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Abstract

Full Text

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THE NATURE OF SYSTEMS OF CONJUGATED BONDS IN COALS

The large class of natural organic substances grouped under the name fossil coals constitutes about 50% of the reserves of organic matter on our planet. Chemists often encounter the formation of coals when carrying out reactions with various organic substances. Despite the fact that chemists often work with natural and artificial coals, their structure is still little known to us. In coal chemistry, three hypotheses on the structure of coals are widespread: low-molecular, colloidal, and high-molecular; moreover, the majority adheres to the last of these. It should be noted that none of them has sufficient grounds to become a theory.

With regard to the nature of the system of conjugated bonds in the main type of coals—humic coals—most researchers have long held the view that it is fundamentally aromatic. The present article is devoted to an analysis of this question.

In nature there exists a natural process of coalification, in which, under the corresponding conditions of occurrence, the carbon content changes from approximately 50 to 98%. The phenomenon of coalification is characteristic of all deposits; for example, in the Donets Basin, seams extending from northwest to southeast over a distance of 40-60 km change from long-flame coal to anthracite.

Modern coal chemistry, in general terms, explains coalification by the growth of aromatic lattices in coals, i.e., by an increase in the degree of aromaticity of its structure ([1,2]). Thus, in coals (96% C), of 101 C atoms, 99, in the opinion of Van Krevelen ([2]), are aromatic; that is, the structural unit already contains about 39 aromatic rings. In this case it follows that anthracite is very close to microcrystalline graphite, containing about 50 rings. In nature, cases of the transition of coal into graphite have been observed only in contact metamorphism, i.e., under the action of the heat of hot magma. It has been established that the activation energies of the process of graphitization of coals are large and reach 90-120 kcal/mole, whereas the process of coalification, according to Kasatochkin ([3]), proceeds with an insignificant entropy effect. In the present case we are faced with a contradiction, which is further aggravated by the fact that the most condensed of the known hydrocarbons, sym-tetrabenzocoronene (11 rings), is soluble and stable in air at 700° ([4]), which has not been observed with respect to anthracites. Many contradictions have accumulated between the

concept of the aromaticity of the skeletal structure of coals and their chemical properties. This circumstance is reinforced by the fact that the very concept of aromaticity in organic chemistry has undergone significant changes, whereas in coal chemistry these changes have not been taken into account.

The second nexus of contradictions lies in the interpretation of the results of coal oxidation. As is known, upon oxidation with HNO_3, NaOH + O_2, NaOH + $KMnO_4$, etc., benzene-carboxylic acids are obtained from humic coals. On average, tricarboxylic acids are obtained, but as coalification proceeds the average composition of the acids obtained shifts nonlinearly toward tetra-

carboxylic acids. The oxidation reaction products contain, in appreciable amounts, substances identical in elemental composition with benzenecarboxylic acids, but not being such acids. In some cases the oxidation products consist exclusively of such substances (5). Acid yields from most coals are below 40%, and if it is assumed that all of them are benzenecarboxylic acids, then the yield in benzene nuclei will be below 20%. It is difficult to judge from such data the aromaticity of the structure of the original coals. It is considerably easier to judge the principle of bond conjugation in coal, since on average there are three COOH groups per one nucleus, showing that conjugation of double bonds in coals can occur quite completely through hexagonal "benzene" rings. With such an interpretation, the following facts, which previously had no explanation, become comprehensible: oxidation with ozone does not give products corresponding to the oxidation products of aromatic compounds (6); oxidation with H_2O_2 in acetic acid gives acidic nonaromatic compounds in high yields (7); oxidative-hydrolytic decomposition according to Shemyakin again leads to nonaromatic compounds (8).

In the modern interpretation of aromaticity, an important factor is resistance to oxidation. With regard to the resistance of coals to oxidation, it is necessary to note their comparatively easy oxidizability (9).

