On the Structure of Humic Acids. An X-ray Diffraction Study

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(Received May 1, 1950)

Introduction

Coal is considered as substance built by independent molecules possessing the same crystallographic meaning and a more or less highly developed aromatic character, but continuously changing van der Waals forces. J. Biscoe and B. E. Warren(1) coined the word "turbostratic" systems to express such crystallographic character for carbon blacks. H.E. Blayden, J. Gibson and H. L. Riley(2) have proved that the coal structure is also described by the word. And they suggested that the peripheral nature of crystallites might be essential for coal properties. By the concept of turbostratic system, however, the carbon cannot be distinguished from the caking coal which shows entirely different rheological characters. The author has shown from the experiments on Young's modulus of coal(3) that the weak van der Waals forces between coal molecules and strong solvation of molecules with inorganic ash are the necessary conditions for essential (caking) properties of coal. The most considerable reason of such differences of the intermolecular forces appears to be in the peripheral conditions of coal molecules. The present study is concerned from this view with humic acids.

The humic acid is defined in this paper as the chocolate-color substance which is produced by the extraction with 1% sodium hydroxide solution up to 90°, and is precipitated by adding the excess of mineral acids. This substance is interesting not only from the peripheral problem of coal molecules but for discussing the coalification mechanism from vegetable debris.

On the structure of humic acid, we have theories rather in confusion. Stadnikoff(4) gave a chain-like molecule for this substance, but W. Fuchs(5) showed from organo-chemical studies some aromatic structure. H. L. Riley(6) suggested recently that there should be a third possible arrangement of carbon structure having tilted benzene rings, but regretfully with insufficient experimental evidence.

The present X-ray diffraction study falls into two sections. The first deals with the humic acids from various "rank" of coal. The second section describes similar diffraction experiments on some derivatives from humic acids of same origin.

As to the X-ray diffraction study we have a study by J. Sedletzky and B. Brunowsky(7) on three samples of humic acids from German brown coal. Most recently the author was informed from the Chem. Abst. that H. Brusset(8) has published an X-ray study on humic acids from lignite and of the products obtained by treating it with dil. HNO_3 and solvents.

Experimental Method and Description of Samples

The generally used Debye-Scherrer diffraction method was used. Copper $K\alpha$ radiation filtered by nickel foil was employed. Exposures of 4.5 hours were necessary at a potential of 30 kv., and a tube current of 6 milliamp. After development, the photographic film was micro-photometered and the lattice parameters were obtained from the maxima on the photometer curve and the values of crystallite dimensions were calculated from the breadth of bands, drawing at both cases the back-ground blackening due to the incoherent scattering.

The descriptions of the samples are in the following. The samples from No. 1 to 5 were made from lignites, i.e. Komatsu, Takayama, Kitomo and Nagasakayama lignite respectively. Extraction by 1% alkaline solution and precipitation by hydrochloric acid were repeated twice, washed by distilled water repeatedly and then dialysed for a week. No. 6 is the humic acid prepared by "Merck." No. 7 is the humic acid extrated from the soil of a pond in Tokyo by the Oden's method.(9) The samples from No. 8

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(1) J. Biscoe and B. E. Warren, *J. Appl. Phys.*, **13**, 364 (1942).

(2) H. E. Blayden, J. Gibson and H. L. Riley, *Proc. Conf. Ultrafine Structure of Coals and Cokes*, London, **1944**, 176; *J. Inst. Fuel*, 1945, Wartime Bulletin, 117.

(3) Katsuya Inouye, Presented at the 3rd annual meeting of the Chem. Soc. Japan, Apr. 1950. The manuscript has just been sent to the *J. Colloid Sci.*, May, 1950.

(4) "*Die Chemie der Kohle*," W. Fuchs, S. 455, 1931.

(5) W. Fuchs, *Angew. Chem.* **44**, 111 (1931).

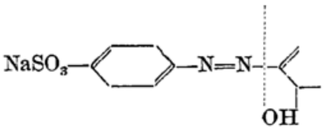
(6) H. L. Riley, *J. Soil Sci.*, **1**, 104 (1947).

(7) J. Sedletzky and B. Brunowsky, *Kolloid-Z.*, **73**, 90 (1935).

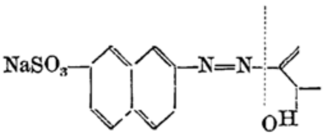
(8) H. Brusset, *Chem. Abst.*, **43**, 6395 (1949). (*Bull. soc. chim. France*, **1949**, 319).

(9) S. Oden, *Kolloid-Beihefte*, **11**, 75 (1919).

to 11 are the so-called "regenerated" humic acids(10) obtained by ca. 150 hours' air oxidation at 150° from the bituminous coals, i.e. Yubetsu producer gas coal, Takashima caking coal and Shishimachi strongly caking coal respectively. Purification was carried out as at the lignite humus. Nos. 12 and 13 are the acid azo dyes from humic acids Nos. 1 and 2 respectively, coupled with diazo-sulfonilic acid in alkaline, solution under cooling. These brown dyes are remarkable to be able to make aqueous solutions easily. No. 14 is another acid dye from humic acid No. 2 coupled with diazo-J-acid. It is noteworthy that this dye has a beautiful violet color entirely different from the original humus. These dyes were purified twice by salting-out method with sodium acetate and alcohol. No. 15 is the methoxy-derivative of the humic acid No. 2 obtained by the reaction with dimethyl sulfate.(11) The methoxy humic acid is less hydrophilic brown powder. (See the figure.)



