preted on a rational basis in terms of definite optical principle. There are many questions of theoretical interest which may be elucidated.
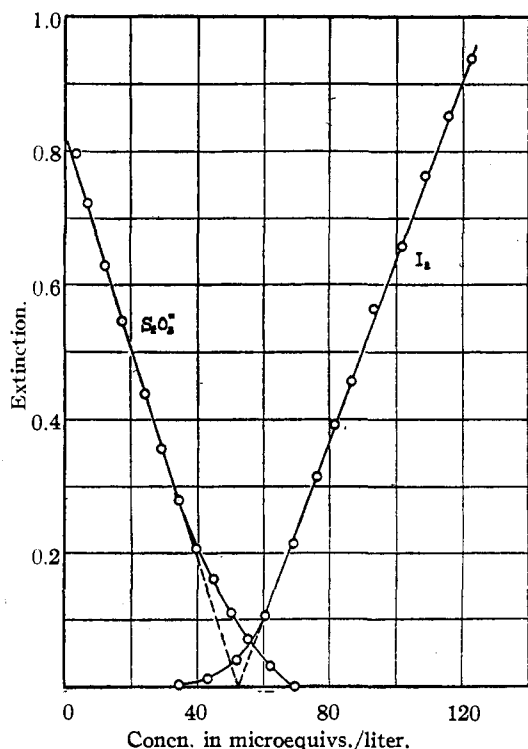

Fig. 5.

For example, the initial course of the extinction curve enables one to calculate the "apparent" dissociation constant of the starch–iodine complex, or alternately to calculate the adsorption equilibria which may be involved. We are deferring such computations until measurements, which are now under way using pure beta amylose instead of starch, are completed.

It should be pointed out that, in general form at least, our equation $E = k(c - c_0)$ has been used before, primarily to correct for deviations at various cup depths.[7,8] Our suggested c_0 is not purely empirical, however, but is definitely related to the dissociation equilibria.

Summary

Photoelectric titrations with approximately monochromatic light have been performed on the starch–iodine system. Beer's law is obeyed beyond a preliminary "dissociation stage." The equation $E = k(c - c_0)$ is satisfactory and may be applied to the Duboscq type instrument. Though admittedly complex, there is nothing about this system which requires the use of purely empirical correction.

(7) M. Winkler, Chem.-Ztg., 56, 86–87 (1932).
(8) H. Ginsberg, Z. anorg. allgem. Chem., 209, 105–112 (1932).

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The Relation of Extract to Residue in a Bituminous Coal

BY BURNARD S. BIGGS

In an earlier contribution from this Laboratory[1] it was shown that the amorphous material which constitutes the bulk of the extract dissolved from a Pittsburgh seam coal by benzene at 260° is composed of hydrocarbon units containing an average of four or five rings interspersed with oxygen-containing heterocycles or other inert oxygen linkages. It was demonstrated that the average molecular weight of these fundamental units is about 300, but that they normally exist in associated aggregates with molecular weights ranging from 450 to about 1600. In this paper evidence is presented in support of the viewpoint that such a structure is typical of the whole coal substance, and that the difference between the residue of benzene pressure extraction and the ex-

tract itself lies more in the size of the aggregate than in the essential chemical structure. The residue, except for a small portion which is very resistant toward hydrogenation, appears to be composed of large groups of nuclei which are associated or polymerized in such a complex manner that the treatment with benzene cannot dissociate them sufficiently to effect their dissolution. This conception of the structure of coal has been suggested previously by a number of investigators in this field.[2] Fischer, Peters and Cremer,[3] to account for the practically complete conversion of coal to "pseudo-bitumens" on mild hydrogenation, have definitely suggested that the residue differs from the extract mainly in its

(1) Biggs, THIS JOURNAL, 58, 484 (1936).

(2) Schrauth, Brennstoff-Chem., 4, 161 (1923); Fuchs, ibid., 12, 266 (1931); Francis and Wheeler, J. Chem. Soc., 127, 2240 (1925).
(3) Fischer, Peters and Cremer, Brennstoff-Chem., 14, 181 (1933).