In bromination of coals, Stahlschmidt (10) and Wheeler (11) noted that the addition reaction predominates, rather than substitution. Only at 65° does the substitution reaction begin to dominate. Fuchs (12) established that bromine is readily eliminated from bromo derivatives by 2/3 with calcium acetate or alkali. In sulfonation, Pictet (13) established that, despite swelling, coals are sulfonated with difficulty; moreover, the more carbonized the coal, the more weakly it is sulfonated. Chlorosulfonic acid does not add to coals (14), and coals are not nitrated without oxidation (15).

The magnetic susceptibility of coals was investigated by Honda and Ouchi (16), who established their diamagnetic constants $\chi = 0.53—0.78 \cdot 10^{-6}$ CGSE at a carbon content of 62–87%. Calculation by the Larmor–Langevin formula gives the value of the mean radius of magnetic orbits as 0.68–0.78 Å, whereas for graphite $R_{av} = 7.8$ Å, and for diphenyl $R_{av} = 1.6$ Å. As is evident, in aromatic hydrocarbons the diamagnetic constant is considerably greater (17) than in coals.

In recent years, extensive spectroscopic studies of coals have been carried out, especially in the infrared region. In deciphering the spectra, tables compiled for aromatic compounds were used. Absorption lines corresponding to CH_{arom} are visible in coals containing up to 89% carbon, in which, according to Van Krevelen (2), there are, per structural unit of 48 C atoms, 37 aromatic and 11 hydroaromatic C atoms. In this case the appearance of a continuum for CH_{atom} becomes incomprehensible, whereas, for example, diffuse lines of C–O and C–O–C groups are still visible (up to 93% C in coals). It should be noted that absorption is absent at 5.8–6 μ, which indicates the absence of unconjugated double bonds. Since the absorption spectrum indicates groupings that are thermodynamically unstable (17, 18), the deciphering of spectra with respect to aromatics in coals is surprising. After all, one of the criteria of aromaticity is the thermodynamic stability of aromatic compounds. Spectra in the ultraviolet region can no longer be deciphered by tables corresponding to aromatic compounds. When individual aromatic compounds are added to coals in amounts of 10 percent or more, the lines of the latter can be detected in the ultraviolet spectrum (19). Concluding the review of the principal contradictions in views on the aromaticity of the structure of coals, it is also necessary to recall the double refraction of coals and dichroism, i.e., coal molecules lack both a center and symmetry.

The refractive index of coals, when the ray travels perpendicular to the bedding, increases from 1.80 (C = 68%) to 1.91 (C = 86%), and when the ray travels parallel to the bedding, from 1.80 (C = 68%) to 1.85 (C = 85%) (20, 21). Birefringence shows that electronic transitions in different planes occur differently; these cases are examined in detail in the chemistry of dyes (for example, almond red, etc.–systems of conjugated bonds with disturbed coplanarity of the molecule). From consideration of the optical properties there follows the possibility of regarding the packing of coal molecules as systems of uniaxial crystals. In X-ray photographs of coals two diffuse bands of different width and intensity are visible, the interpretation of which, by analogy with graphites, is undoubtedly strained (1, 2). It is simpler to regard these lines as specific to the amorphous state, as is done for liquids and amorphous polymers.

It will be more correct to base the structure on a system of conjugated bonds which, according to X-ray structural analysis and optical properties, is not planar (aromatic systems are planar!). Such a system has only partial overlap of π-electron orbitals, and its hexagonal elements provide the perfection of the conjugation system in three dimensions. Depending on the overlap of the π-electron orbitals, the macromolecule, with its generally electronegative character, exhibits one or another chemical activity or inactivity, which are also connected with the effect of hyperconjugation. With such an interpretation, the easy oxidizability of coals, the sharp increase in uncertainty after mild reduction, and the thermodynamic instability of coals become understandable.

Thus, the material accumulated by coal chemistry and the modern concept of aromaticity in organic chemistry contradict the old views established as far back

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as the 1880s. Clearly, at the present stage they must be abandoned.

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