DISCUSSION

THE SECOND EDITION OF THE REPORT OF THE COMMITTEE OF THE ORGANIC CHEMISTRY SECTION OF THE ACADEMY OF SCIENCES USSR "THE STATE OF THE THEORY OF CHEMICAL STRUCTURE IN ORGANIC CHEMISTRY" [1]

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I have had occasion to express my dissatisfaction with the first edition of this report [2]. I cannot remain silent on the second edition of the report as the "corrections and complementary material" introduced into it (page 4)* do not remove the fundamental discrepancy between the interpretation of the authors of the report and my theses [3], on which the report is based, concerning the practical fruitlessness, theoretical inconsistency and methodological fallaciousness of Ingold and Pauling's theory of mesomerism (resonance), its direct contradiction of Butlerov's tried theory of chemical structure and the necessity for a further development of chemical theory along Butlerov's lines. My remarks on the second edition are dictated not only by my obligation as the author of these theses to see that they are used, not to the detriment, but for the benefit of Soviet and world science, but also by my right to disclaim responsibility [10] for the interpretation placed upon the theses by the authors of the report (my silence might be mistaken as approval for the new version of the report). These remarks are all the more necessary because, owing to the great prestige of the committee, the fundamental misrepresentations by the authors of the report are being reproduced in other publications, particularly in textbooks [4].

Outwardly, the conception of the authors is a duplication of my own: a theory is proposed which is considered as a contemporary modification of Butlerov's theory of chemical structure and is opposed to the contemporary Ingold and Pauling theory of mesomerism. The difference consists in the fact that in place of my "new structural theory" a theory is advanced by the authors which is directly opposed to it and identical to the theory of mesomerism (the difference is purely one of nomenclature -- in this connection see the verbatim report of my speeches at the All-Union Conference [2]). The paradoxical nature of the resulting conception has remained unnoticed by the authors because of a number of logical errors in their judgments.

One of the most serious errors of the authors is their interpretation of Butlerov's conception of two categories of mutual influence of atoms (page 7) in the sense of two types of spatial "displacements" in molecules (page 15). In actual fact Butlerov assigned the greatest significance to that variety of the mutual influence of atoms which is accompanied by their chemical change and which is reflected in contemporary (electronic) formulae of chemical structure as the distribution of the electrons between atoms, i.e. as the chemical composition of atoms in molecules (as a result of the yielding or acquisition or sharing of electrons, this composition is different from the electronic composition of free atoms); in consequence, the second -- spatial -- variety of the mutual influence of atoms includes only those electrostatic reactions of atoms having different electrical affinities in molecules which are transmitted along the chains of atoms by an inductive mechanism and determine the distribution of the electron density between the nuclei within the limits of the given distribution of electrons in atoms (in this sense it is possible

*Here and subsequently, the references to page numbers, without an indication of the source, relate to the second edition of the report.

to speak of the physical state of chemical structures). Affirming in every way the fictitiousness of structural-electronic formulae* — as true and well-defined expressions of the chemical structure of stable molecules, ions, bipolar ions, radicals, biradicals, complexes and unstable ones (pseudomeric with the former)** — the authors fail to notice that the mere replacement of concepts of resonance or disturbance by that of mutual influence (without the recognition of the truth of structural-electronic formulae***) is insufficient to convert the "mechanistic," "Machist," "idealistic," "common," "illusory" (pp. 45, 50 theory of Ingold and Pauling into the materialistic, quantum-mechanical, fruitful, contemporary modification of the thoery of chemical structure and mutual influence of Butlerov and Markovnikov. It is obvious, however, that the authors' theory (theory of mesomerism), by its method of multistructural expression**** not so much of the "actual nature of the molecule" (p. 10) as of its properties ("dynamic effects," p. 78) is a modification of Kekule's theory and not Butlerov's, and that it is, therefore, incorrect to represent it as such.

The second extremely serious error of the authors is their neglect of the chemically highly important principle of quantum mechanics concerning the saturability of bonds (p. 22), i.e. the capacity of an electron to pair with only one electron, to take part in the formation of not more than one covalent bond (in consequence of Pauli's principle). The new hypothesis of the authors (p. 32) concerning the nature of conjugation (single electrons remain in monoatomic orbits and "pair" with two electrons which are adjacent and have opposed spin, might have been considered as a hypothesis to the effect that only π-electrons do not obey this principle and as, therefore, not contradicting it as a whole, if the authors had confined themselves to the concept of π-conjugation and had left aside $\pi-\zeta$ and ζ-conjugations (pp. 103-116); by failing to do this, however, the authors in substance oppose this theory to the theory of quantum mechanics as a whole*****. It is evident that the new hypothesis of the authors can only be regarded as an attempt to explain the nature of π-conjugation by the polyradical structure of conjugated systems. At this point, however, a number of objections arise. The hexaradical formula of benzene [6] is not suitable for explaining the alternating polarity in the benzene ring, and while giving the appearance of explaining the causes of the instability of the penta-carbon analog of benzene [7], it cannot provide even this semblance of an explanation in cases of odd-numbered carbon analogs of butadiene and anthracene [8]. In addition, if it is taken into consideration that the paramagnetic properties of radicals are not removed either by the above-mentioned "pairings" of the electron with other electrons (for example, triphenylmethyl, p. 80), or by the even-numbered electronic composition of the molecules (biradicals, p. 83), it will be seen that the hexaradical struc-

