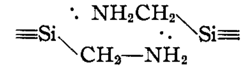
anomalies found for these compounds. It was thought that perhaps the amines were strongly associated, possibly through coördination somewhat as drawn



If such were true, the amines in non-polar solvents might exhibit abnormally high molecular weights. However, no indication of this was found when the molecular weight of trimethylsilylmethylamine was determined cryoscopically in benzene. The nearly ideal values of 102.5 and 104.3 were found. A value of 103.2 was calculated.

From these data the silylmethylamines all appear to be stronger bases than comparable organic amines. Substituents on the nitrogen show no abnormal effects. Substituents on the silicon atom show effects similar in nature to the same substituents in comparable organic amines.

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[CONTRIBUTION FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Nuclear Structure of the Water-soluble Polycarboxylic Acids from Oxidation of Bituminous Coal[1]

BY CLARENCE H. RUOF, T. R. SAVICH[2] AND H. C. HOWARD

The nuclear structures of the polycarboxylic acids prepared by the oxidation of bituminous coal have been studied by fractionation and investigation of the properties of: (1) the free acids, (2) their esters and (3) the methylated nuclei resulting from the hydrogenolysis of the esters. All the physical and chemical properties of these products demonstrate unequivocally the presence of significant amounts of compounds with nuclear structures more complex than the benzene ring. Certain fractions of the hydrogenolysis products contain appreciable amounts of oxygen and have properties corresponding closely to phthalans (isodihydrobenzofurans); the possibility that such ring systems were formed in the hydrogenolysis procedure cannot be excluded. The non-distillable residue of the hydrogenolysis products appears to be a polycyclic structure.

The method of degradation employed—oxidation, followed by esterification, hydrogenolysis and fractionation of the alkylated nuclear structures—is widely applicable to investigations of coal structure. In these reactions the temperature need not exceed 270°, thus minimizing structural changes due to thermal effects.

Controlled oxidation of aqueous alkaline suspensions of bituminous coals results in the conversions of approximately 50% of the carbon to a mixture of water-soluble carboxylic acids, the balance appearing as carbon dioxide.[3] Aliphatic acids—acetic and oxalic acid—have been shown to constitute a minor part of the mixture, usually not more than 10% of the coal carbon, and the balance has been designated as benzenecarboxylic or benzenoid. Individual benzenecarboxylic acids, which are all colorless, stable, crystalline compounds, have been isolated by a number of different workers, using a variety of coals and oxidation procedures. But there are also present yellow, non-crystalline thermally unstable acids which, in aqueous solution, migrate rapidly through parchment; they are not readily volatile but are soluble in low internal pressure solvents such as ethyl ether and the molecular weights of both the free acids and their esters are in the range of the benzenecarboxylic series.

The purpose of the present investigation was to study the nuclear structure of these yellow water-soluble polycarboxylic acids, which appear to be simple enough to offer hope of successful results in structural investigations and yet are sufficiently complex so that information concerning their structure would contribute significantly to our knowledge of coal. The methods used have involved (a) solvent fractionation of the free acids, (b) fractionation of the butyl esters by the action of solvents and by molecular distillation and (c) hydrogenolysis of the butyl esters followed by precision fractionation of the resulting nuclear structures with attached methyl groups. Throughout this series of steps the maximum temperature reached was 270°, thus minimizing thermal alterations of the fragments of the coal polymer.

Determination of molecular and equivalent weights of the acid fractions permits calculation of average functionality and hence average nuclear size. Similar calculations can be made for the ester fractions from values of molecular weights and saponification equivalents and information as to nuclear size follows directly from the molecular weight measurements on the fractions obtained from the hydrogenolysis reaction. In addition, determinations of such properties as density, refractive index, boiling point, viscosity and ultimate composition on the esters and hydrogenolysis fractions has permitted conclusions to be drawn as to chemical structure. The data from all these procedures point to the presence in the mixed acids of nuclear structures of a wide range of sizes—from a single ring to polycyclics of molecular weight of several hundred.

Experimental

Preparation of the Acids.—A suspension of 15 pounds of −100 mesh Pocahontas No. 3 coal in 15 gallons of water and 45 pounds of commercial flake sodium hydroxide was treated with oxygen gas at a total pressure of 900 p.s.i.g. at 270° for 2 to 3 hours in equipment previously described.[4] After cooling to about 90°, the reaction product was pressured out of the autoclave, cooled, filtered, acidified with sulfuric acid and extracted with methyl ethyl ketone in a two-stage countercurrent system. The ketone solution of the acids was concentrated to a sirup in a steam-jacketed

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[1] Presented in part before the Gas and Fuel Division, American Chemical Society, May 9, 1949, Pittsburgh, Penna.

[2] Rensselaer, Indiana.

[3] H. C. Howard, Chap. 9, "Chemistry of Coal Utilization," edited by H. H. Lowry, John Wiley and Sons, Inc., New York, N. Y., 1945.

[4] For a description of the pilot plant for the preparation of these acids see N. W. Franke and M. W. Kiebler, *Chem. Industries*, **58**, 580 (1946). Operating details are given in British Patent 635,088, April 5, 1950.

still and the dry acids finally recovered from the sirup in a laboratory vacuum drum dryer. The caked acids from the dryer were ground in a pebble mill and stored in a closed container. The yield of mixed aromatic acids recovered was 50–60% by weight of coal charged.

