DISCUSSION

A. M. BUTLEROV'S THEORY OF CHEMICAL STRUCTURE AND ITS RECENT SUCCESSES

G. V. Chelintsev

The problems of chemical structure continue to hold the center of the stage in the Soviet chemical world. The existent confusion in chemical theory is a serious obstacle to the scientific, practical, pedagogical, and ideological work of chemists. The contemporary practical and methodological problems of chemical theory can be solved only along the lines of A. M. Butlerov's theory of chemical structure, which has been tested in the widest practical applications and is therefore reliable. An attempt at such a solution was advanced by me some three years ago in my book "Outline of the theory of organic chemistry" (State Chemical Press, 1949). The present article deals with A. M. Butlerov's theory of chemical structure in the light of the recent publication of the volume "A. M. Butlerov. Selected works on organic chemistry" (USSR Acad. Sci. Press,1951) and of the Report of the Commission of the Division of Chemical Sciences of the USSR Academy of Sciences "The state of the theory of chemical structure in organic chemistry" (USSR Acad. Sci. Press, 1951).

I. A.M. Butlerov's Theory of Chemical Structure

A great event has recently occurred in Soviet chemistry--the publication of the volume of A.M. Butlerov's selected works. At last wide circles of Soviet chemists have the opportunity of making direct acquaintance with the theory of chemical structure that served as a guiding star in the development of chemistry nearly 100 years ago. The book is beautifully gotten up, and the papers by A.M. Butlerov have been well selected and edited. The editorial articles by A.D. Petrov and by B.A. Kazansky and G.V. Bykov correctly indicate the tremendous significance of A.M. Butlerov's experimental work in the development of applied and theoretical organic chemistry.

The interpretation of the key idea of A.M. Butlerov's theory of chemical structure given by B.A. Kazansky and G.V. Bykov by way of orientation for the reader in evaluating the significance of that theory and as a reflection of the editors' standpoint produces a painful impression, however. In the conclusion of their article, B.A. Kazansky and G.V. Bykov write: "Naturally enough, the theory of chemical structure has not retained all of its original classical form and has undergone further development. Though A.M. Butlerov found it necessary to distinguish between the concept of chemical structure and the spatial arrangement of the atoms within a molecule...this (such a distinction--G.Ch.) lost any significance for the modern theory of structure long ago. When contemporary theory discusses the structure of a molecule of an organic compound, it conceives of it in the literal sense of the word, that is, it refers to the spatial....arrangement of the atoms comprising it... a definite polarity of its component parts, and the like." (p.583-584) [1]. Thus, the concept of chemical structure advanced by A. M. Butlerov,that is, the fundamental difference between A.M. Butlerov's theory and the views of Kekule or Kolbe, according to B.A. Kazansky and G.V. Bykov themselves (p. 563), is wrong in the opinion of contemporary chemists.

The idea of chemical structure as some higher, supramechanical law of chemical

[1]) Here and elsewhere in this article, unspecified page references refer to the one-volume edition of A.M. Butlerov's selected works.

phenomena, to the establishment and confirmation of which A. M. Butlerov devoted his life, turns out to be false. According to B.A. Kazansky and G.V. Bykov, it is the mechanical concept of chemical structure as nothing but the spatial arrangement of atoms within the molecule, i.e., the "constitution" theory of A.M. Butlerov's ideological opponents, Kekulé and Kolbe, that conforms to contemporary chemical science.

In their endeavor to justify somehow or other their description of A.M.Butlerov as "a great Russian chemist" (p. 583), B.A. Kazansky and G.V. Bykov write that "The concept of chemical structure is not basic to A.M. Butlerov's theory. The central place in that theory is occupied by his postulate of the chemical properties of a compound as a function of its structure....This postulate proved to be wholly revolutionary in its time" (p. 559)..."However, the concept of A.M. Butlerov's concerning chemical structure was a substantial step forward, since...by differentiating the notion of the distribution of the bonds between chemical atoms from the notion of the distribution of the physical atoms in space (the 'relative arrangement of atoms'), it demarcated the real goal of the development of organic chemistry--the establishment of the chemical structure of organic compounds" (p. 558).

B.A. Kazansky and G.V. Bykov regard Butlerov's idea of chemical structure as a lucky mistake that proved to be fertile from the practical standpoint. Kazansky and Bykov try to show that the idea of the dependence of the properties of substances upon the structure of their molecules would be impossible within the confines of a "truly" mechanical concept of chemical structure, such as the arrangement of the atoms in space. In brief, B.A. Kazansky and G.V. Bykov, considering A.M. Butlerov's concept of chemical structure to be erroneous, do all they can (and even more than they can) under these difficult circumstances to prove the decisive part played by his theory in the evolution of organic chemistry.

Acknowledging the good intentions and the heroic efforts of B.A. Kazansky and G.V. Bykov, we cannot but regret that their article is included in the single-volume edition of A.M. Butlerov's selected works. This article hampers a true understanding of A.M. Butlerov's theory of chemical structure. Nor can we fail to regret the publication of the review by B.M. Rodionov in Progress of Chemistry (1951,No.4), in which the article by B.A.Kazansky and G.V. Bykov is appraised enthusiastically. All this aggravates the harm done to Soviet chemical science by the traditional neglect of the great practical and philosophical significance of A.M. Butlerov's theory.

