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STRUCTURES OF THE ACIDS OBTAINED BY OXIDATION OF BITUMINOUS COAL-
THERMAL DECARBOXYLATION OF THE COPPER SALTS

R. S. Montgomery and E. D. Holly
The Dow Chemical Company

ABSTRACT

The chemical structures of the aromatic acids obtained by the controlled oxidation of bituminous coal were investigated by thermal decarboxylation of the copper salts followed by separation and identification of the products. This decarboxylation method allows the identification of the nitrogen-containing nuclei. The use of this method, however, resulted in a less complete decarboxylation and much greater yields of oxygenated nuclei than did the copper-quinoline method.

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STRUCTURES OF THE ACIDS OBTAINED BY OXIDATION OF BITUMINOUS COAL-
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In our previous papers^{1,2} the chemical structure of bituminous coal was studied by investigating the nuclei of the aromatic acids obtained on controlled oxidation. The mass spectrometer was found to be ideally suited to this work because with it very small amounts of hydrocarbons can be identified in rather complex mixtures. In the previous work the decarboxylations were carried out using the copper-quinoline method. This method was found to be generally satisfactory but with it the small amounts of the basic, nitrogen-containing nuclei could not be detected owing to the large quantities of quinoline that are used in the reaction. Therefore, the coal acids have been decarboxylated using an alternate method. The thermal decomposition of the copper salts of the acids will bring about decarboxylation without the use of quinoline and so allow the determination of the nitrogen-containing nuclei in addition to the neutral and acidic nuclei. Another reason for investigating this alternate decarboxylation method was that Entel³, by using this method, found significant amounts of 9-fluorenone, biphenylene oxide, and the lactone of 2-hydroxy-2'-biphenylcarboxylic acid that we were unable to detect using the copper-quinoline method although we had been able to account for substantially all of the nuclei.

EXPERIMENTAL

The acids used in this study were obtained from The Coal Research Laboratory of the Carnegie Institute of Technology and were the same as those investigated in our previous papers. They were obtained by the oxidation of an aqueous alkaline suspension of Pocahontas No. 3 bituminous coal by gaseous oxygen at 270° and total pressures of about 900 psig.

Decarboxylation. - The decarboxylation was carried out by the method used by Entel. A solution of 1.0 kg. of the coal acids in 1.0 l. of water was made and 380 g. of basic copper carbonate (1.7 mole $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) was added in small quantities with stirring. To ensure the completion of the reaction, after cessation of the evolution of carbon dioxide the reaction mixture was stirred and heated for one and a half hours on a steam-bath.

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- (1) R. S. Montgomery, E. D. Holly, and R. S. Gohlke, *FUEL*, Lond. 35, (1956) 49
 - (2) R. S. Montgomery and E. D. Holly, *FUEL*, Lond. 36, (1957) 63
 - (3) J. Entel, *J. Amer. Chem. Soc.* 77, (1955) 611

This aqueous suspension of the copper salts of these acids was made up to a volume of 2.0 l. and charged to a four-liter, stainless steel, externally heated, shaking autoclave. The autoclave was flushed with nitrogen and heating and shaking of the autoclave was started and maintained for 24 hours after reaching a temperature of 250°. The pressure after this length of time was 3180 psig. After cooling to room temperature, the autoclave was vented through two Dry Ice-methylene chloride-filled cold traps. Just 3.6 g. of a very low-boiling liquid was obtained in the cold traps.

Initial Separation. - The autoclave contained two layers. The aqueous layer was almost clear and colorless while the oil layer was rather dark-colored and tarry appearing. The residue on the bottom of the autoclave was washed well with both water and carbon tetrachloride before discarding it. About 2 l. of carbon tetrachloride was used.

The acidic products of the decarboxylation were separated by making the reaction mixture basic and separating the aqueous layer. This aqueous layer was in turn acidified and the acidic nuclei extracted by means of carbon tetrachloride. A large amount of solid material was obtained that was not soluble in either water or carbon tetrachloride. This was presumably the partially decarboxylated acids.

The original carbon tetrachloride solution from which the acidic material had been removed was then extracted with water to which had been added a little sulfuric acid. The basic nuclei were obtained by making this extract basic and then extracting it with carbon tetrachloride. The original carbon tetrachloride solution from which both the acidic and basic components had now been removed contained only the neutral decarboxylation products.

Work-up of the Carbon Tetrachloride Extracts. - Most of the solvent was removed from the carbon tetrachloride solutions of the neutral, acidic, and basic decarboxylation products at atmospheric pressure using a 30 inch concentric-rod type column. The distillation fractions were examined by means of a 200° inlet mass spectrometer and in some cases an ultraviolet spectrometer. The residue from the atmospheric distillation of the carbon tetrachloride solution containing the acidic components was vacuum distilled in order to obtain more accurate estimates of the amounts of the various components. The weights of the components are given in Table 1.