Fractionation of the Acids.—The mixed acids were fractionated with pentane–ether mixtures. Approximately 200 g. of the vacuum-dried acids were refluxed for about 5 hours with one liter of reagent quality ether. About 5% was insoluble and removed by filtration and the filtrate was adjusted to 200 ± 5 g. per liter. Due to the hygroscopic nature of the acids, this filtration was often troublesome in humid weather and it was found best to carry it out in a paper thimble in a Soxhlet extractor and to complete the washing of the insoluble material by reflux in the extractor. The ether solution of the acids was treated with half its volume of commercial *n*-pentane with good agitation. This resulted in the development of two phases, a mobile, nearly colorless, pentane-rich phase and a highly viscous, orange-colored phase, which tended to adhere to the bottom and sides of the vessel. After agitation was stopped, the phases were allowed to separate and the pentane-rich phase was decanted from the vessel. The acids recovered from this solution constituted the first fraction. The viscous material remaining in the vessel was dissolved in ether, diluted to the original volume and treated again with half its volume of pentane. The whole procedure was repeated until the six fractions and a residue were recovered. The viscous residue became nearly insoluble in ether after the greater part of the lower molecular weight material had been extracted.

Preparation of the Butyl Esters.—The butyl esters used in this study were prepared as follows: The vacuum-dried acids, 18.2 kg., were charged to a 35-gallon Pfaudler glass-lined steam-jacketed kettle equipped with a simple distillation head to which was attached a large Dean–Starke type trap. Butanol, 60.6 liters, and concentrated sulfuric acid, 300 ml., were added and heat was applied. The butanol–water azeotrope was stripped off, the aqueous layer which separated was removed, and the butanol was continuously returned to the still. After 24 hours the simple head was replaced by a column, 25 mm. o.d. × 110 cm. packed with $^3/_{32}''$ glass helices (30 plates), which expedited the separation of the total of 4700 ml. of aqueous phase and reduced the esterification time to 80 hours. In previous runs, where the column was not employed, 200 hours were required to remove all the water and reduce the residual acidity to a minimum. After removing 34 liters of butanol by distillation *in vacuo*, 19 liters of toluene was added; the toluene–butanol azeotrope was distilled to remove the last traces of butanol. After cooling, the resulting esters, 26 liters, were removed, dissolved in an equal volume of pentane and washed with vigorous stirring for 3.5 hours with a solution of 1800 g. of Na_2CO_3 in 60 liters of water. About one liter of insoluble tarry material was removed at this point. After separation from the aqueous phase the esters were heated to 150° at 80 mm. to remove the solvent. The average yield of esters from several runs was 87% based on the average equivalent weight of the original acids.

Fractionation of the Butyl Esters.—It was found that fractionation of the mixed esters could be effected either by the action of solvents such as propane or pentane or by molecular distillation. Both separations were on a molecular weight basis. The pentane fractionations could be made either by varying the ratio of solvent to ester or by keeping the solvent–ester ratio constant and varying the temperature.

Molecular distillation was found to be a more convenient method for fractionation. Small scale analytical distillations were carried out on 1-g. samples in a small pot-type molecular still which has already been described.[5] Larger scale distillations were conducted in a centrifugal type still by Distillations Products Industries and the fractions returned to this Laboratory for analysis. Because of the presence in the crude ester mixture of very viscous esters of molecular weight above 1000, the most satisfactory results were obtained by feeding to the centrifugal molecular still a refined product from which some 30% of the high molecular weight material had been precipitated by a dilute solution of stannic chloride in pentane. This refining treatment was carried out as follows: 1800 ml. of crude esters was poured with good agitation into 18 liters of commercial *n*-pentane and to this solution was added 100 ml. of 10% stannic chloride in pentane. After standing for 24 hours the pentane solution was decanted from the tarry residue and again treated with a 100-ml. portion of 10% stannic chloride solution. This operation was carried out for a third time and the recovered pentane solution of the esters then washed with water and the esters recovered by distillation of the pentane. The average yield of refined esters was 70%.

Hydrogenolysis of the Butyl Esters.—One thousand grams of unrefined butyl esters of the coal acids was dissolved in pentane and made up to 5000 ml. of solution. The pentane insoluble residue, 27 g., was removed by filtration. The pentane solution was then passed through a column of anhydrous potassium carbonate to reduce acidity which permitted a smaller number of stages for complete hydrogenolysis. After this treatment 875 g. of esters with an acid number of 4.3 was recovered.

The treated esters, 1000 g., copper–chromium oxide catalyst prepared in this Laboratory,[6] 100 g., and 2000 p.s.i.g. of hydrogen were charged to a 3400 ml. externally heated rocking autoclave and heated to 270° for six hours. The catalyst was removed by filtration from the product after cooling to room temperature and 300 ml. of butanol was used for rinsing the autoclave, catalyst and filter aid. The filtrates were "topped" in a 35-plate column to a head temperature of 130°. The "topped" products from eight such runs were combined and recharged in 1000-g. lots to the autoclave along with fresh catalyst for the next stage. The same procedure was followed for a total of four stages; the saponification equivalents being 510, 1250, 5900 and ∞, respectively. The total hydrogen absorbed was 3.2 moles for each equivalent of ester. The "toppings" contained butanol and hydrocarbons which formed azeotropes; they were combined and freed from butanol by alternate distillation and extraction with water. The butanol-free material was then recombined with the "topped" products to yield a total of 1920 g. of hydrogenolysis products with the following properties: mol. wt., 250; C, 83.48; H, 9.40; N, 0.52; O (by difference), 6.60; empirical formula $C_{17.4}H_{23.3}O_{1.03}N_{0.09}$; and $n^{25}D$ 1.5396.