Contrary to the assertion made by B.A. Kazansky and G.V. Bykov, the idea of a supramechanical--chemical--structure of molecules is the cornerstone of A.M. Butlerov's theory. In A.M. Butlerov's historic report "The chemical structure of substances" (1861), he said: "We do not know the connection that exists within complex molecules between the mutual chemical interactions of the atoms that comprise them and their mechanical arrangement...but nevertheless, even if we leave aside the very notion of physical atoms, we cannot deny that the chemical properties of a complex body are chiefly governed by the chemical relations of the elements that comprise it" (p. 71)... "Up to now I thought it possible to modify the well-known rule to the effect that the nature of a complex molecule is determined by the nature, the number, and the arrangement of its elementary constituents as follows: The chemical nature of a complex molecule is determined by the nature of the elementary constituents, their number, and the chemical structure" (p. 72) [1]. "If we now try to determine the chemical structure of substances and succeed in representing it by our formulas, these formulas will be genuinely rational formulas to a certain extent, even if not entirely so. In the light of this, only one rational

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[1]) A.M.Butlerov used the concept of chemical structure to replace that of arrangement. Therein lies the revolutionary nature of A.M.Butlerov's lecture.

formula will be possible for any one substance, and when we know the general laws of the relationship between the chemical properties of substances and their chemical structure, a formula of this sort will express all these properties." (p. 782).

Thus A.M.Butlerov makes a clear distinction between the concept of the mechanical arrangement of atoms within molecules and the concept of chemical structure and, putting aside for the moment the problem of the relationship between mechanical state and chemical structure, he affirms the decisive importance of the latter in determining the distinct multiformity (a single formula of chemical structure existing for every substance) and chemical properties of substances.

In 1863 A.M.Butlerov thought it necessary to exclude any terminological confusion that might lead to confusion of the concepts of chemical structure and the spatial arrangement of atoms. In his comparison of the terms "constitution" and "chemical structure," A.M.Butlerov expresses his preference for the latter, "as it is more characteristic and is not employed in various connotations, like the word 'constitution,' and hence cannot lead to confusion so readily." In a footnote he adds, "The expression 'the topographical position of atoms' current lately hardly seems to be suitable, since it contains the notion of a determination of the position of atoms in space. I see no need for speaking of this arrangement...when discussing the chemical bond between atoms... As the consideration of the spatial position of atoms is immaterial for chemical purposes...the retention of expressions that presuppose this location will only hamper the desirable unification of differing (though in principle similar) views, which is so extremely important for the advancement of science" (p. 85).

Thus, for the sake of the complete elimination of any confusion of the concepts of atom position and chemical structure, A.M.Butlerov is even ready to accept the temporary exclusion of the former concept from discussions of molecular structure.

In 1885, A.M.Butlerov sets forth his most complete definition of the concept of chemical structure, in his paper on "Chemical structure and the 'substitution theory'":

"1) We are fully entitled to speak of the chemical interrelationship between atoms within a molecule as something real. Putting to one side the problem of the nature of this interrelationship and all spatial notions, we agree to call it by the name of 'compound' or 'bond'.

"2) It is only by some difference in this interrelationship (a difference in the manner of the 'bond') that the phenomenon of isomerism can be explained...

"3) The difference defined above is something constant, residing in the molecule, i.e., it is actually present in it, constituting an inalienable and characteristic part of it. It is this very part, i.e., the definite kind of 'bond' between the atoms, that we call constitution or structure and that we have to deal with when discussing isomers. Moreover, the facts support the view that the difference in the structure of isomers involves a differing distribution of the 'bonds' between the atoms within the molecule. It is the distribution of 'bonds' between the atoms in a molecule that has been given the name of 'chemical structure'." (p. 445-446).

Here, basing himself on his discovery of the agreement between the number of possible isomeric formulas for chemical structure and the number of real isomeric substances, A.M.Butlerov categorically asserts that the idea of chemical structure as determined for each substance by the order of the chemical bond between the atoms within its molecule is not a hypothesis, but rather a true reflection of a most important supramechanical rule (putting aside spatial relations) that applies to chemical phenomena. Here the concept of the chemical bond appears as some singular combining-chemical relationship between the atoms within a molecule that is quali-

tatively different from the general spatial-force (mechanical) relationship of the atoms.

Expanding this latter thought, A.M.Butlerov feels he has to clearly distinguish the concept of chemical structure from the concept of the mutual influences, or the force interrelationships, of the atoms within the molecule. With this in mind, A.M. Butlerov points out the qualitative difference in the mutual influences of atoms that are linked directly and indirectly--that between atoms that are linked together indirectly "the relationship we have called a 'bond' union...is not present...this influence will be one of another kind-- we may call it the mutual influence between atoms that are not directly linked together" (p. 451-452).

It is evident that A.M.Butlerov again and again stresses the supramechanical meaning of the concept of chemical structure. This concept is not equivalent to the concept of the spatial relationships of the atoms nor to the concept of force relationships--" mutual influences." It is clear to A.M.Butlerov that spatial and force--mechanical--relationships are present to a greater or lesser degree among all atoms--within a molecule as well as between molecules, i.e., they are universal relationships. What is more, his discovery of the equivalence of the number of possible chemical structural formulas to the number of real substances convinced A.M.Butlerov that these formulas, as true reflections of molecular structure, furnish direct evidence of the qualitative difference between the relationships of various atoms.