TABLE 1

Compound	Weight, g.
Mass 198 (carboxybiphenyl)*	1.
Mass 196	2.
Mass 172	0.3
Mass 170 (phenylphenol)	1.
Biphenylene oxide	0.2
Mass 166 (phthalic acid)	0.1
Biphenyl	0.1
Toluic acid	3.2
Naphthalene	0.7
Benzoic acid	11.7
Cresol	0.03
Phenol	2.3

* Tentative assignments are given in parenthesis.

The carboxylic acids present represent 0.8 g. of biphenyl, 1.9 g. of toluene, and 7.2 g. of benzene.

The weights of the various basic decarboxylation products are given in Table 2.

TABLE 2

Compound	Weight, g.
Phenanthridine	0.2
Phenylpyridine	4.1
Quinoline	0.3
Pyridine	present

The phenanthridine was identified by means of its ultraviolet spectrum.

The solvent that was stripped from the carbon tetrachloride solution containing the neutral decarboxylation products contained a total of 75.9 g. of benzene, 1.9 g. of toluene, and 18.9 g. of methylethylketone. The total weight of the residue from this distillation was 165 g. A 106.6 g. portion was vacuum distilled. The results are tabulated in Table 3.

TABLE 3

Fraction	Temperature	Weight, g.
1	35°/160 mm. to 48°/160 mm.	10.60
2	76°/1.0 mm. to 97°/0.6 mm.	10.85
3	87°/0.3 mm. to 141°/0.6 mm.	15.68
4	139°/0.7 mm. to 181°/0.6 mm.	20.67
residue		44.55
loss		4.2

These fractions were examined by means of a 200° inlet mass spectrometer and the results given in Table 4. The weights are based on the entire 165 g. rather than the 106.6 g. actually distilled.

TABLE 4

Component	Fract. 1	Fract. 2	Fract. 3	Fract. 4
Terphenyl	---	0.02 g.	0.05 g.	0.6 g.
α -phenyl naphthalene	---	0.07	0.3	4.1
Mass 196	---	0.2	0.2	3.8
Benzophenane	---	0.5	6.4	6.7
9-Fluorenone	---	---	---	7.0
Phenanthrene	---	---	---	6.7
Biphenylene oxide	---	1.7	12.6	1.3
Biphenyl	---	6.5	7.9	0.3
Mass 152	---	---	---	1.
Methylnaphthalene	---	0.2	---	---
Naphthalene	0.02 g.	7.6	0.9	---
C ₂ benzene	0.03'	---	---	---
Toluene	0.6	---	---	---
Benzene	0.3	---	---	---

** This notation indicates benzene substituted with two saturated carbon atoms, i.e. ethylbenzene or xylene.

There were also small amounts of masses 198, 146, 134, 122 and 120. The residue was about 80% non-volatile in the mass spectrometer. It contained terphenyl, biphenyl, and masses 204, 202, 196, 182, 180, 178 and 168.

Chromatography. - An 18.7 g. portion of the fourth fraction of the above vacuum distillation was chromatographed. A 1-1/8 x 20 inch column packed with alumina was used. The material to be chromatographed was applied to the column from 172 g. of carbon tetrachloride. All of the material with the exception of 1.5 g. of a dark-colored tar was soluble. One hundred milliliter fractions of the eluate were taken. The fractions were evaporated under vacuum at room temperature and the residues weighed. Some representative fractions were examined by means of a mass spectrometer. Some of the fractions were also examined by means of an infrared spectrometer and an ultraviolet spectrometer. A total of 14.01 g. was collected but it was estimated that 3.5 g. of this was residual solvent. Therefore quite a bit of the material that was originally absorbed on the column was lost and judging from the fact that the lower molecular weight, more volatile components were considerably reduced in the fractions of the eluate, it was lost by evaporation or sublimation during the removal of the solvent.

The amounts of the various components and the solvents used to elute them are plotted as a function of fraction number in Figures 1 and 2. After the last fraction, a small amount of additional material was obtained by heating the alumina from the column with benzene. The position and shape of the

curves if very informative about the structure of the components. The amounts of the components were estimated by graphically intergrating the areas under the curves, and are tabulated in Table 5. The weights are based on the entire 20.67 g. rather than the 18.7 g. actually chromatographed.

TABLE 5

Component	Weight, g.
Mass 258	0.12
Mass 244	0.078
Mass 232	0.011
Terphenyl	0.48
Mass 228	0.033
Mass 218	0.024
α -phenyl naphthalene	0.77
Mass 202	0.19
The lactone of 2-hydroxy-2'-biphenylcarboxylic acid	2.0
Methyl benzophenone	0.18
Mass 184	0.53
Benzophenone	2.6
9-Fluorenone	2.4
Phenanthrene	2.1
Mass 170	0.004
Total	11.5 g.

