$$H_2O \xrightarrow{HC_2Na} NaOH \xrightarrow{RX} ROH \xrightarrow{HC_2Na} RONa \xrightarrow{RX} ROR$$

Similarly, unless extraordinary precautions are taken to exclude all moisture, ethers may be expected to result from any process in which an alkyl halide reacts in liquid ammonia solution on a sodium compound that is decomposable by water.

Summary

1. It was shown that sodium propylate, butylate, amylate, or phenate react with alkyl bromides in liquid ammonia at pressures of from 1 to 10 atmospheres to give fair yields of ethers. Alkyl chlorides or iodides are not as effective as the bromides in this reaction.

2. A similar reaction was found to result in the formation of ethers as by-products in Picon's synthesis of alkylacetylenes and presumably in other procedures of this type.

3. It was shown that sodium alkoxides in liquid ammonia also behave as dehydrohalogenation agents toward alkyl halides.

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[CONTRIBUTION NO. 22 FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Equivalent and Molecular Weights of Humic Acids from a Bituminous Coal

BY R. C. SMITH AND H. C. HOWARD

Mild oxidation of bituminous coal with such reagents as oxygen, dilute nitric acid, dilute alkaline permanganate, or peroxides results in nearly complete conversion of the organic material of the coal into alkali-soluble products. The alkaline solutions of these oxidation products are dark brown in color and on acidification brown amorphous so-called humic acids are precipitated. Because of the similar appearance of these products to those obtained by acidification of alkaline extracts of brown coal, lignite, peat and other partially decomposed organic material, they have been designated "regenerated" humic acids.[1] While the humic acids obtained from peat and similar materials have been investigated quite extensively, little work has been done on the amorphous acids produced by the oxidation of bituminous coal, with the result that almost no information is available as to even such general properties as equivalent and molecular weights. Since these products are obtained in high yields, through reactions which probably do not result in profound internal structural changes, information as to their properties is obviously of importance from the standpoint of our knowledge of the nature of the units composing bituminous coal.

Previous investigations,[1,2] which have dealt for the most part with acids directly extracted from peat or brown coal, have resulted in values ranging from 134 to 345 for equivalent and 733 to 1445 for molecular weight.

Experimental

Preparation of the Acids.—All humic acids used in this study, except where otherwise noted, were prepared by the oxidation of a bituminous coal[3] by refluxing with 1 *N* nitric acid for approximately a week in the presence of air. The reaction is chiefly an oxidation, since 85–90% of the nitric acid consumed appears in the gaseous products as nitric oxide, when air is excluded from the system. More nitrogen is found in the humic acids than can be accounted for by the original coal. The nature and significance of this nitrogen has not yet been determined.

The acid-soluble oxidation products were separated by filtration and the insoluble residue washed with water until peptization started. This residue was then treated with an excess of ammonium hydroxide and suspended inorganic and organic material separated by sedimentation or filtration. The dark brown alkaline humate solution freed from suspended material was then acidified and the resulting precipitate of humic acids separated by filtration and washed until peptization started. Final purification was carried out by electrodialysis. It was found that inorganic impurities were retained very tenaciously, more than a week usually being required for the complete removal of the precipitating agent by electrodialysis. The mixture of water and purified acids (part of the acids remained in suspension and part deposited on the anode diaphragm) was removed from the cell and evaporated to dryness on the water-bath. The acids

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(1) Francis and Wheeler, *J. Chem. Soc.*, **127**, 2236 (1925).

(2) Odén, "Die Huminsäure," Theodor Steinkopff, Dresden, 1922, p. 86; *ibid.*, p. 91; Bahr and Ehrenberg, *J. Landw.*, **61**, 427 (1913); Biesalsky and Berger, *Braunkohle*, **23**, 197 (1924–25); Erdtmann, *Svensk Kem. Tid.*, **38**, 201 (1926); Kawamura, *J. Phys. Chem.*, **30**, 1364 (1926); Fuchs, Stengel, and Bangert, *Brennstoff-Chem.*, **9**, 181 (1928); Stadnikoff and Korschew, *Kolloid-Z.*, **47**, 138 (1929); Samec and Pirkmaier, *ibid.*, **51**, 96 (1930); Thiessen and Engelder, *Ind. Eng. Chem.*, **22**, 1131 (1930); Stach, *Braunkohlenarch.*, **40**, 1 (1933).