Thus, A.M.Butlerov exhaustively describes the fundamental distinction between his concept of chemical structure and the concepts of space or force interrelationships of the atoms within molecules--the concept of a mechanical molecular state.

All of A.M.Butlerov's creative work is permeated by the idea of the irreducibility of chemical structure to a mechanical state and by the idea of the decisive importance of supramechanical laws in chemical phenomena. To say that this idea is of minor importance in A.M.Butlerov's theory of chemical structure, as is done by B.A.Kazansky and G.V.Bykov, is a crude distortion of Butlerov's theory.

Not only do B.A.Kazansky and G.V.Bykov distort A.M.Butlerov's theory, but they immeasurably minimize the practical and philosophical significance of this theory. At the close of the second citation from the article by B.A.Kazansky and G.V.Bykov cited above, they say that although Butlerov's concept of chemical structure was a false one, it nevertheless was "substantial step forward," since it "demarcated the real goal of the development of organic chemistry--the establishment of the chemical structure of organic compounds."

Everything is in confusion in this evaluation. The real goal of the development of organic chemistry is, of course, not "the establishment of the chemical structure of organic compounds," but mastering the laws of chemical motion in nature and guiding this motion in directions useful to man. Evidently, B.A.Kazansky and G.V.Bykov are not speaking of the goal of the development of organic chemistry, but of the method of its development. Kazansky and Bykov state that A.M.Butlerov's erroneous concept of chemical structure proved to be useful notwithstanding, since it led to the discovery of the most important method in the development of organic chemistry--the method of establishing the structure of organic compounds from their chemical properties (cf. the quotations at the beginning of this article.)

This definition of the most important method in the development of organic chemistry is just as untrue as all the rest. The most important method in the development of organic chemistry is not the establishment of the structure of organic compounds from their chemical properties, but an understanding of the laws of

chemical structure in the multiplicity of organic compounds and thus predicting hitherto unknown substances. It is precisely in their search for the causes governing the possible existence of molecules of various atomic composition, as well as the possible existence of a certain multiplicity of compounds of the same atomic composition, that chemists have discovered the rules of valence numbers, of the octet, the tetrahedron, coordination numbers, coordination, the octahedron, asymmetry, free rotation, and shared and unshared doublets, the combination of which has built up chemists' knowledge of the rules governing the chemical structure of molecules. Formulas for chemical structure subordinated to the foregoing rules proved to be excellent tools to express and predict the individual multifariousness of substances. As for the "method of determining the structure of substances from their properties" or vice versa, this method plays a subordinate role in the development of organic chemistry--the feasibility of using this method depends upon the securing of information on the laws of chemical structure by the first method.

In their paper, B.A.Kazansky and G.V.Bykov depict A.M.Butlerov's theoretical concept as a sort of collection of opinions without any clear logical connection between them. As a result, they have been unable to provide a correct estimate of A.M.Butlerov's theory of chemical structure.

Let us briefly examine the history of the origin and the contents of A.M.Butlerov's theoretical ideas.

We know that structural formulas were written long before A.M.Butlerov. Depicting the valency of atoms by lines and connecting the lines together, chemists explained why atoms do not combine in any quantitative proportions within molecules, but only in certain ones. But the metaphysical thinking of the chemists of the time contained no other notion of molecules than that of mechanical aggregates of atoms coupled in space. Structural formulas, directly expressing some peculiar supramechanical interaction between atoms linked together by valence bonds, were regarded as convenient tools for expressing ways of securing chemical properties or, possibly, the distribution of atoms within molecules, but no one believed that they had any real meaning. The tool that was fated to become the most important tool in chemical science was ready to hand, even though in an extremely crude form. Yet they did not know how to use it.

This knowledge was discovered by A.M.Butlerov. In his study of isomerism, Butlerov discovered that the number of possible structural formulas corresponded to the numerical multiplicity of the real substances. He concluded that structural formulas are not convenient fictive symbols, but true, single-valued expressions of real molecules. Hence, the atoms in real molecules, in exact conformity with the structural formulas, are governed not only by general space-force (mechanical) relationships, but also by some special, supramechanical connecting-chemical relationships. Hence, molecules are not mechanical aggregates of atoms, but chemical compounds subordinated to some supramechanical laws. Hence, the concept of molecular constitution as the arrangement of a molecule's atoms in space must be transformed into the concept of the chemical structure of a molecule as a precisely defined sequence of chemical bonds between the atoms within the molecule. Hence, chemical structure is the most important, fundamental, characteristic feature of a molecule's nature, playing a decisive part in determining its specific diversity and properties. Hence, the chemical structure formulas may be used as a powerful tool for expressing and predicting the specific diversity and properties of substances. These are the theoretical notions of A.M.Butlerov as a whole.

It follows from an examination of this concept that A.M.Butlerov's achievements are not confined to the "fortuitous" discovery of "a method of establishing structure from the chemical properties of substances." Actually, A.M.Butlerov discovered the most important method, described above, of perceiving the laws of chemical

structure from the diversity of substances, comprehended the significance of structural formulas as true reflections of molecules, and showed how to use them as tools for expressing and predicting the specific diversity and properties of substances.

