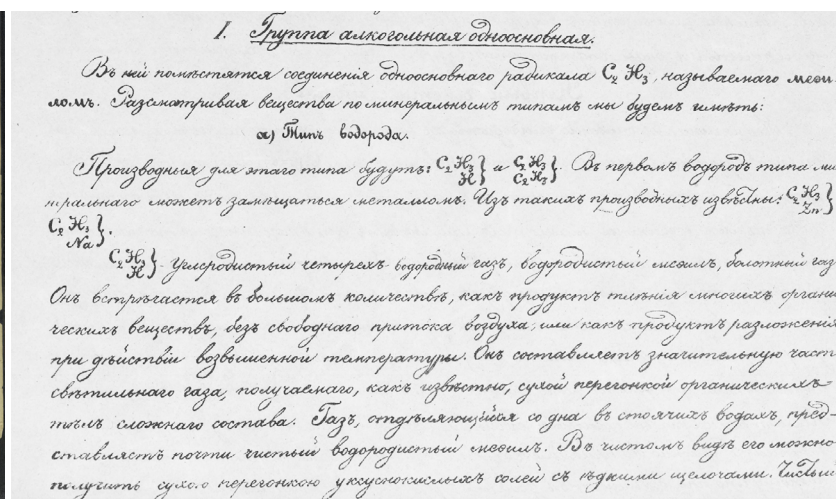
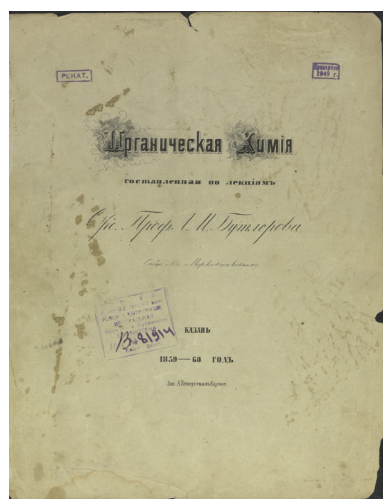


Figure 11. Notes from Butlerov’s lectures for 1859-1860, taken by Markovnikov (top), and for 1862-1863, taken by Bukhvostov (bottom). Note the modern atomic weights used in 1862. Images courtesy of the Lobachevskii Scientific Library of Kazan University.

which was much closer to that of Couper than Kekulé. The notes from this class (30), recorded by his student, Ivan Bukhvostov in 1862-1863 (Figure 11, bottom row), are still extant.

There is another critical document that has a bearing on the question of the timing of Butlerov's conversion from a Type Theorist to a Structuralist. In September 1861, Butlerov attended the 36th Assembly of German natural scientists and medical practitioners in Speyer. Here, in what has become known as "the Speyer paper," he presented his version of structural theory. Emil Erlenmeyer had been in the audience, and pressed Butlerov to publish the paper in his journal, the *Zeitschrift für Chemie und Pharmacie* (31).

In this paper, Butlerov 1) set out his version of Structural Theory, which was now similar to Couper's version; 2) proposed the term, *chemical structure*; and 3) set the limitation that each compound be represented by a single structure, and that a structure represent a single compound. He was, however, careful to point out in the same paper that the *chemical structure* was distinct from *physical structure*, and that it did not imply anything about the location of atoms in the molecule. Even so, it is worth noting that, just three years later, he did suggest that it might be possible at some time in the future to locate the physical atoms in a molecule (32).

Butlerov showed how his theory could be used to predict the existence of new isomers of known compounds (e.g., the amyl alcohols, Figure 12), and he then confirmed those predictions by preparing the compounds themselves. The first of Butlerov's syntheses

was the synthesis of *tert*-butyl alcohol, which he reported twice (Scheme 1). In 1863, he reported (33) that the reaction between phosgene and dimethylzinc afforded a mixture of isopropyl alcohol and *tert*-butyl alcohol. The following year, he reported (34) that acetyl chloride and dimethylzinc gave only *tert*-butyl alcohol, and provided evidence that acetone may not be involved as an intermediate stage in the reaction because the direct reaction between acetone and dimethylzinc was exceptionally slow. From a modern perspective, it is probable that the addition to acetone may

have been catalyzed by the zinc chloride generated during the first reaction, making the reaction autocatalytic, but because the concept of autocatalysis did not emerge until the 20th century, Butlerov did not know to explore this possibility. The same year, he began publication of his textbook of organic chemistry (35), the first based entirely on Structural Theory, with none of the trappings of Type Theory.

