

COMPARISON OF THE THERMAL DECOMPOSITION OF THE COPPER SALTS WITH THE
COPPER-QUINOLINE DECARBOXYLATION METHOD

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ABSTRACT

The copper-quinoline decarboxylation method has produced appreciably different results than has the thermal decomposition of copper salts of the acids obtained by the controlled oxidation of bituminous coal. Therefore, a study was made of these two decarboxylation methods in order to determine their reliability. Essentially complete decarboxylation was obtained with the copper-quinoline method while the other method produced only partial decarboxylation. A portion of the naphthalene obtained by the decarboxylation of naphthoic acid, however, was converted to methylnaphthalene during the course of the copper-quinoline decarboxylation. The thermal decomposition, on the other hand, produced the lactone of 2-hydroxy-2'-biphenylcarboxylic acid and probably other oxygenated nuclei. These peculiarities of the methods must be taken into account in interpreting the results of the decarboxylations of the coal acids.

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Not for Publication
Presented Before the Division of Gas and Fuel Chemistry
American Chemical Society
New York City Meeting, Sept. 8-13, 1957

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The structures of the acids obtained by the controlled oxidation of bituminous coal have been investigated by decarboxylation followed by separation and identification of the nuclei. The results of decarboxylation by the copper-quinoline method^{1,2} and by thermal decomposition of the copper salts^{3,4} were appreciably different. Much larger yields of oxygenated nuclei and less complete decarboxylation of the acids resulted when the thermal decomposition of the copper salts was used. In the present study a model mixture that approximated the coal acids as closely as possible was decarboxylated by both of the methods and the products and their amounts were compared.

EXPERIMENTAL

A mixture of aromatic acids was made that would resemble the mixture obtained by the controlled oxidation of bituminous coal. The approximate proportions of acids possessing the benzene, naphthalene, and biphenyl nuclei were the same although the functionalities of the naphthalene and biphenyl carboxylic acids were lower than the acids of the same nuclei in the coal acid mixture. Furoic acid and an aliphatic acid containing a pyrene nucleus were included in the model mixture although there is no evidence that these nuclei are actually present in the coal acid mixture. This was done because it has been suggested that these types of nuclei were present but not detected owing to the experimental techniques used. The composition of the model mixture is given in Table 1.

TABLE 1

Nucleus	Acid	Proportion, %
Benzene	Benzoic acid	0.94
	o-toluic acid	0.54
	m-toluic acid	0.47
	p-isopropylbenzoic acid	0.47
	o-phthalic acid	12.19

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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
 - (4) R. S. Montgomery and E. D. Holly

TABLE 1 (cont'd)

Nucleus	Acid	Proportion, %
	m-phthalic acid	3.96
	p-phthalic acid	2.89
	trimellitic acid	20.07
	trimesic acid	9.79
	pyromellitic acid	8.87
Naphthalene	1-naphthoic acid	9.59
	2-naphthoic acid	9.48
Biphenyl	diphenic acid	18.85
Propylpyrene	α -(1-pyrene) butyric acid	0.94
Furan	furoic acid	0.94
		<u>100.00</u>

Decarboxylation using the Copper-Quinoline Method. - A 40.0 g. portion of the model mixture was mixed with 12.0 g. of anhydrous copper sulfate and 120.0 g. of freshly distilled quinoline and allowed to stand overnight. The flask that contained the mixture was fitted with a reflux condenser and the condenser vented through a cold trap. It was maintained at 160° overnight and then heated under slow reflux for nine days. The reflux temperature had gone down to 205° after three days but after four days had risen again to 218° where it remained for the duration of the decarboxylation. This was doubtless caused by the formation of benzene and other low-boiling nuclei and the subsequent loss of some of these products. After the reaction mixture had been cooled to room temperature, carbon tetrachloride was added and the resulting solution washed with 325 ml. of 20% hydrochloric acid. The insoluble tar was filtered out of the mixture and the layers separated. The aqueous layer was washed with carbon tetrachloride and discarded. A total of about 575 ml. of carbon tetrachloride was used.