TABLE I

| Humic acid from | Composition, % | | | | | | Mol. wt. | Eq. wt. | Total acidity eq. |
	C	H	N	S	Ash	O			
ES	60.95	4.19	3.76	0.48	0.76	29.86	193	240	181
EI	57.17	3.71	3.09	.34	.95	34.74	217	192	141
Residue	60.17	8.89	3.04	.55	.98	31.37	242	244	162
Whole coal[4]	60.75–62.17	3.12–3.31	2.73–4.05	.65	.95–1.44	28.9–31.9	220–250	232–248	160

degree of polymerization. Smith and Howard[5] have shown that humic acids prepared from a bituminous coal by oxidation with 1 N nitric acid have an average molecular weight of about 250 when dissolved in the polar solvent catechol. This fact is particularly significant when it is considered that these humic acids represent about 70% of the carbon of the coal, and that the reagent used in their preparation is so mild that drastic changes in the original skeletal structure are not likely to have occurred. The development by these investigators of the use of catechol for cryoscopic work on coal products makes available a valuable tool for coal research, and their work on humic acids constitutes the most convincing evidence thus far obtained for the viewpoint described above.

The experimental material presented in this paper consists of comparisons of a number of products derived from both the extract and the residue. These are (1) humic acids prepared from both sources by mild oxidation, (2) bitumens, present as such in the extract, and obtained by mild hydrogenation from the residue, and (3) high-boiling oils, prepared by repeated hydrogenation under mild conditions.

Humic Acids.—Humic acids were prepared from the ether soluble and ether insoluble fractions of the extract[1] and from the residue by oxidation with 1 N nitric acid in the manner of Juettner, Smith and Howard.[4] The yields of purified product, based on the carbon content, were about 54, 43 and 77%, respectively, for ether solubles, ether insolubles and the residue. Comparative figures on these acids are shown in Table I, along with similar data reported by Juettner, Smith and Howard[4] for humic acids prepared from the whole coal. The molecular weights were determined cryoscopically in catechol by the method of Smith and Howard;[5] the equivalent weights, representing the weight of material associated with one carboxyl group, were determined by electrometric titration; and the total acidity equivalents, representing the weight of material

associated with one acidic group (either phenolic or carboxylic), were determined by the method of Ubaldini and Siniramed[6] based on total alkali consumption from a standard alcoholic potash solution. Ether solubles are referred to as ES and ether insolubles as EI.

In addition to those differences apparent in the table, the acids from the ether solubles had a brownish-black color, and intumesced on being heated to a high temperature, whereas the other products were jet black and showed no tendency toward fusion when heated. Their only noticeable reaction to heat was an evolution of carbon dioxide which took place at a temperature above 250°. All three materials were completely insoluble in hydrocarbon solvents, and while all of them imparted some color to oxygenated solvents such as acetone, alcohol and acetic acid, the acids from the ether solubles were definitely more soluble than the others. In all these properties the differences between the humic acids from the ether solubles and those from the ether insolubles were much more pronounced than the differences between the latter and the acids from the residue; and in spite of the minor differences that did exist, the products from the extract fractions were indubitably the same type of substance as the "standard" humic acids obtained from the residue or the whole coal.

Bitumens.—The pseudo-bitumens were prepared by catalytic hydrogenation of the extraction residue at the relatively low temperature of 350°. The fraction of the product that was soluble in benzene after this treatment amounted to 72% of the original residue, and consisted of approximately equal amounts of petroleum ether soluble, ethyl ether soluble and ethyl ether insoluble materials. The close agreement in properties of corresponding fractions of the original extract and of the pseudo-bitumens is evidence that these materials were of very similar nature. In appearance they were indistinguishable, all fractions being brown powders. Their solutions in hydrocarbon solvents were red with green

(4) Juettner, Smith and Howard, THIS JOURNAL, 57, 2322 (1935).
(5) Smith and Howard, ibid., 57, 512 (1935).
(6) Ubaldini and Siniramed, Ann. chim. applicata, 23, 585 (1933).