This does not exhaust the contributions of A.M.Butlerov to the development of chemical theory. With his concept of supramechanical chemical structure, A.M.Butlerov was able to overcome the metaphysical mode of thought of the chemists who were his contemporaries and thus to establish the only creative dialectical-materialist view of the nature of chemical phenomena. In retaining the epithet of dialectical materialist for A.M.Butlerov while asserting that by now Butlerov's concept of chemical structure is equivalent to the concept of the arrangement of atoms in space, B.A.Kazansky and G.V.Bykov have themselves endorsed mechanism.

B.A.Kazansky and G.V.Bykov do not adduce, nor can they (since there are none), any convincing arguments to prove that in the light of modern science the concept of chemical structure boils down to the concept of mechanical state. Regarding molecules as some sort of mechanical aggregates of electrons and nuclei, B.A. Kazansky and G.V.Bykov bypass the question of why these "aggregates" are incomparably fewer than the number of arrangements of electrons and nuclei that are efficient from the standpoint of energy. Rejecting the supramechanical laws of molecular structure as governing the real diversity of molecules and unable to explain this multiformity on the basis of mechanical notions, Kazansky and Bykov take an agnostic position. The laws of chemical structure take on the significance of something handed down from above--unknowable.

By way of proving the correctness of the mechanical concept of chemical structure, Kazansky and Bykov simply refer to the alleged point of view of contemporary chemists. Most contemporary chemists, however, regard structural formulas not merely as conventional and inexact expressions of interatomic distances and bond angles within molecules, but rather as, above all, direct and accurate expressions of the order of the chemical bond linking atoms within real molecules, i.e., in the sense of the Butlerov theory of chemical structure. By "contemporary chemists" Kazansky and Bykov apparently mean only the adherents of the mesomerism-resonance theory of Ingold and Pauling, whose concept of chemical structure is the same as the mechanical concept of Kazansky and Bykov.

The article by Kazansky and Bykov is useful in that it provides an opportunity for defining certain important positions in the current discussion on the problems of chemical structure. Until recently, our domestic supporters of the theories of Ingold and Pauling have categorically rejected the contrast between the theory of chemical structure and the mesomerism-resonance theory given by me (in my Outline of the theory of organic chemistry, 1949) based upon the differences in the concepts of chemical structure employed in these theories. In their articles, the "contemporary chemists" constantly alleged that considering structural formulas as nothing but inexact expressions for the spatial relationships between atoms (or electrons and nuclei) within molecules is in full agreement with the meaning A.M.Butlerov gave them.

Against the background of Butlerov's own definitions of the concept of chemical structure set forth in the one-volume edition, Kazansky and Bykov have been compelled to acknowledge that this concept of chemical structure does not agree with that held by "contemporary chemists." This illustrates the correctness of the above-mentioned contradiction set forth by me. At the same time it indicates that inasmuch as the concept of chemical structure held by "contemporary chemists" is incompatible with A.M.Butlerov's concept of chemical structure, their claims to be his intellectual heirs are out of place. Their concept of chemical structure agrees with the views of A.M.Butlerov's opponents, and they are the latter's intellectual heirs.

Seeing that this uncomfortable state of affairs might be discovered, the "contemporary chemists" are trying to find some way out of the situation. Their last achievement in this direction is the above-mentioned report of the Commission of the Division of Chemical Sciences of the USSR Academy of Sciences to the Conference on the Problems of Chemical Structure convened by the Division of Chemical Sciences. The report states: "The concept of chemical structure introduced by Butlerov by no means boils down to a notion concerning the arrangement of atoms and the distribution of bonds within a molecule. Butlerov repeatedly stressed the need for taking the existence of mutual influences between the individual atoms and groups of atoms within the molecule into account" (p. 6 of the Report).

All of this, it is clear, has nothing to do with the Butlerov definition of chemical structure, which Butlerov distinguished sharply from the concepts of the "arrangement" and the "mutual influence" of atoms within molecules, from the concept of the space and force (mechanical) relationships between atoms within molecules. The Commission combines the concept of the distribution of bonds with the concepts of the arrangement and mutual influence of atoms into a single, allegedly Butlerovian, concept of chemical structure in order to reduce the former--supramechanical--concept to the latter--mechanical--one. As a result of this combination, the concept of the distribution of bonds acquires the meaning of the distribution of the most significant space-force interactions between atoms, while the chemical bond becomes nothing but a quantitative species of the universal general mechanical interrelationships between atoms. The concept of chemical structure is reduced to the status of the mechanical concept of the arrangement of atomic nuclei and electronic density within molecules. The sole difference between the concept of chemical structure held by B.A.Kazansky and G.V.Bykov, on the one hand, and that held by the Commission of the Division of Chemical Sciences is that in the latter the concept of chemical structure is not rejected outright, but is reduced to the level of the concept of mechanical state--in a cautious form. This permits the "contemporary chemists" to maintain for the time being their version that their views are in conformity with the Butlerov theory.

