INTRODUCTION TO AN ENGLISH TRANSLATION, "ON THE DIFFERENT EXPLANATIONS OF CERTAIN CASES OF ISOMERISM" BY ALEKSANDR BUTLEROV

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This rather lengthy paper by Butlerov sought to bolster the case for the structural theory of organic chemistry by reconciling the apparently diametrically opposed views of Friedrich August Kekulé (1) and Hermann Kolbe (2). In retrospect, despite not being called a classic by the Alembic Club or Ostwald's Klassiker, this paper really does represent a watershed in the development of organic chemistry because a neutral third party with credibility in both camps served as the referee for the argument. Part of why it did not achieve "forgotten classic" status at the turn of the twentieth century is almost certainly the fact while that papers by the originators of structural theory, Kekulé and Couper, were recognized as classic contributions, Butlerov's enhancements of the theory, which were critical to its further development and acceptance, were viewed as being a lesser contribution. Butlerov's claims in this arena were also not helped by the blatant politicization of the history of science in the Soviet Union during the heyday of the cold war (3). However, today, as Butlerov's contributions are undergoing an impartial re-appraisal (4), it appears to me that this paper actually does deserve the title of "forgotten classic."

The decade between 1858 and 1868 was a tumultuous one for the discipline of organic chemistry. It saw the rise of the structural theory of organic chemistry from an esoteric theoretical construct to something that was so pervasive that by the end of the decade—still a year before Mendeleev first proposed his Periodic Law of the Elements—that few bothered to even acknowledge the

work of the pioneers in the field (5). In its early years, it provoked a polemical debate over just what was meant by the structure of a compound, so it is perhaps the greatest testament to the success of the theory that, just a scant decade after it was first proposed, it was so widely accepted that it was viewed as a self-evident truth. There were four major participants in the polemical debates that gave rise to the structural theory of organic chemistry as it was used at the end of the decade—three protagonists and one antagonist.

A fierce struggle over priority ensued among the protagonists of the new theory (6). The first of these was Kekulé (1), whose deduction of the structure of benzene (7) assured him a place in the pantheon of great organic chemists. Contemporaneously with, and independent of Kekulé, the Scot, Archibald Scott Couper, working in the laboratory of Charles Adolphe Wurtz, developed his own structural theory of organic chemistry (8), but the delay in its publication led to him not receiving the credit he deserved. His intemperate—even vitriolic—allegations against Wurtz led to extremely bad blood between the two men, and to his summary dismissal from the laboratory. This was followed shortly thereafter by Couper suffering a nervous breakdown; he never again entered the debate. The third individual to enter this debate was Butlerov. Butlerov did not develop the basic concepts of structural theory, but his contribution was far more important. By making the theory easier to use, and by demonstrating its power by using it to predict the existence of compounds—whose existence he then confirmed by synthesis—he underscored just how powerful a tool this theory really was. In many ways, it was Butlerov who really made the new theory acceptable to the organic chemistry community; amongst other things, he wrote the first organic chemistry textbook (9) based solely on the new theory.

The main antagonist of the new theory was another giant of nineteenth-century organic chemistry, Hermann Kolbe. Kolbe was adamantly opposed to most new theories of organic chemistry, believing that *theories* had no place in an exact *experimental* science. Thus, structural theory, in its turn, also earned his unstinted opposition, as did its successor, the tetrahedral carbon of van't Hoff, and the subsequent rise of organic stereochemistry. It is rather a pity that this intemperate diatribe against the tetrahedral carbon atom (10) should be one of the most widely known of Kolbe's legacies, instead of, for example, his synthesis of acetic acid from undeniably inorganic precursors (11), or his electrolysis of carboxylate salts to explore the structure of carboxylic acids (12).

Both Kekulé and Kolbe had their own version of structural theory, which Kolbe spoke of as the rational constitution of the molecule (he eschewed the term, "structure"). Nevertheless, a modern examination of both Kolbe's rational constitutions and Kekulé's structures for a number of compounds, in the light of modern atomic weights and the form of structural theory championed by Butlerov, reveals that they actually give the same structure for the same compound. Indeed, one of Butlerov's early tasks was to show that the formulas of Kekulé and Kolbe, each of whom refused to acknowledge the possibility that the other might be correct, were actually the same. This reconciliation of the two views was not straightforward, since Kolbe used the earlier equivalent weights for carbon (C = 6) and oxygen (O = 8), which thus required the use of double atoms (C^2 and O^2) to get the correct weights of molecules, while Kekulé used the modern atomic weights for these elements, and used the barred symbols to specify this (C = 12 and O = 16). Butlerov first had to demonstrate that the two versions of the formulas of compounds were, in fact, equivalent. At the same time, he advanced a strong argument in favor of the new atomic weights. Kolbe eventually came around to this view, but he was still using the old equivalent weights when Butlerov's student, Markovnikov, was working in his laboratory as a post-doctoral researcher; one verbal battle over the atomic weight of oxygen was recounted by Markovnikov to his mentor (13). What is very interesting in Butlerov's paper is the fact that when one transforms

Kolbe's formulas by using the "new" atomic weights and the barred symbols, they are actually much easier to read and interpret than Kekulé's, and actually much closer to modern condensed structural formulas! Herein lay, in part, at least, the importance of Butlerov's version of structural theory: using it, he was able to reconcile the views of the two most influential chemists of his day—one a fierce protagonist of structural theory, and the other a fierce antagonist of the same theory. Being able to do this was critical to the universal acceptance of structural theory.