TABLE II

Material		Approx., °C. softng. pt.	C	Composition (ash free), % H	N	S	O	Mol. wt. in diphenyl	catechol
Orig. extr.	ES	100–120	86.99	6.44	1.37	0.67	4.53	450	285
	EI	300–350	85.02	5.79	1.77	.73	6.69	1200–1600	285
Pseudo bitumens	ES	110–140	86.40	7.50	1.66	.32	4.12	486	288
	EI	350–400	85.48	7.29	1.88	.42	4.93	1300–1600	320

TABLE III

Material	Wt., g.	C	% H	Ash	O N S	Carbon, g.	% of Orig. Carbon
Original residue	100	72.58	5.29	10.78	13.73	72.58	
Oil	65	87.65	8.45	0.0	3.70	57.0	78.5
Bz sol. pet. ether insol. (contg. catalyst)	6	31.66	2.51	...	...	1.9	2.6
Spent catalyst and unconverted residue in soxhlet cup	60	9.4	..	...	...	5.6	7.7
Gases and loss	...	...	..	...	...	...	11.2

fluorescence. Comparative data are shown in Table II.

It is to be emphasized that 72% of the benzene extraction residue was here converted, in one step, into a material which had a molecular weight, in catechol, of about 300. Fischer, Peters and Cremer[3] have converted 80 to 90% of a Mathias Stinnes bituminous coal into pseudo-bitumens at an even lower temperature (260°) by prolonging the duration of the hydrogenation to five days, and by using μ-size coal. In view of the relative mildness of the conditions used, it appears that the formation of such large yields of pseudo-bitumens from coal must have resulted from the cleavage of relatively weak bonds between nuclei which were already present and which did not undergo very drastic changes during the reaction.

High-Boiling Oils.—In the work reported in the previous paper[1] the extract fractions were converted, by hydrogenation, into oils which were shown to be partially hydrogenated aromatics. The high-boiling fractions of these oils were found to have an average molecular weight of about 250 in both catechol and diphenyl, and apparently represented the hydrocarbon skeletons of the units of structure of the extract. In the present work similar oils have been prepared in high yield from the extraction residue by several repetitions of the procedure by which pseudo-bitumens were obtained, the oils being removed after each step. In five such steps a total of 78.5% of the carbon of the residue was recovered in the form of petroleum–ether-soluble oils. Analyses of the original residue and of the products obtained in the hydrogenation are shown in Table III.

Since such a high percentage of the original carbon was accounted for in the non-gaseous products of the hydrogenations, one is justified in concluding that little decomposition of the nuclear structure had occurred.[7] Further support for this conclusion lies in the fact that the oils still contained almost 4% of oxygen, nitrogen and sulfur, which would very likely have been removed if a very extensive breakdown of the nuclear material had taken place during hydrogenation.

The atomic ratio of carbon to hydrogen of these oils, about 7 to 8, together with boiling points (most of the material boiled between 300 and 460°), and the average refractive index ($n^{25}D$ 1.60) indicated that they were partially hydrogenated polycyclic aromatics, or the type previously obtained from the benzene pressure extract. This is in accord with the great bulk of evidence accumulated in the literature pointing to a foundation of six-membered carbon rings in coal.

Discussion and Conclusions.—The facts that the resinous pseudo-bitumens can be formed by mild hydrogenation of the supposedly humic portion of coal, and that humic acids result from the oxidation of the so-called "resinous" portion of coal constitute such strong links between these materials that they can no longer be considered to differ appreciably in their essential chemical structure. This conclusion does not apply, of course, to the relatively small portion of the residue which is very resistant to hydrogenation and seems to differ from the main body of the coal substance. The fact that bitumens, pseudo-bitumens and humic acids, when dissolved in catechol, have molecular weights falling roughly in the same range of from 200 to 300 indicates

(7) Sachanen and Tilicheyev, "Chemistry and Technology of Cracking," Trans. by Boehtlingk, Brown and Steik, Chemical Catalog Co., N. Y., 1932, p. 341.

that this skeletal structure is composed of units of about that average size. The conversion of both extract and residue, by mild hydrogenation, into oils which are high-boiling, but which are nevertheless distillable, tends to show that the skeletons of these oils constitute the stable portions of the units of coal structure. Little information is available in regard to the role of the oxygen, nitrogen and sulfur of coal in the structure of these units. It has been shown previously[1] that in the extract the oxygen occurs chiefly in the form of inert linkages, either of the ether or heterocyclic type; it is probable that the same is true of the oxygen in the residue.