II. New Achievements of A. M. Butlerov's Theory of Chemical Structure

As we have indicated above, the Butlerov method of learning the laws of chemical structure from the multiformity of substances was the method of development of the theory of organic chemistry. That is how A.M.Butlerov established the structural theory, and that has been how it evolved subsequently. The discovery of excess substances over the number of possible structural formulas led to the evolution of the structural theory into the stereochemical theory with its tetrahedron and free rotation rules. The discovery of the multiformity of substances that did not fit into the framework of the rules of valence numbers and the tetrahedron led to the evolution of the structural theory into the coordination theory with its rules of coordination numbers and the octahedron. The discovery of ions and radicals, electrolytes and non-electrolytes, resulted in the evolution of the structural theory into the electronic theory, in which the notion of two kinds of chemical bonds was advanced: covalent bonds, formed by the sharing of an electron pair in a two-atom orbit and governed by the valence number, octet, and tetrahedron rules; and electrovalent bonds, formed without the sharing of an electron pair in a diatomic orbit (the duplet remaining within the valency shell of a single atom) and governed by the coordination number, coordination, and octahedron rules. The structural, projection, coordination, and electronic formulas of these theories proved adequate for expressing and predicting all the known multiformity and properties of molecules.

During the evolution of the structural theory into the above-mentioned theories we learned how much the mechanical state of molecules depended upon their chemical

structure. The tetrahedron and octahedron rules, discovered chemically (by means of the Butlerov method described above), explained the way in which the bond angles in molecules depended upon the way in which the atoms were linked together. New physical methods made it possible to measure the bond angles and interatomic distances directly, thus confirming the foregoing rules that had been discovered chemically and adding to them the rules governing the variation of the bond lengths (the interatomic distances) with the nature and multiplicity of the bonds. The discovery of these ways in which mechanical state is a function of chemical structure has made the chemical structure formula suitable for judging the arrangement of the atoms within a molecule.

It is obvious that as a result of all this the chemical structure formula has not remained the same. It has retained the significance of a direct and true reflection of the sequence, order (in the configuration sense), multiplicity, and manner of chemical bonding of the atoms within the molecule. Neither the structural formula nor the projection, nor the coordination, nor the electronic formula expressed anything else directly. Judgments from this formula concerning the methods of synthesis, the mechanical state, and the properties of a molecule are mediated by our information concerning their dependence upon chemical structure.[1])

Unfortunately, the neglect of A.M.Butlerov's theory and ignorance of the history of the development of structural problems has made it possible for "contemporary chemists" to see in the chemical structure formulas nothing but expressions of the mechanical state of molecules. When the "contemporary chemists" learned that there existed a supramechanical concept of chemical structure due to A.M.Butlerov, they regarded it as merely outmoded nonsense. They did not take the trouble to reflect that the formulas of chemical structure were governed by rules determining the localization of electron orbits in one or two atoms, the rules of valence and coordination numbers, the tetrahedron and octahedron rules, the octet and coordination rules, the rules of free and restricted motion of atoms in space--rules that are not explainable from the mechanical standpoint. They did not take into consideration the fact that the reality of the supramechanical rules of molecular structure set forth in these rules has been corroborated by the practical employment of formulas based upon these rules in predicting hundreds of thousands of hitherto unknown molecules. The "contemporary chemists" regarded the chemical structure formulas merely as some unknowable, conceptual standards of energetically efficient arrangements of atomic nuclei and electron densities within atoms.

In this scheme everything was very highly oversimplified. They regarded the molecule as an electronic-nuclear aggregate whose properties were determined by its mechanical state. Once they ignored the rules of chemical structure specified above, the possibility arose of "explaining" the various discrepancies between the chemical structure formulas and the experimental data on the arrangement of the nuclei and the electron density within the molecules or on the properties of molecules by some sort of shifts of the nuclei and electron densities in molecules from conceptual standards. In the Ingold formulas, shifts of this sort are represented by bent arrows, while the Pauling formulas represent them by superposing several standards.

Equipped with these formulas, the mesomerism-resonance theory entered chemistry flying the flag of the mechanistic postulate of the delocalization of electrons and bonds within molecules, setting forth the fictitiousness of the classical formulas of chemical structure with their single-valued, localized electron orbits and chemical bonds.

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[1]) Within the confines of the known ways in which mechanical state is a function of chemical structure, there still is an infinity of mechanical states corresponding to each chemical structure formula and differing in the arrangement of the nuclei about the axis of free rotation and in the polar distributions of electron density about the nuclei.

As might have been expected, the mechanical mesomerism-resonance theory proved to be practically sterile. Its viability is due solely to the possibility discovered within the Ingold and Pauling formulas of parasitically employing the stipulatedly fictitious formulas of chemical structure in their usual real meaning. It is apparent that an approach of this sort has no practical advantages. All it does is to make the multiformity and properties of molecules depend upon fictions--the real molecules and the properties turn out to be products of the mind. The mechanism inevitably evolves into the idealism of Machian doctrine.

The methodological defectiveness of the mesomerism-resonance theory is due to the concept of mesomerism that lies at the core of the theory, i.e., the intermediate structure of real molecules when compared to ideal standards. It is upon this concept that the methods of expressing real structures employed in the Ingold and Pauling formulas are based: via "fictitious formulas," which are then used in their real meaning.

A subsidiary role is played by the notion of resonance or disturbance, i.e., some "phenomena," involving an increase in energy, that cause a shift of the nuclei and the electron density from the ideal standards. These concepts make visible the reality of the allegedly fictitious formulas and thus facilitate their parasitical use in their real significance.

The report of the Commission of the Division of Chemical Sciences referred to above is curious because of the way in which the commission, while acknowledging the practical sterility and methodological defectiveness of the mesomerism-resonance theory, contrives to rescue it intact and whole.