Fractionation of the Hydrogenolysis Products.—The hydrogenolysis products, 1920 g., were subjected to precision fractionation in a 100-plate column with a packed section, 13 mm. i.d., 200 cm. high, packed with $^3/_{32}''$ glass helices and equipped with boiling rate and reflux ratio controllers. The first 11.4% was distilled at atmospheric pressure, the next 15.3% at 64 mm. and the next 8.4% at 27 mm. The vacuum distillation was required to maintain the still temperature below 270°. After the removal of this first 35.1%, the remaining still contents were transferred to a perforated plate Hy-Vac column and another 31.4% was distilled at 0.3 mm. before thermal decomposition became appreciable as indicated by gas evolution.

Analytical Methods: Determination of Molecular and Equivalent Weights and Saponification Equivalents.—Molecular weights of the acids were determined by an ebullioscopic procedure which has already been described[7] using benzoic, salicylic and mellitic acids as standards; those of the esters and hydrogenolysis fractions were determined by a similar procedure but using dibutyl phthalate and dioctyl phthalate as standards for the former and terphenyl and fluorene for the latter. The molecular weights of a number of the lower molecular weight fractions of the hydrogenolysis products were also determined cryoscopically in benzene. The dibutyl and dioctyl phthalates and terphenyl were Eastman Kodak Co. products, and the fluorene was Fraenkel and Landau "Reinst"; these materials were used without purification. The molecular weights were usually run at two or three concentrations, and at the concentrations used, the values at infinite dilution did not differ significantly from those at higher concentrations.

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(5) G. Schulz and H. C. Howard, THIS JOURNAL, **68**, 991 (1946).

(6) The copper–chromium oxide catalyst was prepared by the procedure of Connor, Folkers and Adkins, THIS JOURNAL, **54**, 1139 (1932), for catalyst 25KAF with certain modifications. All quantities of materials were doubled; barium nitrate was replaced by an equivalent amount of hydrated calcium nitrate and the amount of 28% ammonium hydroxide was increased to 500 ml. The final decomposition of the ammonium salts was performed in two batches in a 12" × 12" flat metal tray heated on an electric hot-plate and covered by a weighted $^1/_4''$ transite board containing thirteen $^1/_4''$ holes for escape of gases.

(7) N. Berman and H. C. Howard, *Anal. Chem.*, **21**, 1200 (1949).

The equivalent weights of the acids were determined in the usual way by titration with standard alkali, using phenolphthalein as an indicator or when the color was dark, a Beckman model H glass electrode *p*H meter.

Considerable difficulty was experienced in determining saponification equivalents of the esters. The method used was essentially that described by Maglio[8] except that because of its high viscosity the required amount of standard potassium hydroxide in diethylene glycol was weighed into the reaction flask, instead of being measured from a buret, and the saponification period was increased to 4 hours at 125°. With dibutyl phthalate (theoretical, 139.1) the following average values were obtained for 1-, 4- and 16-hour saponification periods: 140, 142 and 141. With fractions of the butyl esters of the acids from the oxidation of coal, the values continued to decrease for saponification periods even up to as long as 16 hours. For example, with a fraction having a molecular weight of 460, the observed saponification equivalents for 1-, 4- and 16-hour heating periods were 145, 143 and 137. It appears possible that this glycol–potassium hydroxide reagent was reacting slowly with some group other than carbobutoxy in the mixed esters.

Analytical Molecular Distillations.—Quantitative molecular distillations were carried out on 1-g. samples using the apparatus and technique which has been previously described for distillation of the methyl esters.[5]

Viscosity Measurements.—Viscosity measurements were made in Cannon–Fenske viscometers, Series 50, 100, 200, 300 and 400 at 25 ± 0.1°. The series 200, 300 and 400 instruments were standardized against API standard oil beta 44 and the 50 and 100 series by intercomparison of ester fractions.

Ultimate Compositions.—The ultimate analyses of the various products in this paper were made by Huffman Microanalytical Laboratories, Denver, Colorado.

Adduct Formation with Stannic Chloride.—The sample to be tested was diluted with about 10 volumes of commercial pentane and treated with a few drops of a pentane solution of stannic chloride (1% by volume of fuming, anhydrous $SnCl_4$ in commercial pentane). The aliphatic cyclic ethers, dioxane, tetrahydrofuran and tetrahydropyran give copious precipitates with this reagent under these test conditions.[9]

Spectra.—Ultraviolet spectra were determined on a Beckman model DU ultraviolet spectrophotometer.

Results and Discussion

Properties of the Acids.—The acids used in this investigation were yellowish-brown, hygroscopic solids, melting with decomposition, very soluble in water, soluble in the lower boiling ethers, and almost insoluble in aliphatic and aromatic hydrocarbons. Ebullioscopic values of molecular weight, in acetone, fell within the range 250–260 and equivalent weights, 75–85, indicating an average functionality of more than 3 and an average nuclear size of 110. A typical average ultimate analysis of a sample dried to constant weight over phosphorus pentoxide at room temperature was: C, 54.4; H, 3.0; N, 0.1; S, 0.4; O (by difference), 42.1. Quantitative determinations indicate that the greater part of the sulfur was present in the form of sulfate which was probably due to incomplete elimination of sulfuric acid after its use in the recovery.