The first decade of predicting new compounds and confirming their existence by synthesis was instrumental in firmly establishing Structural Theory, but the theory would

have stagnated were it not for another brilliant chemist to emerge from Kazan: Butlerov's student, Vladimir Vasil'evich Markovnikov (1838-1904, Figure 13) (36). Markovnikov was the first to apply Structural Theory

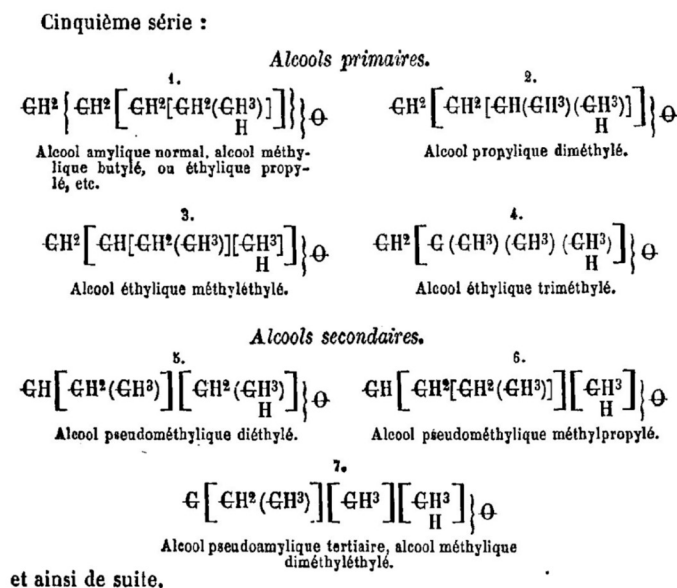
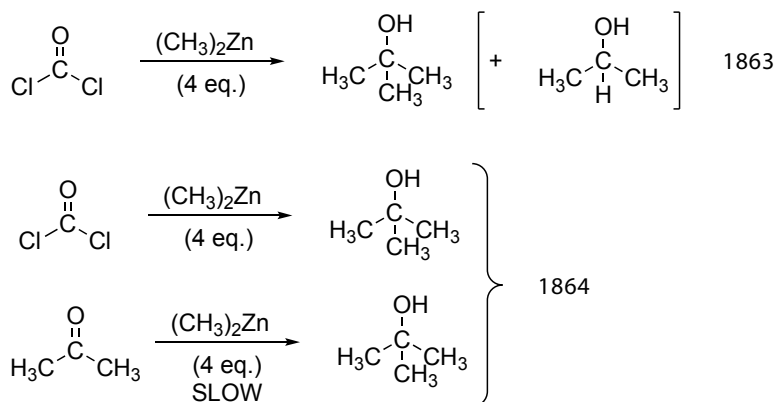


Figure 12. The isomers of amyl alcohol predicted by Butlerov.



Scheme 1. Butlerov's syntheses of *tert*-butyl alcohol, and evidence that acetone may not be an intermediate stage in the reaction.

to the study not only of chemical structure, but also chemical reactivity. It was Markovnikov who moved from simple prediction of isomers to studying the isomer ratios of the products of reactions, what today we would call, "regiochemistry." This application of Structural Theory to reactions was the first of its kind in this author's experience.



Figure 13. Vladimir Vasil'evich Markovnikov (1838-1904).
Image courtesy of the Butlerov Museum of the Kazan
Chemistry School.

Markovnikov was born near Nizhny Novgorod, and entered Kazan University in 1856 as a student in economic science. At the time, Russia was seeking to introduce the Cameral system for educating bureaucrats, so Markovnikov was required to take two years of chemistry as part of his degree. After hearing Kittary, the young Markovnikov had decided to pursue study in technology, but Kittary's departure for Moscow led to him coming under the influence of Butlerov. Butlerov had just returned from western Europe and was slowly developing his own version of structural theory.