The commission criticizes the mesomerism-resonance theory in so far as resonance and perturbation are concerned. The commission correctly points out that inasmuch as the chemical structure formulas used in the Ingold and Pauling formulas are fictitious, the concepts of resonance or perturbation phenomena in the structures corresponding to these formulas are likewise fictitious. The commission proposes that the concepts of resonance and perturbation be discarded from the Ingold and Pauling formulas, and that these formulas be considered simply as expressions of real arrangements of nuclei and electron density as compared with conceptual standards--comparative abstractions (p. 38 of the report).

But how can we then explain the reason for the shift of nuclei and electron densities away from the standards in real molecules? The way out of the impasse was found in the concept of mutual influence. The commission explains this shift as due to the phenomena of mutual influence in the ideal standards, which is accompanied by an increase in energy. But there cannot be any real phenomena in conceptual standards!

The ring has been closed. The commission does not realize it only because it has no doubt about the reality of the concept of mutual influence. It is obvious that this concept, which has been widely used by chemists for a long time to explain singularities in the properties of molecules, is not without real meaning. But concepts are not real by and of themselves, but only in connection with the phenomena that they reflect. The concepts of resonance and of perturbation are likewise real in their proper place. They become fictitious only in the sense of phenomena occurring in conceptual standards. In the same manner, the concept of mutual influence, though a more "chemical" notion, is just as fictitious as the concepts of perturbation and resonance when used to refer to phenomena occurring in conceptual standards.

The commission's desire to save the mesomerism-resonance theory is so strong that it deems it possible to eliminate the practical sterility and methodological

defectiveness of Ingold's and Pauling's theory simply by substituting the words "mutual influence" for "resonance" or "perturbation." We must acknowledge the inventiveness of the "contemporary chemists" in their efforts to evade the necessity of admitting their errors. But one might have expected something more substantial from the report of the Commission of the Division of Chemical Sciences of the USSR Academy of Sciences.

A.M.Butlerov wrote: "...the facts that are not explainable by existing theories are most valuable for science, and the development of the latter in the near future must be expected to result principally from the exploration of these facts" (p.425).

Recent facts of this sort in organic chemistry have been the experimental data secured by physical methods that doubtless indicate a discrepancy between the generally accepted formulas for conjugated compounds (including the aromatics) and the actual mechanical state of their molecules. The exceptionally great importance of these findings is illustrated by the fact that there are hundreds of thousands of conjugated compounds, constituting a large proportion of all organic substances. It cannot be said, of course, that chemists have been wholly satisfied with the generally accepted formulas for conjugated compounds, such as Kekule's formula for benzene, even before the publication of these findings. Such formulas did not allow for the absence of the isomeric ortho disubstitution derivatives of benzene, the saturation of aromatic rings, the orientation phenomena of benzene-ring substitutions, the orientation phenomena of additions to conjugated systems, and for many other "singularities" of conjugated systems, grouped under the general concept "of an aromatic nature."

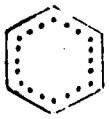
There was no urgent need for replacing the generally accepted formulas by new ones. Even if we ignore for the moment Kekule's oscillatory hypothesis, the absence of any ortho disubstitution derivatives of benzene might be explained as due to the instability of the second isomer--its pseudomeric relationship to the first one. Even if we ignore the hypothesis of alternating polarity, the orientating properties of conjugated systems might be explained as due to the production of ionized quinone structures that were pseudomers of the usual ones in the reactions. In this manner the major discrepancy could be explained away within formulas with localized orbits and within the concept of tautomerism (pseudomerism).

The situation was not so good insofar as the findings on the stability or saturation of conjugated systems were concerned. To explain these findings they had recourse to Thiele's formula, which crudely violated the valence and octet rules. It is curious that the practical importance of Thiele's formula was confined to this merely episodic role, the usual formulas continuing to be employed in representing molecules and reactions. The lack of faith in Thiele's formulas was so great that even the concept of conjugation did not acquire its sole possible real meaning--a continuous multiplicity of bonding between the atoms of conjugated systems--but retained a purely formal content that explained none of their singularities--an alternation of single and multiple bonds in conjugated systems. In essence, chemists associated the notion of the alternation of single and multiple bonds with various singularities in the properties of substances and simply ignored the problem of the origin of these singularities: of an aromatic nature, and so forth.

The exceptional importance of the above-mentioned findings, secured by physical methods, lies in the fact that they have made evident the continuous multiple bonding of atoms in conjugated systems. The substitution of new formulas that directly express the continuous multiple bonding of the atoms in conjugated systems for the generally accepted formulas for conjugated compounds, with their alternating single and multiple bonds, has become obvious.

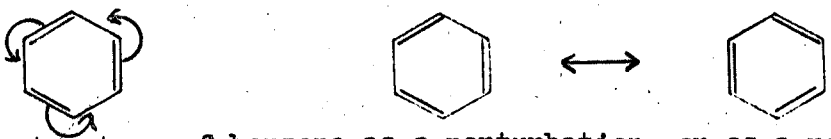
As will be shown below, these new formulas can be found within the framework of the Butlerov theory of chemical structure. Regrettably enough, the Butlerov theory has been forgotten, and it is the mechanistically minded "contemporary chemists" who have busied themselves with the search for new formulas.