Following his reconciliation of the superficially divergent views of Kekulé and Kolbe, Butlerov—who first proposed the existence of double bonds in the alkenes, and triple bonds in the alkynes—then proceeds to explain in detail his version of structural theory. The treatment is highly logical, and he takes great pains to indicate where the point being made requires assumptions. He follows this by justifying those same assumptions with clear logic, and he thus slowly builds a coherent framework for use. With the exception of the formulas that he uses, his structures and his explanations of isomerism appear remarkably modern (although the emergence of stereochemistry would eliminate some of his errors—including an assertion that methyl chloride might possibly—he says, "probably"— exhibit isomerism).

Butlerov's French is relatively straightforward and easy to read, although he has a penchant for using semicolons to generate extremely long sentences to build logic strings. Many of his paragraphs consist of a single sentence made up of several clauses linked by semicolons. I have chosen to break up these sentences into segments that are more compatible with modern English prose. There are a number of terms that were current at the time that Butlerov was writing that are now relatively ambiguous or obscure. For this reason, I have translated "chemical force" by "chemical combining power," "atomicity" by "valence," "oxygenated carbon" by "carbonyl carbon," and "hydrogenated carbon" by "saturated alkyl carbon." Thus, a tetraatomic carbon atom becomes a tetravalent carbon atom. One word that has been especially problematic is "body." While a logical translation of this word in most places that it occurs is "substance," in other places, the word "molecule" is better; the word "species" is also used in places. The word "carbonyle" is also problematic, since Butlerov uses it two ways: to refer to what we call a carbonyl group today (>C=O), as well as to the methylene unit (>C=). Likewise, the verb "admettre" is translated variously as "acknowledge" or "accept." The word "exprimer" is

generally translated as "express," but in places, it is better translated as "describe."

A referee has raised the question of why Butlerov wrote this paper in French. This is an excellent question. Butlerov was fluent in both German and French, and had become acquainted with the new structural theory during his 1857-1858 *komandirovka* in western Europe. During that study abroad, he had spent six months in Paris, with Wurtz, and the remainder of the time in Germany, where he had met both Kekulé and Erlenmeyer. By his return to Russia, he had become an ardent proponent of structural theory, and immediately began teaching it as the basis for the study of organic chemistry (14).

At the same time, he clearly recognized Kolbe's pre-eminence and respected his abilities as a synthetic chemist; no fewer than three of his top students (K. M. Zaitsev, A. M. Zaitsev, and V. V. Markovnikov) studied with Kolbe. Although the younger Zaitsev (A. M.) was flexible (to the point of apostasy, in the eyes of Markovnikov, at least—he submitted an unsuccessful hand-written dissertation for the *kandidat* degree (15), describing Kolbe's views on rational constitution of organic and inorganic compounds)—Markovnikov resolutely defended his mentor's structuralist views in discussions with Kolbe (13).

The paper that is the subject of this translation culminates five years of work with structural theory on Butlerov's part. His first foray into the field was a comment (16) on Couper's paper of 1858, published in the *Annalen*. In the ensuing two years, Butlerov made a practice of publishing his synthetic work in French or German. It is interesting to note how the majority of papers that he published in French during this time also appeared in German. The converse was not true, which makes the referee's question particularly apropos. Unfortunately, I have no clear answer to it beyond mere speculation, which has no place in a scholarly journal.

I have followed the lead of Jensen and Kuhlman (17) in converting the footnotes in the original paper to sequentially numbered endnotes, placed after the body of the translation in conformity with the practice in the *Bulletin for the History of Chemistry*.

There is one place in the text (p 114 of the original) where Butlerov does appear to have mixed up the two compounds that he is discussing—ethylidene dichloride, CH₃CHCl₂, and ethylene dichloride, ClCH₂CH₂Cl. I have translated the text as originally written, but have made a translator's notation that this section appears to

be in error (otherwise his statements make absolutely no sense, and diverge from the careful argument that he has constructed). Likewise, there are places in the text where the structures given in the original are obviously wrong (fortunately, Butlerov provides examples immediately adjacent to the incorrect structures, so they are relatively obvious, and the correction required is also relatively obvious); in those cases, I have used the corrected structures in the body of the translation, and placed the original versions in the endnotes. All chemical structures have been re-drawn using modern drawing software to give a cleaner presentation in the translated paper than is available by simple scanning of the original document; the rigorous checking for accurate reproduction of the original was vital in identifying the errors alluded to above.

As with any translation, there are places where a literal rendering of the original language leads to stilted, or even ambiguous prose. In those cases, I have allowed myself a limited license to paraphrase the original French in order to convey the writer's meaning clearly and correctly to the English reader. These instances have been relatively rare, and have not, I believe, altered the meaning conveyed by the original work. This notwithstanding, any deficiencies in the current translation are the responsibility of the author.

References and Notes

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