The type of linkage by which the units are bound to each other is unknown. As pointed out by Smith and Howard,[8] the fact that the physical properties of bitumens, pseudo-bitumens and humic acids are not compatible with the low molecular weights observed in catechol seems to indicate that the linkages between units are weak enough that they can be disrupted by the dissociating influence of this polar solvent. The ease with which the units are broken apart by hydrogenation similarly suggests that they are held together by relatively weak forces.

Experimental Part

Preparation of Humic Acids.—The 16–20 mesh residue from benzene pressure extraction was ground to 200 mesh, and was freed of benzene in vacuum at 100°. The extract fractions were used as they were prepared previously,[1] the ether insolubles being in the form of a fine powder, just as they were flocculated from the benzene solution, and the ether solubles being ground in a mortar as finely as their relatively low softening point would allow. Samples (5 g.) of each material were suspended in 200 cc. of 1 N nitric acid, and the latter was kept at its boiling point under reflux for seven days. The strength of the oxidizing agent was maintained by daily additions of strong nitric acid in the required amounts as indicated by titration. At the end of the arbitrarily chosen period of time the acid insoluble products were filtered, washed, dissolved in alkali, centrifuged to remove alkali insoluble material, reprecipitated with nitric acid and finally purified by electrodialysis. The humic acids thus obtained were dried first in a vacuum desiccator over fused sodium hydroxide, and finally in vacuum at 100°. Analytical and other data are given in Table I.

Pseudo-Bitumens.—A 100-g. sample of the residue from benzene pressure extraction, ground to 200 mesh, was treated with 100 atmospheres of hydrogen (cold pressure) for twenty-four hours in the presence of 10% of its weight of Adkins copper–calcium–chromium oxide catalyst.[9] The reaction was carried out in an American Instrument

Company one-liter stainless steel bomb. The temperature measured in a thermocouple well which extended to the center of the heated portion of the bomb was 350°; that measured between the wall of the bomb and the wall of the furnace, midway in the heated portion, was 390°. The maximum temperature inside the bomb was probably not greater than 380°. When the bomb was cool the contents were transferred to a Soxhlet cup and extracted exhaustively with benzene. The extract was divided into petroleum ether soluble, ethyl ether soluble and ethyl ether insoluble fractions by the same procedure used on the original benzene extract.[1] Data on both the original bitumens and the "pseudo-bitumens" are shown in Table II.

Preparation of High-Boiling Oils.—The conversion of the residue to high-boiling oils was accomplished by several repetitions of the procedure by which pseudo-bitumens were obtained. The petroleum ether soluble products of the first hydrogenation were set aside and all the other fractions—pseudo-bitumens, insoluble residue and spent catalyst—were returned to the bomb along with a fresh portion of catalyst in the same amount as was used in the first step. A second hydrogenation was then run under the same conditions as were used before. The product was again transferred to a Soxhlet cup and extracted with benzene. The benzene solution was concentrated to 200 cc., the heavier fractions were flocculated by addition of four parts of petroleum ether, and the flocculate was separated by filtration. The filtrate was freed of solvent on a waterbath and 800 cc. of fresh petroleum ether was added to the oily residue. Most of the material dissolved, but a small amount of solid residue was left and was removed by filtration. The filtrate contained the true petroleum–ether-soluble portion, which was freed of solvent and set aside. All precipitates and residues, including the material in the Soxhlet cup, were dried, powdered and returned to the bomb, with a fresh portion of catalyst, and the whole process was repeated again. In five such steps 65 g. of oils was obtained from 100 g. of benzene extraction residue, the yields in each step in a typical run being respectively 21, 16, 13.2, 9.9 and 4.4 g. There was still a small amount (6.0 g.) of material soluble in benzene but not soluble in petroleum ether, heavily contaminated with particles of catalyst which escaped from the Soxhlet cup; and an appreciable amount of the carbon of the residue remained in the cup, mixed with the spent catalyst. Analytical data are given in Table III.

Acknowledgment.—The author is indebted to F. C. Silbert and T. B. Smith for the elementary microanalyses, and to R. C. Smith for aid in the hydrogenations.