Ultraviolet absorption spectra of a methanol solution of the mixed acids are compared with those for acids of the benzenecarboxylic series in Fig. 1. The spectra for acids of the latter series all fall within a definite envelope with a marked hump in the range of 260–300 mμ, while the mixed acids from coal show absorption outside this band and especially at the longer wave lengths where the multi-ring condensed types are known to exhibit absorption.

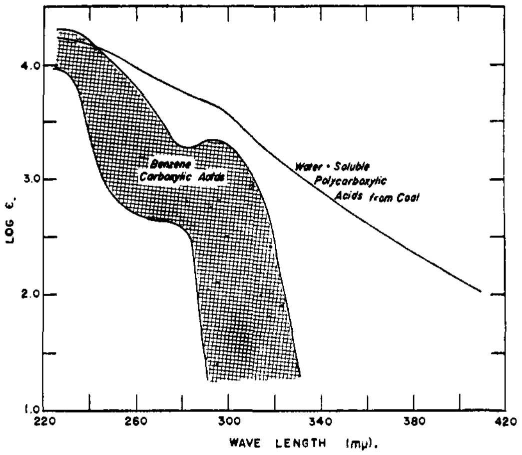

Fig. 1.—Ultraviolet absorption spectra of benzenecarboxylic acids and acids from coal.

Orthophthalic, isophthalic, trimellitic, 1,2,3,4-benzenetetracarboxylic acid, pyromellitic and pentacarboxylic acids, all members of the benzenecarboxylic series, have previously been isolated from this mixture in this Laboratory and the best available data on the amounts and types of various acids indicated that approximately 35% of the mixture was benzenecarboxylic, distributed as 10% di-, 15% as tri- and 10% tetracarboxylic. The only triacid isolated was trimellitic and the predominating tetra- was pyromellitic.

Data from the solvent fractionation of a 2-kg. sample of the mixed acids using ether and pentane are shown in Table I. This procedure effected a rough separation on the basis of molecular weight and it will be noted that equivalent weights increased with molecular weights but not in proportion, so that the number of functional groups per molecule had to increase as indicated under Functionality. The calculated size of average nucleus, even in the lowest molecular weight fractions, is greater than that for a benzenecarboxylic acid and in the higher fractions, indicates a number of rings. The mixed acids were subjected to sublimation with the results shown in the last column. It will be observed that only 87% of the first fraction sublimed although mellitic acid, the least volatile of the benzenecarboxylic acids, rapidly and completely sublimed under the conditions used.

TABLE I

SOLVENT FRACTIONATION OF THE MIXED ACIDS

	G.	%	Cum. %[a]	Mol. wt.	Equiv. wt.	Functionality	Nucleus	Sublimable, %
Ether-insoluble	129	6.3						
Fraction 1	463	22.5	24.0	199	82	2.4	94	87.0
2	499	24.2	49.9	235	86	2.7	116	81.8
3	284	13.7	64.5	256	93	2.7	137	70.5
4	97	4.7	69.5	280	96	2.9	153	66.2
5	39	1.9	71.5	326	97	3.3	181	63.6
6	17	0.8	72.4	374	103	3.6	215	57.3
Residue	535	25.9	100.0	442	112	3.9	271	29.4
	2063							

[a] Adjusted to make ether-soluble, 100%.

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[8] M. M. Maglio, *Chemist-Analyst*, **35**, 39 (1946).

[9] C. H. Ruof and H. C. Howard, "Stannic Chloride Adducts with Coal Degradation Products," presented before the Gas and Fuel Division, American Chemical Society, 118th National Meeting, Chicago, Ill., Sept., 4-8, 1950.

In Fig. 2, calculated nuclear size of these fractions is plotted against cumulative mole per cent. About 75% of the acids on a molar basis have estimated nuclear sizes of less than 150, but it should be noted that such an average nuclear size could include two- and possibly some three-ring structures such as fluorene.

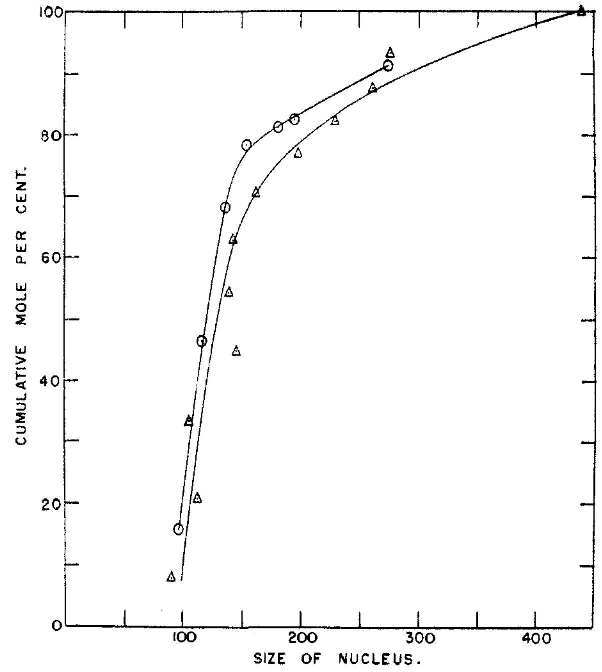

Fig. 2.—Distribution of nuclear sizes: ⊙, solvent fractionation of acids; △, molecular distillation of butyl esters.