Traces of the following masses were also found: 246, 220, 210, 208, and 150.

Identification of Masses 204, 196, 180 and 168. - All of the important components found in the previous papers were identified with the exception of mass 204. This mass was tentatively identified as phenylnaphthalene. This component was concentrated from chromatographic fraction number two by crystalization and its mass and infrared spectra compared with that of an authentic sample of α -phenylnaphthalene. The spectra were found to be identical and so it was concluded that mass 204 is indeed α -phenylnaphthalene.

In the present work three new components were found. Mass 196 was identified as predominately the lactone of 2-hydroxy-2'-biphenyl carboxylic acid by its mass and infrared spectra. A small portion of mass 196 was identified as methylbenzophenone by its mass spectrum and its position in the eluate (see Fig. 1). Mass 180 and mass 168 were identified as 9-fluorenone and biphenylene oxide respectively by their mass and infrared spectra. This lactone, 9-fluorenone, and biphenylene oxide were all found by Entel using the same decarboxylation method.

Total Amount of Nuclei Found. - The total amount of the various nuclei can be computed by summing up the components in each of the fractions. The various carboxylic acids that were found were calculated as neutral nuclei and included in this sum. The nitrogen-containing nuclei are tabulated in Table 6 and the neutral and acidic nuclei tabulated in Table 7.

TABLE 6

Compound	Yield, g./kg.	Portion of total nitrogen, % *	Portion of total nuclei, % **
Phenanthridine	0.2	1.	0.04
Phenylpyridine	4.1	19.	0.9
Quinoline	0.3	6.	0.07
Pyridine	present	---	----
Total	4.6	26.	1.0

* Based on 0.2% nitrogen in the original acids.

** Based on a theoretical yield of 453 g. of nuclei per kilogram of coal acids.

TABLE 7

Compound	Yield, g./kg.	Compound	Yield, g./kg.
<u>Neutral Nuclei</u>			
Mass 258	0.12	Mass 184 (C ₁₄ H ₁₆)	0.53
Mass 246	present	Benzophenone	13.6
Mass 244	0.078	9-Fluorenone	8.2
Mass 232	0.011	Phenanthrene	9.9
Terphenyl (m- and p-)	0.82	Biphenylene oxide	16.6
Mass 228	0.033	Biphenyl	19.0
Mass 220	present	Mass 152	0.95
Mass 218	0.024	Mass 150	present
Mass 210 (C ₁₄ H ₁₀ O ₂)	present	Methylnaphthalene	
Mass 208	present	(α- and β-)	0.17
α-phenylnaphthalene	4.5	Naphthalene	10.6
Mass 202	0.19	C ₂ benzene	0.03
Lactone of 2-hydroxy-2'-biphenylcarboxylic acid	7.4	Toluene	3.8
Methylbenzophenone	0.18	Benzene	83.1
<u>Acidic Nuclei</u>			
Mass 170 (phenylphenol)	1.0	Phenol	2.3
Cresol	0.03		

In addition to these nuclei, 18.9 g. of methylethylketone was obtained. This was doubtless a residue of the solvent used to isolate the coal acids from the original aqueous reaction mixture.

DISCUSSION

By using the thermal decomposition of the copper salts of the coal acids it has been possible to identify about 26% of the nitrogen containing nuclei. The nitrogen-containing nuclei probably amount to only about 4% of the total nuclei of the coal acids but their structures are important in that they provide information about the condition of the nitrogen atoms in the original coal structure. Phenanthridine, phenylpyridine, quinoline, and pyridine have been found. Entel found similar amounts of phenylpyridine, quinoline, and pyridine but the more highly condensed structure, phenanthridine, has not been reported before. The presence of these compounds in the decarboxylation products demonstrates the presence of nitrogen-containing condensed aromatic systems in bituminous coal.

In the present work, mass 204 which occurs in significant amounts in the decarboxylation products was definitely identified as phenyl-naphthalene. It was also possible to definitely identify methylbenzophenone.

This decarboxylation method yielded smaller amounts of nuclei than did the copper-quinoline method used in our previous papers. This is due to a less complete decarboxylation as evidenced by the relatively large amounts of carboxylic acids present in the products. In addition, this decarboxylation method yielded greatly increased amounts of oxygenated nuclei. The oxygenated compounds amounted to about 48 per cent of the neutral nuclei (excluding benzene) where by the copper-quinoline method they amounted to only 3 per cent. Almost twice as much benzophenone was obtained and large amounts of three oxygenated nuclei that did not occur in the products of the other decarboxylation method were found. These three nuclei were the lactone of 2-hydroxy-2'-biphenylcarboxylic acid, 9-fluorenone, and biphenylene oxide. With the exception of these oxygenated nuclei, the decarboxylation products were similar to those found previously by the other method.

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