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Abstract

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ON THE HYDROLYTIC DECOMPOSITION OF OXIDIZED HARD COALS

(Presented by Academician M. M. Shemyakin on 12 I 1960)

In coal chemistry, much attention is paid to humic acids, the formation of which from coals is closely connected with the hydrolysis of the organic mass of coal in alkaline media ([1]). The introduction of polar functional groups into the coal macromolecule considerably facilitates the course of the hydrolysis reaction ([2]). However, the low-molecular-weight compounds obtained in this process contain a considerable number of double bonds and polar groups, which makes their study difficult. In accordance with these data and with M. M. Shemyakin' s theoretical scheme of hydrolytic decomposition ([3]), it was decided to use the Kolbe carboxylation reaction, which proceeds smoothly for higher phenols.

We give the characteristics of an oxidized hard coal from the Kaa-Khem deposit of the Tuva ASSR, which was first beneficiated by the method of I. I. Ammosov ([4]), and then chemically (10% HCl and 4% H_2F_2):

Chemical composition of the coal (in percent)

Petrographic composition, %	A	Stotal	C	H	N	O by difference	COOH groups*	Phenolic OH groups*	Yield of humic acids
99.9 clarene	0.12	0.30	67.22	3.88	1.59	27.01	1.97	3.69	43—45

* Determined by the chemisorption method, in milligram-equivalents per 1 g.

As is seen from these data, the coal under study may be regarded as a peculiar polyphenol, for the carboxylation of which the Kolbe reaction ([5]) may be used

$$ROH \xrightarrow{NaOH;\ CO_2} R(OH)COONa \tag{I}$$

with subsequent hydrolysis of double bonds of the olefinic type (³)

$$>C=C<+\mathrm{H_2O}\rightarrow>\mathrm{CH}-\mathrm{C(OH)}<\rightarrow>\mathrm{CH_2}+\mathrm{O}=\mathrm{C}< \qquad \text{(II)}$$

The simultaneous course of the two reactions should reveal the previously unknown specificity of the structure of the organic substance of coals.

To 40 g of coal were added 400 ml of a 15% aqueous solution of NaOH, through which, after homogenization with stirring, a stream of CO_2 was passed at a rate of 1.2–1.3 l/hour. The experiment lasted 24 hours at 94–98°, after which the mass was acidified to pH 3. The precipitate was filtered off, washed, and treated with hot 70% alcohol, which extracted 22.1% of a resinous, brown, acidic product. The residual coal on the filter was almost completely soluble in alkalis, i.e., it consisted of humic acids. It was established that eightfold repetition of these operations makes it possible to transfer into the alcoholic solution 94.7% of the organic substance of the coal. As shown by M. M. Shemyakin and I. A. Red' kin (⁶), under the conditions described by us it is possible

Table 1

Characteristics of low-molecular-weight hydrolysis products

Fraction	Name	C	H	N	S	Br	OCH_3	O by diff.	C/H atom.	H/O atom.	Acid number	Oxidation number	Mol. wt.
Acid	Acids	55.78	4.13	1.44	0.76	–	1.51	39.33	1.13	1.69	76.9	102.5	–
Acid	Reduction product	68.80	5.85	1.58	1.36	–	–	28.39	0.98	3.22	–	–	–
Acid	Bromination product	48.84	3.35	–	–	22.45	–	~25.36	1.27	~1.84	–	–	120.5 (in H_2O)
Acid	Oxidation product	44.25	3.85	–	–	–	–	~51.40	~1	~1	320.5	270.5	–
Neutral	Neutral	71.37	8.42	0.75	–	–	–	16.46	0.73	7.81	–	273	163.2 (dioxane)
Neutral	Bromination product	44.82	5.60	–	–	37.53	–	~12.05	0.67	~7.4	–	–	–
Neutral	Their 2,4-dinitrophenylhydrazone	39.51	3.7	27.36	–	–	–	29.42	–	–	–	–	–