Summary

Comparisons have been made of a number of products derived from the benzene pressure extract of a Pittsburgh seam coal and from the extraction residue. These products are (1) humic acids, obtained by oxidation with 1 N nitric acid, (2) bitumens, present as such in the extract, and prepared from the residue by mild hydrogenation, and (3) high-boiling oils, obtained by

(8) Smith and Howard, THIS JOURNAL, **58**, 740 (1936).
(9) Connor, Folkers and Adkins, *ibid.*, **54**, 1142 (1932).

repeated hydrogenation under mild conditions. The close agreement between the properties of corresponding products from the extract and residue indicates that these materials are very similar in their essential chemical structure. It is concluded that coal structure is made up of fundamental units with an average molecular weight of about 300, held together in larger aggregates by some relatively weak type of linkage, and that the extract differs from the residue mainly in the degree of this association.

Condensations by Sodium. VI. Malonic Acids from Mercury Dialkyls

BY AVERY A. MORTON AND INGENUIN HECHENBLEIKNER

The recent discovery[1] that malonic acids could be obtained by interaction of sodium, alkyl chlorides and carbon dioxide has directed our attention to the behavior of a possible intermediate, the sodium alkyl. Organo-metallic compounds of this class are conveniently prepared by action of sodium on mercury dialkyls. Analyses by Schlenk and Holtz[2] have shown close agreement with the theoretical value for a monosodium compound. Originally it was our purpose to prepare the alkyl sodium and study its decomposition products at different temperatures by carbonation. We accordingly varied the procedure from that employed by Schlenk and Holtz in order to obtain larger quantities of material. It was apparent, however, that it was unnecessary to heat the supposed amyl sodium in order to obtain other products besides caproic acid. Butylmalonic acid was always obtained in considerable amounts upon carbonating what was expected to be a monosodium compound only. This interesting result caused us to turn our attention to a study of the factors affecting the proportions of the several products from the reaction. Conditions were found whereby diamyl mercury was made to yield as high as 40–50% of butylmalonic acid. It is a reasonable inference that amylidene disodium was an intermediate product. When a similar reaction was carried out with diethyl mercury, methylmalonic acid was likewise formed although the factors needed for high yield in this case were not surveyed.

The over-all equations assumed to express the formation of the products before carbonation are
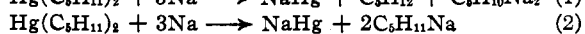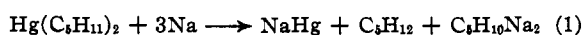
$$Hg(C_5H_{11})_2 + 3Na \longrightarrow NaHg + C_5H_{12} + C_5H_{10}Na_2 \quad (1)$$
$$Hg(C_5H_{11})_2 + 3Na \longrightarrow NaHg + 2C_5H_{11}Na \quad (2)$$

The above equations do not picture the mechanism by which the malonic acids were formed. A few possible paths are by disproportionation or decomposition (splitting out of sodium hydride[3] and addition of two sodium atoms to the amylidene so formed) of the monosodium compound, by disproportionation of the free radical, and by direct formation of amylidene (Michael's[4] mechanism) or amylidene disodium. Although it would be possible to reflect at some length on these possibilities we believe that a better opinion can be formed after more studies. A few inconclusive tests on the formation of sodium hydride are presented in the experimental portion of this paper.

Variations in the ratio of butylmalonic to caproic acid were interesting to observe because they afforded some knowledge of the conditions for increased yields of the malonic acid. Whether the total yield of acids was high or low seemed to have little bearing on this ratio but increasing the amount of solvent from 50 or 100 to 200 ml. changed the ratio from an average of 0.5 to 1.7 (see reactions 1 to 8 as compared with 11 to 14 in Table I). The cause of the variation is not clear. Possibly it is related to a change in the amount of mercury compound adsorbed on the surface of the sodium in the initial stage of the reaction. Higher ratios were also obtained when carbon dioxide was bubbled through the mixture during or immediately after the addition of diamyl mercury. (Reactions 15 to 17 and 9. Reaction 10 showed no increase.) This ratio change appears to be related chiefly to a decrease in the amount of caproic acid formed rather than to any substantial increase in the malonic acid. We were somewhat surprised that the quantity of caproic acid was so

(1) Morton, LeFevre and Hechenbleikner, THIS JOURNAL, **58**, 754 (1936).

(2) Schlenk and Holtz, Ber., **50**, 262 (1917).

(3) Carothers and Coffman, THIS JOURNAL, **51**, 588 (1929).

(4) Michael, Am. Chem. J., **25**, 429 (1901).