(3) For a detailed description of this coal see U. S. Bureau of Mines, Technical Paper 525 (1932).

were brought to constant weight over phosphorus pentoxide in vacuum. The yield was 75 to 85% of the weight of the coal. The carbon originally present in the coal is distributed in the oxidation products approximately as follows: CO_2, 15%; volatile acids, 8%; non-volatile, acid soluble products, 9%; humic acids, 60%; unattacked residue, 8%.

The freshly precipitated acids resemble ferric hydroxide. They dry to shining black particles with conchoidal fracture. On being heated they give no evidence of melting and furnish no volatile combustible products.

The ultimate composition of three typical preparations was: carbon 60.75–62.17%, hydrogen 3.12–3.31%, nitrogen 2.73–4.05%, ash 0.95–1.44%, and oxygen (by difference) 28.9–31.9%, sulfur (one preparation) 0.65%. The average empirical formula neglecting nitrogen and sulfur, calculated arbitrarily on the basis of six carbon atoms, is $C_6H_{3.8}O_{2.2}$.

Determination of Equivalent Weights.—Because of the dark color of humate solutions only electrometric titration methods are suitable. Potentiometric titrations were carried out with hydrogen, quinhydrone, and antimony electrodes. The most satisfactory procedure consisted in solution of a known amount of the humic acid 0.2–0.5 g. in excess of standard alkali 2–3 m. e. and determination of the excess alkali with standard acid, potentiometrically, using the antimony electrode. The method of differential plotting was used in all cases to determine the end-point.

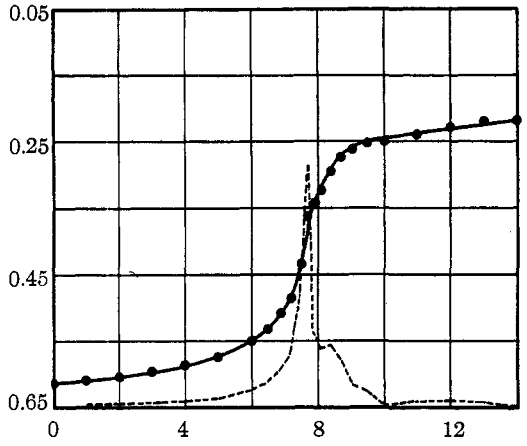

Fig. 1.—α-Naphthoic acid.

Titration curves for a known carboxylic acid, α-naphthoic, and for a typical humic acid preparation, made and dried as described above, are shown in Figs. 1 and 2. The e. m. f. of the antimony-saturated calomel cell is plotted as ordinate and cubic centimeters of standard acid used in the back titration, as abscissa. The derived curve is shown in broken lines.

The results of determinations on benzoic, salicylic, β-resorcylic and α-naphthoic acids agreed with the theoretical value within ±1%. Duplicate determinations on a given humic acid preparation were within 2%. In three different preparations the equivalents ranged from 232 to 248.

Workers with humic acids from other sources have emphasized the importance of the effect of drying temperature on the properties of the acids.[4] Determinations made upon one preparation after drying at room temperature over phosphorus pentoxide and at 150 and 250° in vacuum gave values of 245, 238, and 273, respectively. It is probable that only loss of water or other sorbed products takes place up to 150°, and that at 200° some carboxyls may split off with consequent loss in acidity and increase in equivalent weight. Biesalsky and Berger[3] have reached similar conclusions for brown coal acids.

Humic acids from peat and soil have been separated roughly into two large groups by extraction with alcohol, the soluble hymatomelanic acids and the insoluble humic acids.[5] Markedly smaller equivalent and molecular weights have been reported for the former.[2,6] Because of the possibility of ester formation, with alcohol, we employed acetone as a solvent to effect a separation. After approximately two weeks in a Soxhlet, 28% of our humic acids had passed into the extract. The difference found in the equivalents for the acetone soluble and insoluble fractions, 210 and 277, respectively, is significant but not marked.

Equivalent weights of humic acids from other sources were also investigated. Humic acids, prepared by alkaline extraction of "Rhenisch braunkohle," followed by the same purification process used on the humic acids from the oxidation of bituminous coal gave a value of 244, those obtained by the action of gaseous oxygen on an alkaline suspension of bituminous coal at approximately 90°, 251, and the products recovered from the oxidation of catechol[7] with alkaline persulfate, 199.