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*The authors criticize Ingold and Pauling's theory for its use in the real sense of concepts of resonance or disturbances in fictitious structures expressed by structural-electronic formulae ("valence systems," "imaginary forms," pp. 42-50). The opinion expressed by the authors that "valence systems" were devised in quantum mechanics for convenience in calculations (pp. 42-43) is incomprehensible if only because it also applies to the Ingold formulae which were known long before these calculations originated.

**At the present time the reality of the usually listed unstable "intermediate products" of reactions is beyond doubt. The authors' interpretation of my conception of "electronic pseudomers" as the multistructural quality of molecules (p. 55) in no way corresponds to what I wrote in my "Essays" [3] and "Lectures" [9], to which the authors refer.

***Such a recognition is impossible because the mesomeric method of multistructural expression of the structure of the molecule (Ingold and Pauling's formulae) used by the authors in their theory, rests on the necessity to affirm the fictitiousness of "structures."

****The authors prefer to use the abbreviated notation of Ingold, which consists in taking one of the structures and marking the others on it by curved arrows. At the same time the authors recognize the equivalence of the theories and the formulae of Pauling and Ingold (pp. 48, 49, 118).

*****The fallaciousness of the conception of $\pi-\zeta$ and ζ-conjugations ("hyper-conjugation," "Nathan-Baker effect") has long been demonstrated [5]. The authors cannot abandon this concept because it is precisely in this sphere that the most important Soviet contribution to the theory of mesomerism, the affirmation of whose scientific value is the concern of the report, has been made.

ture of benzene does not agree with its diamagnetic properties. Finally, it must be pointed out that polyradical formulae are inapplicable in cases of π-conjugated systems of types of carbonate and guanidine ions, the cations of cyanine dyes, nitro and amino groups, etc., characterizing similarly conjugated systems of hydrocarbons by the coplanicity, by the straightening out of bonds over their length, by valance angles of the order of 120°, by the reduction in energy, etc. (this similarity makes it necessary to apply the hypothesis of π-conjugation in all instances). The fallaciousness of the authors' new hypothesis of conjugation is indicated by the fact that when they give factual data they do not use polyradical structures but Ingold's mesomeric formulae; this hypothesis only creates an illusion of a difference between the theory of the authors and Ingold and Pauling's theory of mesomerism.

The second attempt of the authors to retain Ingold and Pauling's formulae by reconciling the mesomeric conception of the fictitiousness of the formulae of chemical structure with Butlerov's conception of chemical structure has led, as might have been expected, only to a further accumulation of logical errors.

LITERATURE CITED

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[2] Verbatim Report of the All-Union Conference on "The State of the Theory of Chemical Structure in Organic Chemistry." Academy of Sciences USSR Press (1952). *

[3] G. V. Chelintsev. Essays on the Theory of Organic Chemistry, State Chem. Press (1949).*

[4] A. E. Chichibabin. The Principal Bases of Organic Chemistry, Vol. 1, State Chem. Press (1953); *O. A. Reutov. Theoretical Problems of Organic Chemistry, Moscow State University Press (1956).*

[5] G. V. Chelintsev, Bull. Acad. Sci. USSR, Org. Chem. Sec., 1949, 410; 1950, 536; M. I. Batuev, J. Gen. Chem., 26, 1888 (1956); * 27, 876 (1957). * *

[6] A. E. Chichibabin, ibid., p. 123.

[7] O. A. Reutov, ibid., p. 322.

[8] G. V. Chelintsev, Problems of Philosophy, No. 6, 190 (1953).

[9] G. V. Chelintsev. Six Theoretical Lectures in the Organic Chemistry Course. K. E. Voroshilov VAKhE Press, 11, 48, 87-92 (1953).

[10] I. Moyer Hunsberger, J. Chem. Educ., 1954, 504.

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* In Russian.

** Original Russian pagination. See C.B. Translation.