Markovnikov took the fourth course in organic chemistry from 1 October 1859 to 1 April 1860, and during this year, Butlerov taught Type Theory. However, Markovnikov was ill at the end of the year, so he could not take his final examinations. Butlerov allowed him to take the final examination late. Markovnikov arrived at Butlerov's home and the two men went to the park. There, Butlerov gave him an oral examination. The ques-

tion that he posed was simple, and suggestive: "What is your opinion of mechanical types?" (37).

Butlerov had marked Markovnikov as a candidate for the Professorship, so immediately after he had taken his *Diplom* in Economic Science, Markovnikov began research for the degree of *kandidat* under Butlerov's direction. This degree, which was, at the time, basically equivalent to the B.Sc.(Hons.) degree in the British system or an M.S. degree in the U.S., was the first step up the academic ladder. Markovnikov submitted his dissertation (Figure 14), "On Aldehydes and their Relationship to Alcohols and Ketones," (38) on October 7, 1860. It was based on Type Theory and equivalent weights.

Thus, it seems clear that Butlerov was not yet a Structuralist at the end of October, 1860. Had he been, it would have been extremely unlikely that he would not have brought his favorite student into the Structuralist camp. Regardless, everything had changed by September 1861. That month, Butlerov presented a paper at the *Versammlung deutscher Naturforscher und Ärzte zu Speyer*. At the urging of Erlenmeyer, he published this paper in the *Zeitschrift für Chemie und Pharmacie* (Figure 15) (31).

This paper essentially restates Couper's theory, but in much clearer and more useful terms. In it, he stated:

The well-known rule that says that the nature of compound molecules depends on the nature, the quantity, and the arrangement of its elementary constituents can for the present be changed as follows: the chemical nature of a compound molecule depends on the nature and quantity of its elementary constituents and on its chemical structure.

Although Butlerov had criticized Couper's structures in 1859, at the end of his Speyer lecture in 1861 he made the following telling comment:

I am even obliged to remark that the theory and formulas of Couper—whose too absolute and exclusive conclusions I disputed at that time—contained similar thinking. It was, however, neither clearly enough perceived nor expressed.

So what happened to cause this complete reversal of Butlerov's position in the space of less than a year?

It seems reasonable to suggest that something in late 1860 may have been the triggering event. I posit that the trigger may have been Markovnikov because this period coincides with the time that Markovnikov began to work closely with Butlerov. The two men rapidly became more friends and colleagues than mentor and student. One must