Properties of the Butyl Esters.—The properties of a typical sample of the mixed butyl esters directly from the esterification process were as follows: mol. wt., 470; sapn. equiv., 151; acid number, 9; $d^{25}{}_4$, 1.09; centistokes at 37.8°, 218. The color was too deep to measure on the Gardner scale, >#18. The products from the stannic chloride–pentane refining process showed similar analytical properties, but were much improved in color and fluidity, as follows: mol. wt., 475; sapn. equiv., 145; acid number, 3; $d^{25}{}_4$ 1.06; centistokes at 37.8° 105; Gardner color number, 15–16. Molecular distillation of 1-g. samples of the crude esters up to 340° gave 76.4% distillate, 17.3% residue and 6.3% gas and loss. The distillations of larger samples in the centrifugal molecular still are given in Table II. These figures show that the material removed by the stannic chloride–pentane treatment did not contain distillable products; in fact, the yield of distillate from the refined product calculated back to the crude ester basis is somewhat higher, 63 compared with 59%.

TABLE II

DISTILLATIONS IN CENTRIFUGAL MOLECULAR STILL

Sample	Maximum temp., °C.	Distillate, % Recovered	Distillate, % Crude ester basis
Crude esters, 527 g.	206	58.9	. .
Refined 2.1 kg.	250	91.7	64.2
Refined, 10.6 kg.	185	89.8	62.8

The properties of the fractions from the 10.6-kg. distillation have already been reported in detail.[10] With the exception of the low boiling material recovered from the cold-trap, which contained some butanol, the densities and refractive indices of all the fractions point definitely to compounds of cyclic nuclei. The distribution of calculated nuclear sizes is given in Fig. 2 for comparison with those of the free acids. The nuclear sizes calculated from the esters are somewhat larger throughout; 65% of the esters have nuclear sizes less than 150 compared with 75% for the acids. Intermolecular condensations during the esterification process cannot be excluded and would result in some shift in the distribution of nuclear sizes.

The ultraviolet spectra of a number of the distillable fractions and the residue are shown in Fig. 3. The spectra of the higher fractions of these esters show the absorption beyond 300 mμ, characteristic of condensed cyclic structures.

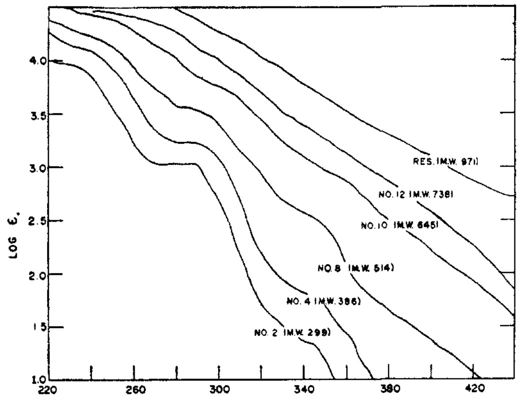

Fig. 3.—Ultraviolet spectra of butyl ester fractions: Nos. 2, 4, 8 and 10 in isoöctane and No. 12 and residue in chloroform.

Plots of cumulative yield and of refractive index against molecular weight are given in Fig. 4. The former shows that about 20% of the material falls in the molecular weight range of 450 to 500; the molecular weights of the tri- and tetrabutylbenzenecarboxylic esters are 378 and 478, respectively. There is also a marked change in the slope of the refractive index–molecular weight curve in the same

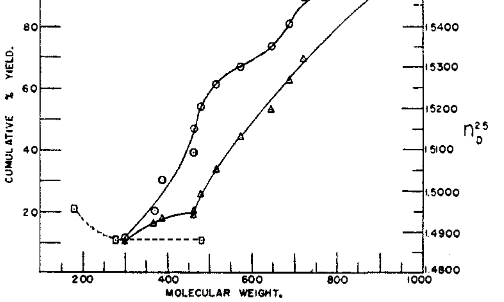

Fig. 4.—Yield and refractive index–molecular weight relations of butyl esters: ⊙, cumulative % yield (coal acids); △, n^{25}D (coal acids); ⊡, n^{25}D (benzenecarboxylic acids).

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(10) N. Berman and H. C. Howard, *Fuel*, **29**, 109 (1950).

molecular weight range and the steadily increasing value of refractive index with molecular weight indicates a marked change in nuclear structure. The addition of carbobutoxy groups to the benzene ring produces little change in refractive index as is evident from the plot of the best data available for butyl benzoate, dibutyl phthalate and tetrabutyl pyromellitate.

Figure 5 shows the relation between functionality and molecular weight calculated for the butyl esters of carboxylic acids of various types of nuclear structure. Where the increase in molecular weight is due solely to addition of carbobutoxy groups, there will necessarily be obtained a series of straight lines of identical slope, but with intercepts on the abscissa corresponding to the size of the nucleus. This plot also shows the large increase in nuclear size with increase in molecular weight of the butyl esters of the coal acids.