Fraction	Name	C	H	N	S	Br	OCH_3	O by diff.	C/H atom.	H/O atom.	Acid number	Oxidation number	Mol. wt.
Basic	Bromination product of coal	40.07	2.65	–	–	42.81	–	~14.47	1.27	~2.76	–	–	–
Basic	Oxidation product of coal	45.16	4.84	3.32	–	–	–	46.68	0.8	1.83	373.8	306.4	94.5 (in H_2O)

one may expect, besides formation according to scheme II of ketones, the production of certain amounts of acids and alcohols. We investigated the low-molecular-weight alcohol-soluble products obtained at the first stage of coal hydrolysis. In the transparent colorless liquid obtained after acidification of the reaction mass, acetic acid was found (yield based on the organic mass of coal–0.75%, or 3.28% of the total amount of low-molecular-weight products) and formic acid (less than 0.001%). The alcohol-soluble product, by successive treatment with 10% HCl and 10% NaOH, was separated into three parts: acidic, basic, and neutral (yields 88.9, 0.091, and 10.92%). Table 1 gives the analytical characteristics of the products obtained.

In alkaline solution the acids react with benzyl chloride, giving acidic amorphous esters (increase in weight 16.4%). With thionyl chloride the acids form amorphous acid chlorides, from which amides, anilides, and esters can be obtained. In alcoholic solution the acids react with semicarbazide (increase in weight 11.3%). Replacement of oxygen in rings by nitrogen was carried out in 25% NH_4OH saturated with NH_4Cl at 155-160° in ampoules for 12 hours. The product obtained in this way is similar to those described earlier (^{2}), but differs from them in that, with $FeCl_3$ in a weakly hydrochloric-acid medium, it gives an intense dark-crimson coloration characteristic of pyrrole rings. The X-ray pattern of the acids has only one broad band. Absorption spectra in the infrared region show the presence of

$$>\mathrm{CO}, \quad -\mathrm{COOH}, \quad >\mathrm{CH_2} \text{ and } -\mathrm{CH_3}$$

and the absence of conjugated bonds. Bromine derivatives were obtained by the action of bromine water on the corresponding products; reduction products–by reduction of alcoholic solutions with Zn + HCl. Oxidation was carried out by the method of Diels (^{7}), by carefully adding perhydrol to an acetic-acid solution. The yield of light-yellow amorphous oxidation products was not less than 80%.

A color transition characteristic of quinones of the chromium series was noted, and in determining the saponification numbers of the oxidation products

a decrease in the numbers with time was established. Both of these facts are analogous to the observations made by John (8) and Hooker (9) in a series of chromans, which, in our opinion, is connected with phenomena of ring opening and ring closure. The molecular weights of the products (see Table 1) were determined cryoscopically; dioxane and water were used as solvents. To determine the average value of the molecular weight of the mixture of acids, the sodium salts were used; consequently, of the value of the molecular weight of the acids it may be said that it is not less than 420 and not more than 800. Thus, the experimental data obtained by us clearly show that, during the carboxylation of coal, its hydrolytic decomposition also takes place. Consequently, in the present case we observe a dual specific reactivity of coal, which on the one hand behaves as an aromatic compound and on the other hand as an olefin. As Fuchs (10) showed, an analogous phenomenon is observed in the bromination of coals (1). In our opinion, this peculiarity of the reactivity is connected, on the one hand, with the nonplanarity of the structure, which is unambiguously shown by X-ray structural analysis, and, on the other hand, with the homonuclear character of addition reactions. The composition and properties of the products of hydrolysis and oxidation of coal indicate that the basis of its structure is a specific system of conjugated double bonds, and not hexagonal aromatic structures, as van Krevelen (11) assumes. The ease with which the carboxylation reaction proceeds is also noteworthy. These data make it possible to suppose that in nature, in the soil, under certain conditions humic acids can be formed even without the participation of plants and animals, i.e., there is probably yet another important pathway by which the carbon cycle in nature also takes place, but which previously had not been taken into account in geochemistry (12). In accordance with theoretical ideas about hydrolysis (3), the proposition concerning the role of water in the metamorphism of coals (13) also needs revision. Indeed, without concepts of hydrolysis it is impossible to understand why in nature there are no coals that do not contain water.

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