The "contemporary chemists" have made use of the data obtained by physical methods to proclaim the fictitiousness of the chemical structure formulas and to affirm the correctness of the Thiele formulas, with their delocalized orbits and bonds. It was soon found, however, that the Thiele formulas were of no use in explaining the orientating properties of conjugated systems. It was the Ingold and Pauling formulas that managed to "eliminate" this contradiction. These formulas made it possible to continue using the previous chemical structure formulas to describe the properties of conjugated systems. The convenience of the Ingold and Pauling formulas lay in the fact that in explaining the "equalization" of the bonds and the "decrease" of energy in conjugated systems, the chemical structure formulas entering into the Ingold and Pauling formulas could be set down as fictions, wholly equivalent to the Thiele formulas.



This apparent way out of the difficulty proved to be a blind alley. At bottom, the episodic attraction of the concept of fictitiousness plays the same role as that formerly played by the episodic attractiveness of the Thiele formula.

The mesomerism-resonance theory does not provide any new formulas for the chemical structure of conjugated compounds but merely a modernized way of circumventing such formulas. All we need do to convince ourselves of the unsatisfactoriness of the Ingold and Pauling formulas as expressions of the structure of conjugated compounds is to examine the mesomeric and resonance formulas for benzene:

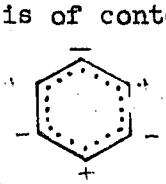


Expressing the structure of benzene as a perturbation, or as a resonance, or as a mutual influence in the molecule of the hydrocarbon cyclohexatriene does not resolve the problem of the structure of benzene but merely glosses over it.

As might have been expected, the mechanist approach to the problem of the chemical structure of conjugated compounds proved to be fruitless. The Thiele formulas could not reflect the findings on the orientating properties of conjugated compounds, while the Ingold and Pauling formulas, ignoring "the facts that are most valuable for science," constituted a brake upon the development of organic chemistry, no matter what the trappings with which they were presented.[1]

The new data secured by physical methods, together with the data on the "singularities" of conjugated systems that have been common knowledge up to now, must be reflected in the new formulas for the chemical structure of conjugated systems if these latter are to encompass all the available data. These new, true, formulas must be a straightforward and single-valued expression of the chemical interrelationships among atoms and among atoms, electrons, and nuclei within molecules--the chemical structure of conjugated compounds.

Within this framework, let us consider the central problem--the structure of benzene. The only possible, and practically complete, formula for benzene on the basis of contemporary electronic and nuclear concepts is the benzene formula reproduced herewith. This formula expresses the alternation of positively and negatively charged carbon atoms in the benzene ring, identically linked to each other by double electrovalent-covalent homopolar bonds. This formula makes use of the classical concept of electrovalent bonds, established without the sharing of



[1]Mechanism is thus not merely the gnoseological root of idealism in chemistry, but also hampers its development.

electronic duplets in two-atom orbits, so that it does not violate the rules of the localization of electron orbits in one or two orbits, of the octet, and of valence numbers. This formula combines all the experimental data on the properties and the mechanical state of benzene, of its analogs, its homologs, and its derivatives. And, lastly, this formula, directly and unequivocally expressing the sequence, the multiplicity and the manner of the atomic bonds, fully conforms with the Butlerov concept of chemical structure.

There are three obstacles to the recognition and spread of the formula cited. The first is of a superficial nature. Inasmuch as the concept of an electrovalent bond is usually associated with the notion of bond polarity, the formula will be regarded as failing to agree with the presence of an axis of symmetry of the sixth order in the benzene molecule. If we bear in mind that the plus and minus signs in the cited formula represent the atomic charges rather than the electron distribution, the first--superficial--obstacle to its adoption is eliminated automatically.

The second impediment is more serious. We have to overcome the customary notion of the electrovalent bond as that of a polar bond. We have to convince chemists of the feasibility of a homopolar electrovalent bond.

Notwithstanding the apparent paradoxicality of the concept of a homopolar electrovalent bond, it has a logical foundation. Let us start with the classical notion of an electrovalent bond as one formed by the sharing of an electron pair in a two-atom orbit. Within this framework we cannot reject the assertion that in the formation of an electrovalent bond between two equally electronophilic atoms (say, between two carbon atoms), the electron density ought to be distributed uniformly owing to the deformation of the electron shells of the atoms. There remains the problem of what may serve as the cause of the formation of an electrovalent bond between equally electronophilic atoms, rather than a covalent bond. The answer may be found in a comparison of the new formula for benzene with the hexatriene formula for its pseudomer. The six electrovalent bonds doubtless represent an increase in energy over three covalent bonds. The reason for the formation of an electrovalent bond between equally electronophilic atoms may be the increase in energy that accompanies the conversion of one covalent bond into two electrovalent bonds. Thus, the concept of a homopolar electrovalent bond is not logical nonsense. The reality of this concept is given by the fact that it is the only one that opens up the possibility of providing a practically and methodologically complete solution of the problem of the structure of conjugated compounds.

The third obstacle to the adoption of the formula we have cited is of an ideological nature. The justification for the concept of a homopolar electrovalent bond is founded upon the notion of the supramechanical phenomenon involved in the attachment of electrons to nuclei. This concept is in conformity with the Butlerov concept of chemical structure--the qualitative difference between the relationships of linked and unlinked atoms being due to the qualitative difference in the relationships between the electrons and the nuclei. From the mechanical standpoint, however, the attachment of electrons to nuclei is a matter of the distribution of electron density about the nuclei, so that the notion that, in addition to the general space-force relationships between electrons and nuclei within molecules, there exist some other, peculiarly combining-chemical relationships does not enter the mind of the "contemporary chemists."