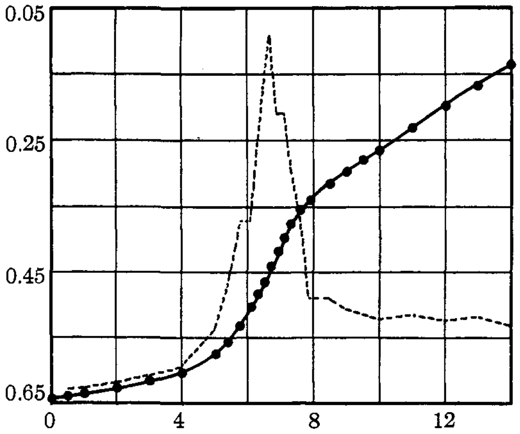

Fig. 2.—Humic acid No. 1.

Determination of Molecular Weights.—The humic acids prepared by the oxidation of bituminous coal, like those directly extracted from peat, are relatively insoluble in the common ebullioscopic and cryoscopic solvents. The di- and trihydroxybenzenes, however, were found to be satisfactory solvents for all the humic acids except those from the German brown coal. Because of thermal stability and moderate melting point, catechol was selected

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(4) Brandl, *Brennstoff-Chem.*, **9**, 89 (1928); Eller and Schoppach, *ibid.*, **7**, 19 (1926); Fuchs and Stengel, *ibid.*, **10**, 303 (1929).

(5) Hoppe-Seyler, *Z. physiol. Chem.*, **13**, 66 (1889).

(6) Odén, "Die Huminsäure," Theodor Steinkopff, Dresden, 1922, p. 110.

(7) Eller and Koch, *Ber.*, **53**, 1469 (1920).

as the most suitable for cryoscopic measurements. The cryoscopic constant for catechol is stated to be 71.3° per mole per 100 g. of solvent.[8] Our preliminary work indicated an average value of 59 when the following substances were used as solutes: benzoic acid, salicylic acid, 1,3,2-xylenol, β-naphthol, *sym*-tribromophenol, resorcinol, phenetol, naphthalene, 1,5-dihydroxyanthraquinone and fluorescein. Calculation from the heat of fusion[9] gave a value of 57.3. The experimentally determined value has been used throughout in this investigation.

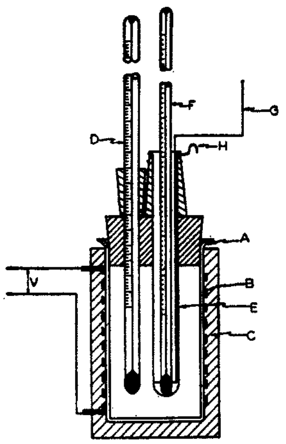

Fig. 3.—Freezing point apparatus.

A special technique was developed for the freezing point determinations. A tall form of 300-cc. Pyrex beaker, "A," Fig. 3, without lip, was provided with a nichrome winding, "B," and supported in an insulating container, "C." A large cork placed in the mouth of the beaker supported a thermometer, "D," for indicating the temperature of the air-bath, and the standard 15-mm. test-tube, "E," which contained the cryoscopic solvent, a thermometer, "F," and an automatically operated loop type of stirrer, "G." Thermometer "F" was a Koppers Refined Products, total immersion, range 70–120°, graduated in tenths and read by means of a magnifier to hundredths. The test-tube was provided with a small loop of nickel wire "H" which served as a means of suspension in the weighing operation. The empty test-tube was weighed to the nearest milligram and 6–8 g. of catechol introduced into the bottom of it by means of a short wide-stem funnel. Thermometer "F" and the loop stirrer were placed in position and the catechol fused by immersing the test-tube in a glycerin bath maintained at about 125°. The test-tube was then placed in the air-bath, the temperature of which had previously been adjusted to 95 to 100° and agitation started. Several freezing points were obtained for the pure solvent. It was usually found that after the first fusion these values were constant to two-hundredths of a degree. The test-tube was then removed from the air-bath, the catechol melted and thermometer and stirrer withdrawn from the liquid catechol, special care being taken to avoid smearing the catechol up the sides of the tube. Any catechol adhering to the sides of the tube was removed by evaporation or wiping with a cotton swab, and thermometer and stirrer were cleaned and dried. After the tube and contents had reached room temperature, it was weighed to one-tenth of a milligram, the sample was introduced through a large stemmed funnel reaching nearly to the top of the fused catechol, the funnel removed and tube, catechol and sample weighed again. The weight of sample was determined by the difference between the last two weighings. The weight of the catechol was obtained by the difference between the weight of the empty tube and that of the tube plus catechol; 50 to 100 mg. of solute was used with 6 to 8 g. of catechol. Freezing points were obtained for the solution in the same way as for the pure solvent.