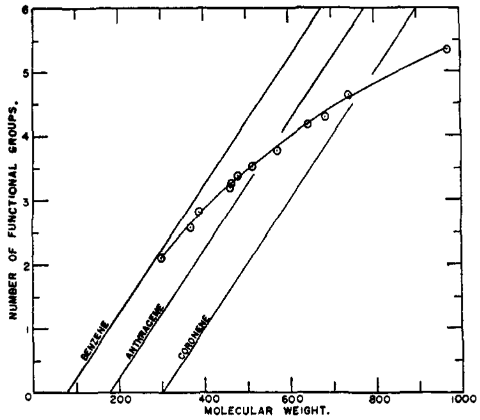

Fig. 5.—Functionality and molecular weight relations of the butyl esters.

Plots of specific refraction as a function of molecular weight have been used as a tool in studying the structure of petroleum hydrocarbons[11] and in investigations on coal hydrogenation products.[12] A similar type of plot for butyl esters is shown in Fig. 6. The only experimental data available for the butyl esters of the benzenecarboxylic series are for butyl benzoate and dibutyl phthalate. From these data the specific refractions for the higher members of the series have been calculated. Values have also been calculated for the butyl esters of acids with benzene, naphthalene, benzofuran, indene and diphenyl nuclei. It is evident that additions of carbobutoxy groups lower the specific refractions of any given nucleus and that the higher fractions of the butyl esters of the coal acids have specific refractions lying well above the values of the benzenecarboxylic series and in the range of the polycyclic structures.

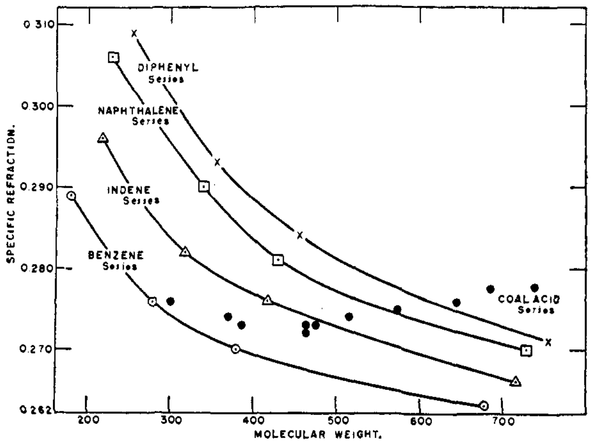

Fig. 6.—Specific refraction–molecular weight relations of butyl esters of various nuclear structures.

Several relations have been developed for relating viscosities and molecular weights of liquids. The simple log η–molecular weight relation, which has been shown to hold approximately for homologous series of aliphatic esters[13] and more recently,[14] at certain temperatures, for fractions of molten coumarone–indene polymers, is plotted for these butyl ester fractions in Fig. 7. Data for butyl esters of two members of the benzenecarboxylic series are also plotted for comparison.

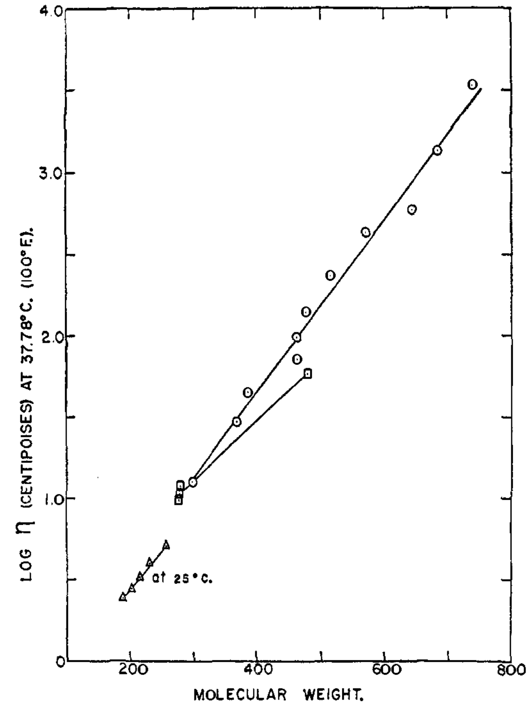

Fig. 7.—Log viscosity–molecular weight relations: ⊙, butyl esters of coal acids; △, ethyl esters of Dunstan and Thole; ⊡, butyl esters of benzenecarboxylic acids.

Ultimate compositions of three of these distilled ester fractions and for the non-distillable residue are given in Table III. Despite the wide range in molecular weights—from 386 to 971—there is surprisingly little difference in ultimate composition, indicating that the higher molecular weight material is probably built up of the same units found in the lower. The empirical formulas for the nuclear

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[11] J. C. Vlugter, H. I. Waterman and H. A. Van Westen, *J. Inst. Petroleum Tech.*, **21**, (a) 661, (b) 707 (1935).

[12] C. D. LeClaire, THIS JOURNAL, **63**, 343 (1941).

[13] A. E. Dunstan and F. B. Thole, "Viscosity of Liquids," Longmans, Green, and Co., London, 1914, p. 35.

[14] E. T. Pieski and A. C. Zettlemoyer, "Viscosities of Molten Coumarone-Indene Resins," presented before the Division of Paint, Varnish and Plastics Chemistry, American Chemical Society, Chicago, Ill., Sept., 1950.

structures were calculated by subtracting from the empirical formula for the given fractions, the number of C, H and O atoms in the carbobutoxy groups—obtained by multiplying the number of atoms of each in the carbobutoxy group ($C_5H_9O_2$), by the average number of functional groups per molecule for that particular fraction. The increase of oxygen atoms in the nucleus, with molecular weight, is noteworthy and indicates that the nuclear structures of these esters are not entirely hydrocarbon in character.