Decisive proof of the reality of the notion of supramechanical relationships between electrons and nuclei is afforded by the fact that the dependable formulas of chemical structure, with orbits localized in one or two atoms, which have been tested in a vast number of experiments, become fictions outside the framework of this notion.

Inasmuch as only the Butlerov affirmation of the truth of chemical structure formulas leads to an understanding of the laws of chemical phenomena and to a mastery of these rules for practical ends, as the history of the development of organic chemistry has shown, it is evident that the notion of supramechanical relationships between electrons and nuclei conforms to reality.

These are the three obstacles to the adoption and the spread of the benzene formula cited above. They will be overcome. This formula deserves to live, since it alone provides a way out of the practical and methodological blind alley into which chemical theory has been led by the "contemporary chemists." The solution of the problem of the structure of conjugated compounds provided by this formula is another splendid triumph of A. M. Butlerov's theory of chemical structure.

A. M. Butlerov wrote: "Now that we have established the major facts, it will not be wholly superfluous to say a few words about a minor matter--formula notation. Remembering that what matters is not the form, but the essence, the concept, the idea, and bearing in mind that the formulas representing isomerism must logically express actual molecules, i.e., certain chemical relationships existing within them, we readily see that any notation may be satisfactory, provided it satisfactorily expresses these relationships... If terms are not defined adequately, however, another notation may result in misunderstandings" (p.455).

The notation comprised in the Ingold and Pauling formulas has resulted in a quandary pregnant with evil consequences. The wide acceptance of the mesomerism-resonance theory has been due to the fact that most chemists have erroneously taken the curved arrows in Ingold's formulas to be merely graphic symbols of the order in which the electron orbits are redistributed during reactions, while the double-ended arrows of Pauling's formulas have been taken to be merely graphic symbols of the tautomeric and equilibrium interrelationships of structures connected by these arrows. To avoid perplexities, we now have to stop using the Ingold and Pauling formulas. The employment of curved and double-ended arrows as graphic symbols without any mesomerism-resonance significance should be postponed until the Butlerovian significance of chemical structure formulas has been clearly understood.

Strange though it may seem, the significance of chemical structure formulas still remains unclear. The possibility of judging the methods of synthesizing substances and their properties as well as the mechanical states of molecules, from chemical structure formulas has created the impression that these formulas are the direct expressions of these methods, properties, and states. The plurality or the variability of the latter has led to the conclusion that the chemical structure formulas are inexact and have to be developed into Ingold or Pauling formulas. The single-valued numerical correspondence between the formulas of chemical structure and the molecules is lost, and chemical theory is transformed into a Machian scholasticism.

We must understand the decisive significance of Butlerov's principle of the direct and single-valued representation of molecules for the scientific classification of known substances and the prediction of unknown ones--for chemical theory. Butlerov's idea of chemical structure has the qualities of genius because he was able to find, among the multiform and variable characteristics of molecules, the one major and only invariant characteristic that defines the discreteness and specificity of the molecule, the loss of which suddenly transforms the molecule into a different one. Butlerov discovered the meaning of a chemical structure formula as a scientific abstraction that truly and

directly expresses the qualitative definiteness of a molecule and thus converted this formula into one of the most important tools for the development of chemistry.

It must be borne in mind that that a chemical structure formula is not abstract in the sense that such a formula alone is not enough to represent clearly the given states and properties of a molecule (that is the meaning in which the term "abstraction" is employed in the report of the Commission of the Division of Chemical Sciences), but rather in the sense that it directly expresses nothing but the chemical interactions of atoms with atoms, electrons with nuclei, within molecules; a chemist's judgments, of given methods, properties, and states (or conversely) from this formula are mediated by his knowledge of how the latter depend upon chemical structure and are governed by the decisive importance of the qualitative definiteness of the molecule for all its other multiform and variable characteristics. Efforts to transform a chemical structure formula into an expression of multiform and variable mechanical states or chemical properties are absurd and harmful.

Full comprehension of Butlerov's idea of chemical structure is needed to avoid the serious quandaries which result from the Ingold and Pauling formulas.

In conclusion, it may be useful to define the interrelationships of the various theories aiming to solve the structural problem. The structural, stereochemical, coordination, and electronic theories, enriched with the Butlerov concept of chemical structure, constitute in the totality A. M. Butlerov's theory of chemical structure; therein lie the developments of the future. The "new structural theory" I have advanced is nothing but a refinement of the electronic theory in the light of the Butlerov theory of chemical structure and an endeavor to apply this theory to solve the problem of the structure of conjugated substances.

As for the mesomerism-resonance theory, in all its modifications, it is the direct opposite of A. M. Butlerov's theory of chemical structure and represents nothing but an expression of a mechanistic viewpoint in chemistry, an unscientific Machian concept that is sterile in practice.

A. M. Butlerov's theory of chemical structure resembles D. I. Mendeleev's periodic system in that the latter reveals the supramechanical laws governing atomic structure, thus making it possible to predict the multiformity and properties of atoms, while the former reveals the supramechanical laws governing molecular structure, thus making it possible to predict the multiformity and properties of molecules. The theories of D. I. Mendeleev and A. M. Butlerov, in combination, provide a practically and methodologically complete solution of the most important problem of chemical theory--the structural problem.

Received October 1, 1951.