V. I. KASATOCHKIN and N. K. LARINA

1957-01-01T00:00:00+00:00

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

V. I. KASATOCHKIN and N. K. LARINA

STUDY OF THE STRUCTURE OF HUMIC ACIDS OF FOSSIL COALS

(Presented by Academician P. A. Rehbinder, 24 XI 1956)

The study of the structure and properties of humic acids is of general interest from the standpoint of investigating the chemical structure of the organic matter of hard coals.

Table 1

Sample of humic acids	W^d	A^d	C^g	H^g	A^c	C/H
	in percent	in percent	in percent	in percent	in percent	
From coal D, oxid. H_2O_2	7.55	0.31	63.81	3.62	0.35	17.6
From coal G, oxid. H_2O_2	5.72	0.25	64.42	3.50	0.28	18.4
From coal PZh, oxid. H_2O_2	8.38	0.42	64.75	3.25	0.47	19.9
From coal K, oxid. H_2O_2	6.37	0.40	65.48	3.20	0.46	20.4
From coal G, oxid. HNO_3	8.37	0.37	61.60	3.14	0.41	18.7

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

In the present study, humic acids were obtained by oxidizing Donets hard coals of the grades D, G, PZh, and K with hydrogen peroxide, and coal G with nitric acid under mild conditions, followed by dissolution in a 2% sodium hydroxide solution (see Table 1). The following methods of investigation were used: measurement of the optical density of alkaline solutions, determination of the precipitation threshold with $CaCl_2$, infrared spectroscopy, and X-ray diffraction study.

Figure 1 presents the results of measurements of the optical densities of alkaline solutions of humic acids from hard coals of a successive metamorphic series, reduced to the same carbon concentration. The course of the optical-density curves indicates a continuous absorption spectrum and may be interpreted from the standpoint of the structure of humic acids, characterized by a combination of an aromatic network of carbon atoms with lateral aliphatic chains ([1]). From this standpoint, the continuous absorption spectrum is explained by the mobility of π-electrons in the atomic carbon network, which constitutes a system of conjugated double bonds. The optical density increases regularly for the humic acids of coals along the metamorphic series ([5],[6]), which directly indicates an increase in the ratio of carbon organized in networks to carbon contained in the side chains of humic-acid molecules.

When coal G was oxidized with hydrogen peroxide, different yields of humic acids were obtained: 3.5 and 26.5%. The optical-density curves for these samples proved to coincide within experimental error; consequently, the character of the humic-acid molecules does not change during the oxidation process.

Infrared absorption spectra in the region from 2.8 to 10 μ for humic acids were obtained on an IKS-11 infrared spectrometer with LiF and NaCl prisms. In the region of stretching C—H vibrations there are absorption maxima corresponding to methylene groups, at 3.42 and 3.50 μ,

aromatic CH groups at 3.3 μ, as well as the maximum of terminal methyl groups CH_3 at 3.38 μ. Just as for the original coals, the intensity of the maximum corresponding to aromatic CH groups in humic acids increases along the metamorphic series of the original coals ([2]), which serves as an indicator of a decrease in the degree of substitution of aromatic carbon networks by side radicals in the series of humic acids of coals of a successive metamorphic series (Fig. 2). In the spectral region from 8 to 10 μ, absorption bands appear at 5.9 and 8.0 μ, corresponding to vibrations of the C=O and C—O bonds.

Fig. 1

Fig. 2

Fig. 1. Optical densities of solutions of humic acids from coals of the metamorphic series:

Fig. 3. Precipitation thresholds of humic acids of coals of the metamorphic series

Figure 2: Fig. 3. Precipitation thresholds of humic acids of coals of the metamorphic series

a –from (weathered); *b* –from G, oxidized with HNO_3; *v* –from K, oxidized with H_2O_2; *g* –from PZh, oxidized with H_2O_2; *d* –from G, oxidized with H_2O_2; *e* –from D, oxidized with H_2O_2; *zh* –from brown coal.

Fig. 2. Spectral absorption curves of humates and humic acids of hard coals: *a* –humic acids from PZh coal, oxidized with H_2O_2; *b* –Na humates of PZh coal; *v* –Ba humates of PZh coal; *g* –Ca humates of PZh coal; *d* –humic acids from G coal, oxidized with HNO_3; *zh* –products of exchange of humates with HCl; *z* –product of deuterium exchange of humic acids of PZh coal; *e* –mixed Na–Ba humates of PZh coal.

In the spectrum of the products of deuterium exchange, obtained by treating the humic acids of PZh coal with deuterium oxide D_2O, the intensity of the absorption band at 8.0 μ is significantly reduced. The spectra of Na, Ca, and Ba humates are characterized by the disappearance of absorption bands at 5.9 and 8.0 μ, associated with the transition of the carboxyl group into the ionic form (^{3}).

Comparison of the spectra of deuterated humic acids and humates shows that the absorption bands at 5.9 and at 8.0 μ in the spectrum of humic acids should be assigned to the atomic groupings C=O and C–OH in carboxyl groups.

When humates are treated with hydrochloric acid, the spectra of humic acids are restored, which is connected with the reversibility of the exchange of mobile hydro-

of carboxyl groups by metal ions. The similarity of the spectrum of Ba humates precipitated from alkaline solutions of humic acids (Fig. 2) to the spectrum of Na humates indicates partial replacement of Na ions by Ba ions and the formation of molecules of mixed Na and Ba humates with a small content of the latter, sufficient to lower their solubility.