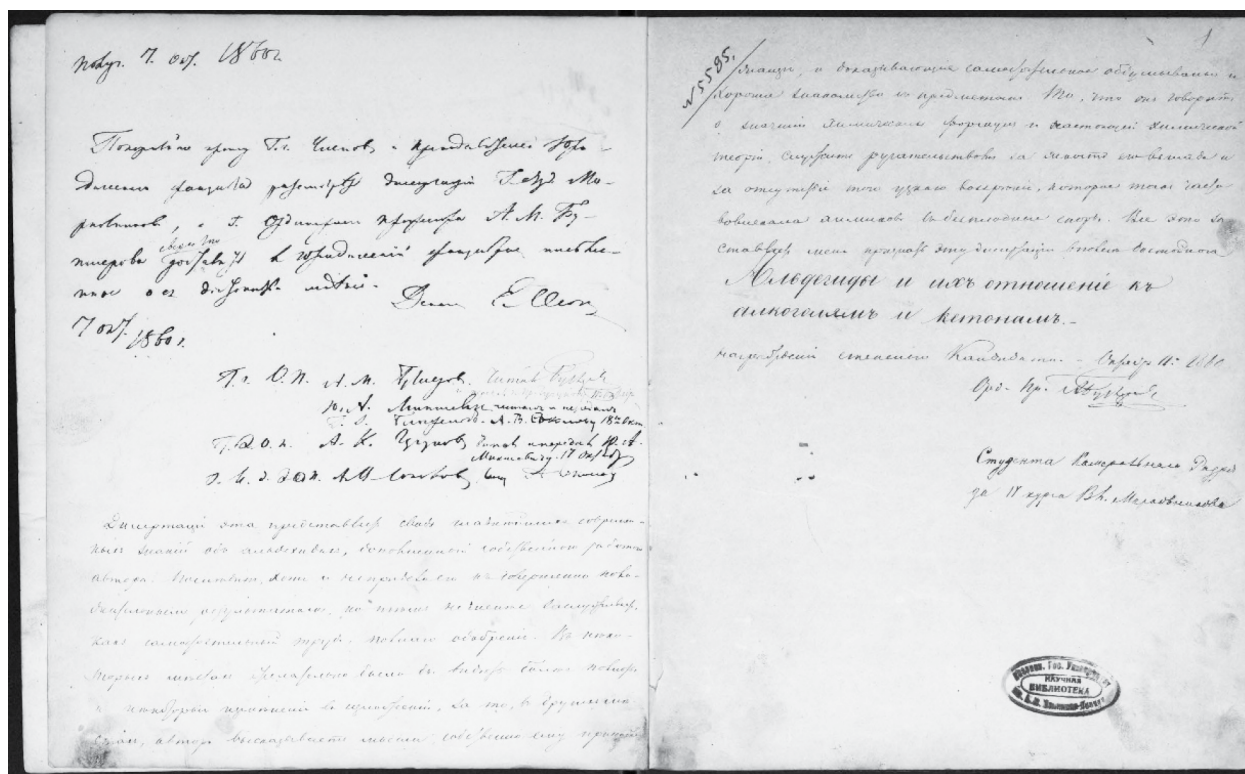


Figure 14. The title page of Markovnikov's dissertation for the degree of kandidat. This page also carries the Examiners' report, which accounts for its messy appearance. Image courtesy of the Lobachevskii Scientific Library of Kazan University.

ask oneself, "Is it coincidental that Butlerov's conversion to committed Structuralist coincides with when he began to work closely with the most brilliant young theorist of his generation?" It is my contention that this is exactly what happened. Between them, they made a formidable intellectual team. The last page of Markovnikov's *kandidat* dissertation contains the following statement:

The similarity of the properties of aldehydes with their [enol] isomers is explained by the similarity of the methods of their formation: aldehydes can be obtained by the method of Piria and Limpricht by the dry distillation of salts. *Obviously, such similarity of properties makes one assume that in these bodies there is an almost identical arrangement of their atoms.*

[Insertion and italics mine—DEL] This certainly appears to presage one of the foundational tenets of Butlerov's version of Structural Theory.

We know that up to his return to Russia in 1859, Butlerov had resisted Structural Theory despite being in Paris, where he was present as Couper developed his version of structural theory and despite meeting Kekulé during the gestation of his. The first course he taught following his return to Russia was based not on

Niņiges über die chemische Struktur der Körper.
 Von Prof. Dr. A. Butlerow.
 (Vorgetragen in der chemischen Section der 36. Versammlung deutscher Naturforscher und Aerzte zu Speyer am 19. Septbr.)

Bei dem gegenwärtigen Zustande der Chemie, wo wir in den Besitz einer Masse ebenso unerwarteter als interessanter Thatsachen gekommen sind, lässt es sich ziemlich allgemein fühlen, dass die theoretische Seite unserer Wissenschaft ihrer tatsächlichen Entwicklung nicht genug entspricht.

In der That, die jetzt fast allgemein angenommene typische Betrachtungsweise, obgleich sie erst vor wenigen Jahren entstanden, und für die Entwicklung der Chemie ungemein fruchtbar gewesen ist, genügt uns doch kaum.

Es sind sogar in der neuesten Zeit einige Thatsachen entdeckt worden, welche viel mehr für die Wahrheit mancher älteren Ansichten sprechen. In der That spricht die Bildung der von Wurtz neu entdeckten Oxyäthylbasen zu Gunsten der Ansicht von Berzelius, welcher die Alkaloide als copulirte Ammoniake betrachtete, und die Aethylen-theorie der Aethylverbindungen erscheint bis zu einem gewissen Grade richtig, wenn man der Bildung des Alkohol's aus Aethylen und Wasser, der Bildung des Jodäthyl's aus Aethylen und Jodwasserstoff u. s. w. gedenkt.