TABLE III

ULTIMATE COMPOSITIONS OF CERTAIN ESTER FRACTIONS

Fract.	Mol. wt.	Analyses, % C	H	O (By difference)	O (From sapon. equiv.)	Nuclear composition
4	386	67.01	7.75	25.24	23.3	$C_{7.5}H_{4.4}O_{0.4}$
8	514	67.15	7.65	25.20	21.9	$C_{11.2}H_{7.4}O_{1.0}$
12	738	68.23	7.43	24.34	19.9	$C_{18.7}H_{12.5}O_{1.9}$
Res.	971	68.70	7.03	24.27	17.6	$C_{28.8}H_{19.6}O_{4.05}$

Hydrogenolysis Products.—The esters are extremely high boiling. If, however, they are subjected to hydrogenolysis, the ester group is replaced by a methyl group and the resulting lower boiling methylated nuclei can be separated by precision fractional distillation. Thus, the hydrogenolysis of dibutyl phthalate, b.p. 340.7°, over copper-chromium oxide catalyst produces good yields of *o*-xylene, b.p. 144.4°. Furthermore, characterization of these nuclei with attached methyl groups is more readily possible because (1) their physical properties are more indicative of the nucleus when it is no longer surrounded by such large substituents and (2) more adequate descriptions of these lower boiling materials are available in the literature. It is recognized, of course, that in addition to the replacement of the ester group by a methyl group, the hydrogenolysis procedure may also effect partial reduction of ester groups to alcohols, saturation of double bonds, reduction of carbonyl groups, and possibly the rupture or synthesis of heterocycles.

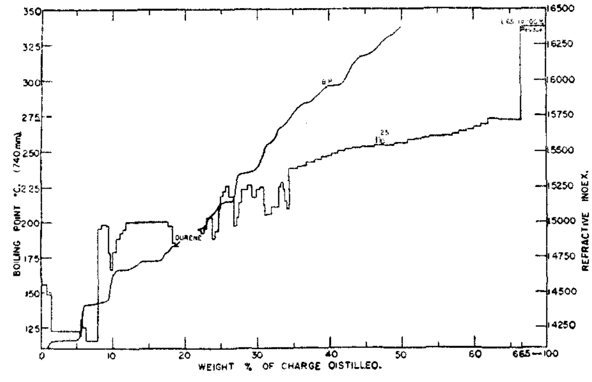

Fig. 8.—Fractionation of the products of hydrogenolysis of the butyl esters.

Decarboxylation would appear to be more advantageous than hydrogenolysis in a study of the nucleus—all benzenecarboxylic acids should yield benzene instead of mixtures of methylbenzenes. However, the temperatures of 400° necessary compared with 270° for hydrogenolysis and the undesirable nuclear condensations often accompanying decarboxylations make the use of this reaction less advantageous.

The hydrogenolyses were performed in three stages until the amount of residual esters was negligible as determined by saponification equivalents. The hydrogenolysis of dibutyl phthalate (1000 g.) under these conditions confirmed the statement[15] that good conversions to the methylated nuclear hydrocarbon—in this case *o*-xylene—could be obtained. In addition to the *o*-xylene, small amounts of butyl butyrate (4 g,), hexahydrophthalan (9 g.) and 2-methylcyclohexanemethanol (15 g.) were found in one experiment.

The distillation data for the products from the large scale three-stage hydrogenolysis of the butyl esters of the coal acids are presented in Fig. 8; the boiling points of fractions taken at reduced pressures were determined at atmospheric pressure in micro boiling point tubes. Data for fractions boiling above 350° are omitted in the graph due to extreme thermal effects in the determination. The expected di-, tri- and tetramethylbenzenes were isolated in this distillation; 1,2,4,5-tetramethylbenzene, durene, separated as a crystalline solid. This latter material was undoubtedly derived from pyromellitic acid and was identified by boiling point, melting point, ultraviolet spectrum, molecular weight and ultimate composition. Although no other individual chemical compounds have been identified or isolated in pure form, much general information has been obtained on the various fractions.

The bulk of the product, however, boils considerably higher than durene and contains nuclei definitely more complex than the benzene ring. For example, only 33% of the hydrogenolysis products distilled up to 264° (760 mm.); this is the boiling point of the highest boiling polymethylbenzene,[16] hexamethylbenzene, which has a molecular weight of 162. The residue, molecular weight 547, which amounted to another 33% could not be distilled up to 270° at pressures as low as 0.3 mm. The index of refraction of the residue is 1.638; this is considerably higher than that exhibited by pentamethylbenzene, $n^{25}D$ 1.52, which is the highest reported[16] for the polymethylbenzenes.

Many of the fractions boiling above durene contain appreciable quantities of oxygen. Those fractions boiling in the range 210–230° possess properties resembling phthalans, which are isomeric with dihydrobenzofurans and which form insoluble adducts with $SnCl_4$. It is impossible to state that such structures are present in the nucleus of the coal acids since they may have been formed in the hydrogenolysis reactions. Isolation of less than 1% of hexahydrophthalan from the hydrogenolysis products of dibutyl phthalate indicates that hydrogenolysis may result in the formation of the hetero-ring; however, it cannot be assumed that all the oxygen-containing molecules remaining in the hydrogenolysis products resulted from this reaction. It is of significance in this respect that the esters always contained more oxygen than could be

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(15) H. Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wis., 1937, p. 101.

