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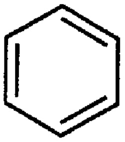
BOOK NOTES

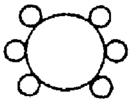
Chemische Studien and *Konstitutions-Formeln der Organischen Chemie in Graphischer Darstellung*, Johann J. Loschmidt, Reproductions of the Original 1861 and 1913 Editions, Aldrich Chemical Company, Milwaukee, WI, 1989. 54 pp. and 152 pp. Paper (Typeset) $12.00 each.

These volumes, issued by the Aldrich Chemical Company, are reproductions of the famous pamphlet published by the Austrian physicist, Johann Josef Loschmidt (1821-1895), in 1861 and of the later annotated edition of the same work, published by Kekulé's biographer, Richard Anschütz, in 1913 as part of Wilhelm Ostwald's famous series, *Klassiker der Exakten Wissenschaften.* Loschmidt's story certainly has all the elements of a romance of the "forgotten genius" genre: born in poverty, forced to privately publish his ideas on chemical structure - many of which appear to have anticipated the work of Kekulé and others, forgotten and then rediscovered after his death by Kekulé's biographer, etc., etc. Indeed, in the article in *Aldrichimica Acta,* in which the republication of these pamphlets is announced, William J. Wiswesser lists a dozen "firsts" in the theory of chemical structure supposedly contained in Loschmidt's masterpiece (1).

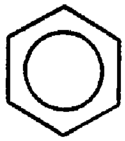
Unfortunately, many of Wiswesser's claims involve the exercise of a good deal of historical hindsight and others are simply wrong. The most serious of these is his contention that Loschmidt proposed the first correct cyclic structure for benzene (II) four years before Kekulé (I) and that his structure even anticipated aspects of the delocalized MO structure used today (III), a premise which he illustrates pictorially by comparing the three formulas:



I

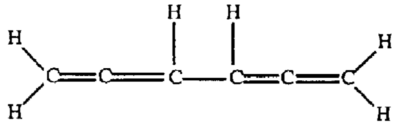


II

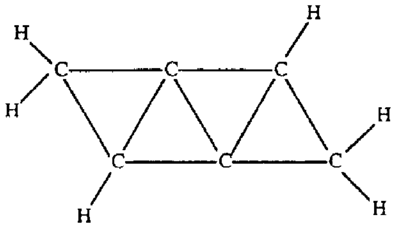


III

This assertion suggests that Wiswesser has not carefully read the work he so enthusiastically recommends to others, for though Loschmidt did propose two structures for benzene in his pamphlet, neither correspond to Kekulé's ring formula. Translating Loschmidt's formulas into modern notation, his first proposal corresponds to a chain stucture:



and his second to a polycyclic structure:



However, he quickly rejected both as inconsistent with the known chemical properties of benzene, and concluded that:

> In any case, it is at present impossible to arrive at a definitive result on this [subject], and we can hold our decision *in suspenso*, since our constructions [i.e., formula] are completely independent of it. We take for the C_6^{VI} nucleus the symbol in figure 184 and will treat it as though it were a six-sited [i.e hexavalent] element.

The symbol referred to in the quote is a large circle and, like all the circles in Loschmidt's formulas, it stands for a two-dimensional projection of the spherical domain of influence for the atom in question. In other words, the benzene circle in Loschmidt's formulas does not stand for a ring of six carbon atoms but for the spherical domain of a large, undifferentiated, hexavalent pseudoatom or "element" composed in some unknown manner of six carbon atoms. Because this aromatic pseudoatom persists unchanged in the structures of other aromatic derivatives, there is no reason to speculate on its internal structure, and Loschmidt promptly proceeds to use it to successfully write the formulas for 121 aromatic derivatives.

Also questionable is Wiswesser's claim that the pamphlet is the "first picture book of molecules, containing graphic displays with atomic domains, rather than abstract bond lines." In fact, Loschmidt's symbols are a throwback, with modifications to represent multiple bonding, to the symbolism used by Dalton 50 years earlier:

Like Loschmidt's circles, the circles in Dalton's formulas represent spheres of atomic influence and included not only the material atom itself but its surrounding envelope of repulsive caloric. As Meldrum noted many years ago, Dalton held to a simple and very literal physical picture of atoms and molecules (compound atoms) and there is little doubt that his atomic diagrams were intended to represent not only the composition but the structure (however unjustified this might have been experimentally) of the molecule in question (2). Though this aspect was never emphasized by Dalton, he did use it to physically justify his famous rule of simplicity (3):

> When an element A has an affinity for another B, I see no mechanical reason why it should not take as many atoms of B as are presented to it, and can possibly come into contact with it ... except in so far as the repulsion of the atoms of B among themselves [is] more than a match for the attraction of an atom of A. Now this repulsion begins with 2 atoms of B to 1 of A, in which case the 2 atoms of B are diametrically opposed; it increases with 3 atoms of B to 1 of A, in which case the atoms of B are only 120° asunder ... and so on in proportion to the number of atoms. It is evident then from these propositions, that, as far as powers of attraction and repulsion are concerned (and we know of no other in chemistry) ... *binary* compounds must be first formed in the ordinary course of things, then *ternary* and so on, until the repulsion of the atoms of B ... refuse to admit any more.