Die Sache ist so, dass die Mehrzahl der älteren und, ebenso die neue Ansicht, nur einem gewissen Kreis von Thatsachen angemessen sind, und zwar denen, auf welche sie sich hauptsächlich stützen.

Dieser Kreis ist natürlicherweise viel grösser für die neue Ansicht.

Zeitschrift f. Chemie. 1861. 36

Figure 15. The beginning of Butlerov's "Speyer paper" (Ref. 31).

Structural Theory, but on Type Theory; he seemed to be trapped by an inertia that inhibited his embrace of new ideas. Markovnikov, on the other hand, was a firebrand with the intellect of a true genius, but his mercurial tendencies needed moderating. Butlerov, the steadier of the two, was the ideal moderating influence over his younger colleague. The two built a team, like a charioteer and a horse, that allowed them to popularize Structural Theory so effectively that within a decade, it was the conventional wisdom.

I have always found it a coincidence, which I have heretofore ignored, that Butlerov's conversion from Type Theorist to Structural Theorist coincided with the beginning of Markovnikov's studies for the degree of *M. Khim.*, in January, 1860. In retrospect, I now find this coincidence much harder to ignore—it is too facile an action to dismiss it entirely. Unfortunately, there is not yet any documentary evidence to provide direct support for this hypothesis.

Nevertheless, I do hypothesize that the characters of the two men, and their closeness as friends, are entirely consistent with Markovnikov feeling comfortable about broaching ideas similar to those that Butlerov had dismissed in Couper's paper as over-reach. In these discussions between the two men, it may be that Butlerov re-evaluated Couper's version of Structural Theory, and realized what it *could* be. In the end, it was Butlerov who was responsible for taking these ideas and forming them into a cohesive whole. Obviously, this question will require substantial further research, the first step of which will be the transcription and translation of the two sets of lecture notes (29, 30) to find an acceptable answer. This work is underway.

Acknowledgments

Nobody gets an award like the HIST Award without the direct or indirect help of a support network, to all of whom I express my very real gratitude. My network consists of the members of HIST, who have read my work; the *Bulletin* and its Editors (Carmen Giunta and the late Paul Jones), who have published my work; my peers, who have reviewed my work; my students, who have made the work fun to pass down to the next generation; and—especially—my wife, Debbie (Figure 16), who has stood with me through it all.



Figure 16. (l-r): Our interpreter, Academician Aleksandr Ivanovich Konovalov, David E. Lewis, Mrs. Deborah Lewis, Professor Igor Sergeevich Antipin and Ms. Gul'nar Mel'nikova in the Butlerov auditorium of the Butlerov Museum of the Kazan School of Chemistry (November 2013). Author's photograph.

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About the Author

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Call for Nominations for the 2020 HIST Award

The Division of History of Chemistry (HIST) of the American Chemical Society (ACS) solicits nominations for the 2020 HIST Award for Outstanding Achievement in the History of Chemistry. This award, formerly known as the Dexter Award and then the Edelstein Award, continues a tradition started in 1956. The award is sponsored by and administered by the Division of the History of Chemistry (HIST). It is international in scope, and nominations are welcome from anywhere in the world. Previous winners of the Dexter and Edelstein Awards include chemists and historians from the United States, Canada, Germany, France, the Netherlands, Hungary, and the United Kingdom.

Each nomination should consist of

- a complete curriculum vitae for the nominee, including biographical data, educational background, awards, honors, list of publications, and other service to the profession;
- a letter of nomination summarizing the nominee's achievements in the field of the history of chemistry and citing unique contributions that merit a major award; and
- at least two seconding letters.

All nomination materials should be submitted (either as e-copy or as hard-copy in triplicate) to the Division of the History of Chemistry, for arrival no later than December 31, 2019. Send e-copy to Vera V. Mainz at mainz@illinois.edu OR alternatively send three (3) hard-copy sets to:

Vera V. Mainz, HIST Sec/Treas
2709 Holcomb Drive
Urbana, IL 61802
USA