(16) A. W. Francis, *Chem. Revs.*, **42**, 107 (1948).

accounted for in the ester groups (*cf.* Table III) and could be partially precipitated with $SnCl_4$ in pentane under conditions where the carbobutoxy group itself is not responsible for the precipitate.

The bulk of the material boiling above durene averaged less than one oxygen atom per molecule. Removal of the oxygenated molecules from these fractions by adduct formation with stannic chloride followed by adsorption on silica gel resulted in the recovery of hydrocarbons having properties corresponding closely to the polymethylindans.

The non-distillable residue had an average composition of $C_{38.37}H_{45.85}O_{2.48}$ with an average molecular weight of 547; while it is possible that this residue might be a polymer of simpler hydrogenolysis products, the polymeric unit cannot be a single benzene ring. This residue was reddish-brown, brittle and resinous and in these respects strongly resembled commercial coumarone and indene resins. However, a secondary hydrogenolysis at 375° resulted in a decrease in average molecular weight to only *ca.* 375, while a commercial "cumar" resin with an average molecular weight of 647 was degraded under less drastic conditions, 350°, to products of much lower average molecular weight, 138. In the hydrogenolysis of this non-distillable residue at 375° the oxygen was 85% eliminated with only a moderate change in average molecular weight which indicates that linear oxygen links are not an important part of the structure. Condensation type polymers with polycyclic nuclei which may be analogous to truxene must be present, although addition type of polymeric structures may also be present.

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[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Hygroscopicity of Amino Acids and Its Relationship to the Vapor Phase Water Absorption of Proteins[2,3]

BY EDWARD F. MELLON AND SAM R. HOOVER

The marked influence of the polar groups upon the vapor phase water absorption of proteins has led to a study of the water absorption of these same polar groups in a number of model substances. In this manner the influence of interactions between polar groups upon the water absorption phenomena could be studied. This paper reports the water absorption results obtained for the amino acids and a number of peptides and other amino acid derivatives. The results indicate that under conditions where the polar groups can be expected to be very highly coördinated into the crystal structure, they absorb little if any water even at high humidities. However, all types of water absorption phenomena, including hysteresis, were shown to be possible within these relatively simple substances. The evidence presented indicates that the polar groups of the proteins must be comparatively uncoördinated and completely available to water molecules. This is a situation similar to that required by the polarization theory of adsorption and, therefore, it is not surprising to find that the polarization theory isotherm describes the water absorption curve of proteins from 6 to 93% relative humidity.

Introduction

The vapor phase water absorption of proteins has been the subject of many investigations and there are still several different explanations propounded for this phenomenon. The coördination of water by polar groups proposed by Lloyd and Phillips[4] has been supported by more direct experimental evidence than any of the other explanations. Sponsler, Bath and Ellis[5] have demonstrated the nature of the binding and the location of the water by infrared absorption and X-ray diffraction measurements on gelatin. Earlier papers in this series[6,7,8] have obtained a more quantitative measure of the absorption due to specific polar groups. Since some of these polar groups are present in the individual amino acids, it has been of considerable interest to determine the hygroscopicity of these amino acids in the pure state and compare the results with the hygroscopicity of peptides and proteins.

Experimental

Purification of Amino-Acids.—The amino acids were of the purified grade obtainable from regular chemical supply sources. These were used directly as received except for glycine, alanine and arginine hydrochloride which showed traces of hygroscopicity. These three amino acids were recrystallized several times: glycine from water, alanine from 50% alcohol, and arginine hydrochloride from water by the addition of alcohol. Proline, which showed a marked hygroscopicity, was subjected to a more vigorous purification. It was converted to the picrate which was recrystallized twice from water. The picrate was decomposed with 40% sulfuric acid. The picric acid was extracted with ether. The sulfuric acid was removed with barium hydroxide and the water evaporated. The residue was recrystallized twice from hot absolute alcohol.

Preparation of Amino Acid Derivatives.—Hippuryl amide and benzoylglycylglycine were prepared from hippuric acid by the method of Fischer.[9] Ethyl hippurate was prepared from hippuric acid in absolute alcohol by the introduction of anhydrous hydrogen chloride. After removal of

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[2] Presented before the 117th Meeting of the American Chemical Society at Philadelphia, Penna., April, 1950.

[3] This is paper VII in a series on the Water Absorption of Proteins.

[4] D. J. Lloyd and H. Phillips, *Trans. Faraday Soc.*, **29**, 132 (1933).

[5] O. L. Sponsler, J. D. Bath and J. W. Ellis, *J. Phys. Chem.*, **44**, 996 (1940).

[6] E. F. Mellon, A. H. Korn and S. R. Hoover, THIS JOURNAL, **69**, 827 (1947).

[7] E. F. Mellon, A. H. Korn and S. R. Hoover, *ibid.*, **70**, 3040 (1948).

[8] E. F. Mellon, A. H. Korn, E. L. Kokes and S. R. Hoover, *ibid.*, **73**, 1870 (1951).

[9] E. Fischer, *Ber.*, **38**, 605 (1905).