Infrared absorption spectra of humic acids isolated from coal G upon treatment with nitric acid contain an absorption maximum at 6.55 μ, which corresponds to vibrations in the NO_2 group.

The precipitation thresholds were determined from the smallest amount of $CaCl_2$ (mg-equiv) required for the onset of precipitation of humic acids from alkaline solutions adjusted to a definite carbon concentration. A regular decrease in the precipitation thresholds is observed with increasing rank of the initial coal (Fig. 3) (^{7}).

Fig. 3. Precipitation thresholds of humic acids of coals of the metamorphic

series

The interaction of alkaline solutions of humic acids with $CaCl_2$ may be represented as an ion-exchange process with the formation of complexes of two or more humic-acid molecules, in which the carboxyl groups are linked through calcium. As a result, the stability of humic-acid molecules in solutions decreases and precipitation processes of mixed Ca and Na humates are ensured ([4]), corresponding to a low Ca content.

The precipitation thresholds of humic acids isolated upon oxidation of coal G with HNO_3 are higher than the precipitation thresholds of humic acids obtained upon oxidation with H_2O_2, owing to the presence of excess hydrophilic nitro groups.

The decrease in stability in alkaline solutions of humic acids of coals along the metamorphic series, observed from precipitation-threshold measurements, is associated with an increase in the fraction of carbon organized in atomic networks (as a result of a decrease in the degree of substitution by side radicals) and, consequently, is determined by the increasing role of the hydrophobic core of the molecules.

X-ray diffraction patterns of samples of coals, humic acids, and humates were obtained with filtered Cu radiation in cylindrical cameras of radius 45 mm. Table 2 gives the average distance between the networks, (d_{002}), and the angular half-width of the interference band (002), (^{ }_{002}), which is a measure of the orderliness of the mutual arrangement of the carbon networks ([1]). Bands with indices (100) for all the samples studied have the same diffuse character, indicating small and essentially unchanging linear dimensions of the carbon networks.

Table 2

Samples	Initial coals (d_{002}), Å	Initial coals (^{ }_{002})	Humic acids (d_{002}), Å	Humic acids (^{ }_{002})
Coal D	3.5	7.5	3.5	7.5
Coal G	3.5	7	3.5	7
Coal PZh	3.5	6.5	3.5	6.5
Na humates (PZh)	–	–	6.0	6.5
Ba humates (PZh)	–	–	–	–

Comparison of the X-ray diffraction data for humic acids and the initial coal shows similarity both in the dimensions of the carbon networks and in the interlayer ordering.

In the X-ray diffraction patterns of Na humates, a shift of the (002) band toward small angles is observed, indicating a significant increase in the interlayer distance—to $(d_{002} = 6)$ Å—compared with humic acids and the initial PZh coal, for which $(d_{002} = 3.5)$ Å. For Ba humates, the interference band (002) is not detected at all, which serves as evidence of complete disorder in the mutual arrangement of the carbo-

carbon networks. The increase in the inter-network distance should be attributed to additional electrostatic repulsive forces of the peripheral carboxyl groups present in Na humates in ionic form. The disordered arrangement of the networks in Ba humates is due to the formation of strong bonds through Ba between carboxyl groups. The observed effects of changes in inter-network distances and ordering in Na and Ba humates are direct evidence of the absence of bonds between carbon networks in an alkaline solution of humic acids and confirm the concept of a true solution of humic acids in the form of individual carbon networks with side radicals.

The experimental material presented on the study of the structure of humic acids of hard coals confirms the previously proposed scheme of the structure of humic-acid molecules in the form of individual flat aromatic carbon networks with side radicals bearing various oxygen-containing and other functional groups (1). In this connection, the process of oxidation of coal substance may be described as a process of oxidative destruction of the macromolecule with the separation of individual structural units, which pass into alkaline solutions owing to the presence of carboxyl groups formed in the process of oxidation. However, in our view, refinement of this structural scheme in the form of a chemical structural formula (8) is impossible, for the reason that the carbon networks constituting the nuclei of the molecules, as well as those in the structural units of the original coals, have a certain distribution in size, and the functional groups are statistically distributed among the molecules.

The importance of investigating the structure of humic acids for the study of the chemical structure of the organic matter of hard coals follows from the fact that the carbon skeleton of humic-acid molecules is quite similar to the carbon skeleton of the structural units of coal substance.

Received
29 X 1956

CITED LITERATURE

[1] V. I. Kasatochkin, Izv. AN SSSR, OTN, No. 9 (1951); No. 10 (1953); DAN, 88, 759 (1952). [2] I. K. Brown, J. Chem. Soc., 1955, 744. [3] L. I. Bellamy, *The Infra-red Spectra of Complex Molecules*, London, 1954. [4] G. L. Stadnikov, *Koll. Zs.*, 47, 136 (1929). [5] M. M. Kononova, N. P. Bel' chikova, DAN, 72, 125 (1950). [6] T. A. Kukharenko, DAN, 89, 133 (1953). [7] N. P. Bel' chikova, Tr. Pochv. inst. AN SSSR, 38, 33 (1951). [8] W. Fuchs, *Die Chemie d. Kohle*, Berlin, 1931.