Acid dyes Nos. 12 and 13.



Acid dye No. 14.

Table 1

No.	Sample	Lattice parameter		Crystallite dimension	
		a	c/2	a	c
1	Lignite Humus (Komatsu)	2.11Å.	3.66Å.	8.9Å.	9.4Å.
2	Lignite Humus (Takayama)	2.19	3.70	8.5	9.1
3	Lignite Humus (Tomowo)	2.16	3.60	7.2	9.7
4	Lignite Humus (Kitomo)	2.17	3.65	11.2	8.8
5	Lignite Humus (Nagasakayama)	2.19	3.58	8.3	10.9
6	Humic acid "Merck"	2.19	3.67	8.9	9.6
7	Soil Humus	1.63	3.43	—	—
8	Regenerated Humus (Yubetsu)	2.32	3.54	12.4	12.3
9	Regenerated Humus (Takamatsu)	2.27	3.57	9.6	17.5
10	Regenerated Humus (Takashima)	2.32	3.54	14.3	21.0
11	Regenerated Humus (Shishimachi)	2.12	3.44	7.8	17.9
12	Sulfanilic dye (1)	2.15	3.85	10.3	10.8
13	Sulfanilic dye (2)	2.29	3.63	8.7	10.8
14	J-acid dye (2)	2.40	3.73	—	—
15	Methoxy Humus (2)	2.24	3.70	7.0	13.2

Results and Discussions

The obtained bands are highly diffused and generally give only two reflections with sufficient intensity to permit of their use in particle size determinations. The calculated lattice parameters for these bands and crystallite dimensions are tabulated in Table 1.

It is noteworthy that all these parameters, with the only exception of No. 7, suggest these samples to possess the so-called "amorphous carbon" lattices. So naturally the author has to recognize, at least from the X-ray stand-point, the humic acid is essentially of the "turbostratic" carbon structure. The soil humus, however, shows different a-parameter and there remains little doubt that this does not yet form the highly aromatic lattice for its low maturity.

One of the results from these data is the fact that the "humic" substances, namely of the same chemical character, show various crystallite dimensions according to the maturity of their original coals. Even in the series of lignite humus, the samples from relatively high rank lignites, for example, of Kitomo or Nagasakayama lignite, have larger dimensions. Furthermore, the "regenerated" humus shows remarkably large dimensions, because of the crystallographic development of the crystallites. In other words, the coal molecules grow up in spite of the same chemical "humic" nature when they are added some peripheral groups.

In the other way from the data of derivatives of humic acids, we can understand the changing of chemical nature only by adding peculiar radicals to the peripheries of the molecules. By adding some diazo radicals, "humic" molecules change soluble in water and furthermore if we choose the adequate kind of added groups, the color can change from brown to violet.

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(10) G. T. Morgan and J. I. Jones, *J. Soc. Chem. Ind.*, **1938**, Sept., 289.

(11) The author is indepted to Mr. Kozo Higuchi for preparing these derivatives (No. 12—15). He is going to publish the preparation and characteristics of these substances. According to his analysis, diazo components are coupled at the *o*- or *p*- positions for phenolic radicals up to almost saturation, and methoxy radicals are produced by substituting the phenolic hydroxyl groups.

In the chemical common-sense, these dyes are of never "humic" nature, but they have the same crystallographic dimensions as of the original samples. (Compare Nos. 13 and 14 with No. 2, and also No. 12 with No. 1). The same consideration is available for the data of methoxy derivative which has lost hydrophilic character of humus. These facts appear to be another evidence of the importance of periphery of molecule to the nature of coal.

The long oxidation of coal means the addition of some oxygen containing radicals to periphery, and in consequence of the strengthening of intermolecular forces, as generally known, the caking properties of coal diminish and in alkaline solution the coal molecules can dissolve to produce the "regenerated" humic acid, followed by, perhaps, base-exchange reactions. It seems therefore interesting to note that the base-exchange capacities of lignite humus and regenerated humus are almost same as shown in Table 2. These data were measured by treating the sample with 200 times of 0.1 N sodium chloride solution during seventy hours.

Table 2

Sample	No. in Table 1	Base-exchange capacity
Lignite Humus	2	3.6×10^{-2}meq./g
Lignite Humus	4	5.5
Regenerated Humus	10	4.8
Regenerated Humus	11	3.9

Conclusion

Some organic chemists discuss the structure of the humic acid and often reach the conclusions in confusion. It seems not to be of essential meaning to discuss the chemical structure as if there exists a definite substance named humic acid. From the above described data and considerations, "humic" is naturally the name for a nature, not for a definite substance. The coal molecule "grows up" with same "humic" nature and on the other hand the chemical character can be changed at our option by adding adequate peripheral radicals, and the peripheral conditions appear often to be of the fundamental meaning to the essential properties of coal.

The diffraction apparatus used in this study was lent to use by the Chemical Institute, the University of Tokyo, and the author takes great pleasure in acknowledging his indebtedness to Dr. Hideo Akamatsu, without whose kind permission the author doubts whether he could have done the work, and also to Mr. Hiroshi Takahashi for his help in taking photometer curves.

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