Both Eastman catechol, without preliminary purification, and a product purified by vacuum sublimation were used. Although the purified product melted approximately 0.3° higher, its use was found to have no significant effect on the molecular weight measurements.

The first measurements on humic acids were made with products dried over phosphorus pentoxide at room temperature, and molecular weights of approximately 200 were obtained. This value was so much lower than that reported for acids from peat and brown coal that consideration was given to factors which might cause low results. Of these the most probable appeared to be the liberation of sorbed water from the humic acid by the cryoscopic solvent. The effect of rigorous drying in vacuum of these humic acids on apparent molecular weight is illustrated by the data in Table I. It was observed that the heated samples dissolved in the catechol much less rapidly. Drying of the acids at 300° was started, but when a temperature slightly above 250° was reached an almost explosive gas evolution took place and a large part of the sample was lost. The heating was continued, nevertheless, for the requisite period at 300°, but the product recovered was almost completely insoluble in fused catechol and in aqueous alkali.

TABLE I

EFFECT OF DRYING ON MOLECULAR WEIGHT

Drying temp., °C.	Loss in wt., %	Concn. g./100 g.	Av. ΔT	Mol. wt.
		Humic Acid No. 1		
25 (over P_2O_5)	..	1.64	0.44	220
150	5.6	2.01	.35	340
200	8.8	1.04	.17	360
		1.16	.20	340
		Humic Acid No. 2		
25 (over P_2O_5)	..	1.95	.46	250
150	8.78	1.39	.27	300

In the work on equivalent weights it was shown that there was a difference in equivalents between the acetone soluble and insoluble fractions. Molecular weight determinations on these same materials are shown in Table II. These data indicate a difference in molecular weight of the two fractions of the same order as that found for the equivalent weights.

It has been shown that humic acids from brown coal can be esterified.[10] Esters of the bituminous coal humic acids were prepared by agitation with absolute ethanol saturated with dry hydrogen chloride. Five esterifications yielded a total of 23.3% of the original humic acids as an alcohol-soluble product. Molecular weight measurements on both the alcohol soluble material and on the residue are shown in Table II. It is

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[8] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1926, Vol. IV, p. 183.

[9] Andrews, Lynn and Johnston, THIS JOURNAL, **48**, 1274 (1926).

[10] Fuchs and Stengel, *Brennstoff-Chem.*, **10**, 303 (1929).

TABLE II

MOLECULAR WEIGHTS

Substance	Concn. g./100 g.	Av. ΔT	Mol. wt.
Humic acid no. 1	Catechol ($K = 59$)		
Acetone soluble fraction[a]	1.40	0.43	190
	2.94	.79	220
	1.58	.39	240
Acetone insoluble fraction[a]	1.68	.38	260
	4.40	.95	270
	1.92	.38	300
Esterification product, alcohol-soluble fr.	1.49	.23	380
Esterification product, alc. insoluble fr.	1.44	.27	315
Catechol fusion product	1.04	.28	220
	1.49	.38	230
Humic acid no. 2			
Hydrogenation product	2.01	.46	260
	Tribromophenol ($K = 204$)		
Hydrogenation product	0.748	0.30	510
	Diphenyl ($K = 80$)		
Hydrogenation product	1.92	0.13	1200

[a] Material dried at 100°, all others at 150°.

worthy of note that these products which had been subjected to a strongly dehydrating solvent medium show molecular weights of the same order of magnitude as the starting material.

Since the preceding experiments seemed to preclude the possibility of loosely bound water being a factor in the low results obtained, consideration was given to other possible causes. Solvation causes low values, but for a substance of molecular weight of, say, 1200 to give an apparent value of 300, three-fourths of the solvent must be bound to the solute. At a concentration of 1 g. per 100 and catechol as the solvent, m. w. 110, each mole of solute, m. w. 1200, would have to bind more than 800 moles of solvent. This seems highly improbable.

Another possible cause of low values would be a chemical condensation with elimination of water. If each mole of a solute, m. w. 1200, reacts with catechol with the formation of three moles of water, the apparent molecular weight of the solute will be 300. Such a reaction is possible, but opposed to it is the fact that low values for molecular weight are obtained *immediately*. Solution in the catechol took place in most cases in a few minutes and the values for ΔT usually did not change more than 10% over the first hour although a lowering in melting point was often observed if the melt was allowed to stand for several hours, unprotected from air and moisture. If the sample is free from sorbed low molecular weight impurities it is difficult to see how the *first* value for molecular weight can be too *low*, unless a condensation reaction takes place instantaneously, although it may easily be too high due to incomplete solution.