The drawings of binary, ternary and quaternary molecules given by Dalton in his famous *New System of Chemical Philosophy* are consistent with the predictions of his repulsion model of molecular structure. Indeed, it is tempting to speculate that the inability of Berzelius' atomic symbols to represent this structural aspect with equal clarity was at least partly responsible for Dalton's well-known dislike of Berzelius' proposals, just as it was responsible for the superior clarity of Loschmidt's formulas over those of his contemporaries.

Both pamphlets are attractively reproduced and reasonably priced, though there are some breaks in the thinner print and line drawings, the portrait of Loschmidt in the 1913 edition has the resolution of a poor photocopy, and the glued bindings have a tendency to give out almost immediately. Nevertheless, in spite of these minor physical shortcomings and the questionable historical motives, the Aldrich Company must be enthusiastically applauded for making this classic available again to both chemists and historians.

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References and Notes

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3. Quoted in reference 2, p. 9.

TRANSLATIONS

The Answer to Last Issue's Puzzle

The reaction between "cuperous nitre" and tin described by Cavallo was discovered by the British chemist Bryan Higgins in 1773 (1). Though the editor was unable to find mention of an equation describing the reaction in the standard reference books, the most likely representation is:

$$Sn(s) + Cu(NO_3)_2{\cdot}3H_2O(s) \rightarrow SnO(s) + CuO(s) + 3H_2O(l) + 2NO_2(g)$$

Cuperous nitre is, of course, copper dinitrate trihydrate and the observation that "copious nitrous fumes" are emitted, as well as the facts of thermodynamics, make it likely that the nitrate ion, rather than the copper ion, is the primary oxidizing agent. $\Delta H°$ for this reaction is -220.97 kcal/mol, $\Delta S°$ is 189.2 cal/K mol and $\Delta G°$ at 298K is -277.4 kcal/mol. An alternative reaction with $Cu(OH)_2(s)$, $Sn(OH)_2(s)$, $NO_2(g)$ and only 1 mole of H_2O as products is slightly more exothermic but less favorable overall due to a smaller entropy change. The moisture in the copper nitrate is necessary to kinetically initiate the reaction and the folding of the foil minimizes heat loss to the environment, thus helping to make the reaction thermally self-accelerating.

A recent twist on the use of copper nitrate as an oxidizing agent is the development of a new laboratory reagent called *claycop*, which is short for clay-supported copper nitrate (2).

References and Notes

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AWARDS

The Dexter Award

The 1989 Dexter Award for outstanding accomplishment in the history of chemistry has been awarded to Dr. Dean Stanley Tarbell of Vanderbilt University. The award, which consists of a cash prize of $2000 and an engraved plaque, was presented to Dr. Tarbell at the Fall National Meeting of the American Chemical Society in Miami Beach.

Dr. Dean Stanley Tarbell

Born in Hancock, New Hampshire, in 1913, Dr. Tarbell received both his undergraduate and graduate training in chemistry from Harvard University, taking a Ph.D. in organic chemistry under Dr. Paul Bartlett in 1937. Most of his academic career (1938-1967) has been spent as an organic chemist at the University of Rochester. In 1967 he became Distinguished Professor at Vanderbilt University and Professor Emeritus in 1981. Dr. Tarbell's work in the history of chemistry, which has been done in collaboration with his wife, Dr. Ann Tracy Tarbell, has largely centered on the development of organic chemistry in the United States, and has resulted in numerous articles and two books: a biography of Roger Adams (*Roger Adams; Scientist and Statesman*), published in 1981, and *Essays on the History of Organic Chemistry in the United States*, published in 1986.

The Division would at this time also like to solicit nominations for the 1990 Dexter award. Nominations should include a complete vita for the nominee, consisting of biographical data, educational background, awards and honors, publications, and presentations and other services to the profession; a nominating letter summarizing the nominee's achievements in the field of the history of chemistry and citing unique contributions which merit a major award; and at least two seconding