In order to determine whether some such rapid condensation reaction were taking place between the humic acids and the catechol, a sample of humic acids was fused with the catechol, using approximately the concentrations of the molecular weight determinations (1%), and kept in a fused state for an hour. The acids were separated from the cooled melt by addition of an excess of dry ethyl ether, in which catechol is readily soluble. After filtration and further washing with dry ether the recovered acids were dried at 150° in vacuum for twenty hours. The yield was 96% of the starting material. Qualitative solubility tests indicated no difference between the reaction product and the original material. Both were insoluble in the common organic solvents and soluble in catechol. Molecular weight measurements, which are shown in Table II, indicate that no condensation reaction has taken place during the fusion with catechol.

Hydrogenation Products.—It was found possible by hydrogenation to convert these humic acids to brown amorphous bitumen-like bodies, melting under 200° and burning with a smoky flame. These products were insoluble in aqueous alkali, indicating absence of acidic properties, but readily soluble in a number of organic solvents as well as in catechol. Molecular weight measurements made on these hydrogenation products in a series of solvents of varying polarity are shown in Table II. The molecular weights in catechol are of the order to be expected if the values for the original acids are correct. The results obtained in the other solvents were surprising. We seem to be dealing with a class of substances which associates or polymerizes to a marked degree in non-polar solvents. Similar series of measurements made upon the brown, amorphous bitumen-like products obtained from this coal by distillation in high vacuum, and upon the so-called solid bitumens from benzene pressure extraction, showed these substances also to possess this remarkable associating power.

Discussion

These humic acids "regenerated" from bituminous coal are similar in appearance, in solubility, in equivalent weight, and in composition to those extracted directly from peat and brown coal and for which the evidence indicates molecular weights of 700–1400. Their behavior on pyrolysis is also the same, *i. e.*, they do not melt and they yield almost nothing but low molecular weight decomposition products, water, and carbon dioxide, and a carbonaceous residue, up to 500°. No organic compound of which we have knowledge, with the carbon, hydrogen, oxygen ratios of these acids and a molecular weight of the order indicated by the measurements in catechol shows such behavior on heating. The explanation which appears to be in best accord with the facts is that solution of these products in catechol results in breakdown into units of the average size indicated by the freezing point depressions. Catechol possesses a relatively high moment, 2.1 D compared with tribromophenol (1.5) and diphenyl (0.0), and should be a "dissociating" solvent.[11] Solutes like benzoic acid which associate badly in non-polar solvents such as diphenyl, yield normal values in catechol. There is evidence[2,10] to indicate that the humic acid molecule contains hydroxyl and carboxyl, and these are strongly associating groups. It therefore seems probable that the failure of these acids to distil is due to the existence, between units, of attractive forces which cannot be overcome by thermal agitation except in the presence of a highly polar solvent. Our work indicates that phenolic as compared with hydrocarbon solvents such as benzene exert some specific depolymerizing action on coal and products derived from it. This point of view is supported by the conclusions of other workers.[12]

Summary

Equivalent and molecular weights of humic acids prepared by the oxidation of bituminous coal have been determined, equivalent weights potentiometrically with the antimony electrode, and molecular weights cryoscopically in catechol. The equivalent weights found ranged from 200 to 300 and molecular weights were of the same order of magnitude. It was shown experimentally that the low values for molecular weight were not due to sorbed moisture or a condensation reaction and that solvation to the extent necessary to account for the observed values is highly improbable.

Prolonged extraction of the acids with acetone resulted in separation into two fractions which did not differ markedly in equivalent or molecular weight. Esterification resulted in products of the same order of molecular weight as the starting acids. Hydrogenation of "regenerated" humic acids converted them to bitumen-like substances which showed molecular weights in catechol of the order of magnitude of the original acids. The apparent molecular weight of the hydrogenation products, in the non-polar solvent, diphenyl, was approximately four-fold that in catechol.

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(11) Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., New York, 1931, pp. 195, 198, 202.

(12) Bone, "Coal and its Scientific Uses," Longmans, Green and Co., London, 1919, p. 95; Pertierra, *Fuel*, **13**, 23 (1934); Lowry, *Ind. Eng. Chem.*, **26**, 321 (1934); Soum and Podbreznik, *Bull. inst. pin.*, **57**, 61 (1929).

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