The carbon tetrachloride layer was extracted with 100 ml. of 5% sodium hydroxide solution and the basic extract, in turn, acidified and extracted with about 100 ml. of ether. After the ether had been allowed to evaporate at room temperature, a residue of 0.03 g. of a viscous yellow oil was obtained. This oil was examined by means of a 200° inlet mass spectrometer and the results are given in Table 2.

TABLE 2

Component	Weight, g.
Mass 170 (phenylphenol)*	0.002
Mass 142	0.0006
Mass 136 (C ₃ phenol)**	0.0002
Mass 122 (C ₂ phenol)	0.002
Mass 108 (cresol)	0.001
	<u>0.006</u>

* Tentative identifications are given in parenthesis

** This notation designates phenol substituted with three saturated carbon atoms, i.e. propylphenol, methylethylphenol, or trimethyl phenol.

The mass spectrum also indicated that in addition to the components listed, the oil contained a complex mixture of high molecular weight materials.

The low-boiling material obtained from the cold trap was also analyzed by means of a mass spectrometer. In addition to sulfur dioxide and water, it contained 0.09 g. of furan, 0.9 g. of benzene, and 0.04 g. of toluene.

Most of the solvent was removed from the carbon tetrachloride solution containing the neutral components using a 12 inch Vigereux column. In addition to the carbon tetrachloride, the distillate contained 4.5 g. of benzene and 0.09 g. of toluene. The residue was examined using a 200° inlet mass spectrometer and the results are tabulated in Table 3.

TABLE 3

<u>Component</u>	<u>Weight, g.</u>
Biphenyl	4.66
Methylnaphthalene	0.37
Naphthalene	5.78
C ₃ benzene	0.16
Toluene	0.13
	<hr/> 11.1

Decarboxylation using Thermal Decomposition of the Copper Salts. - A 40.0 g. portion of the model mixture was mixed with 16.0 g. of basic copper carbonate ($\text{CuCO}_3 \cdot \text{Cu(OH)}_2$) in enough water to produce a solution volume of about 160 ml. The mixture was heated for 2 hours on a steam bath and then charged to a 320 ml. stainless steel autoclave. The autoclave was heated at 150° for about 2 hours and then maintained at 250 - 260° for 26 hours. After this length of time, the pressure had reached 750 psi. The autoclave was carefully vented and the contents washed out with both water and carbon tetrachloride. The mixture was made basic and the dark colored, insoluble residue filtered out and discarded.

The aqueous, basic extract was then acidified thereby precipitating a tan-colored material. The composition of this tan, insoluble material was investigated using a 200° inlet mass spectrometer. It contained 3.7 g. of benzoic acid and 2.6 g. of naphthoic acid. A significant amount of a mass 73 fragment ($-\text{CH}_2-\text{CH}_2-\text{COOH}$) was also found but no peak was detected at the molecular weight of this component. The mixture also contained small amounts of mass 198 (α -phenylbenzoic acid), 196, 170 (phenylphenol), 168, and 164 (isopropylbenzoic acid).

Most of the solvent was removed from the carbon tetrachloride solution of the neutral components using a 12 inch Vigereux column. The distillate contained 0.65 g. of benzene, 0.1 g. of toluene, 0.18 g. of naphthalene, and 0.21 g. of biphenyl in addition to the carbon tetrachloride. The composition of the residue as determined by its mass spectrum is given in Table 4.

TABLE 4

Component	Weight, g.
Biphenyl	3.5
Naphthalene	3.2
C ₃ benzene	0.05
Toluene	0.05
	<u>6.8</u>

In addition to the nuclei listed, small amounts of masses 202, 196, and 168 were also found.

Since small amounts of unexpected nuclei were found in the residue, it was chromatographed so that they could be more positively identified. A 9.60 g. portion was chromatographed using a 1 x 14 inch column filled with about 150 g. of alumina. The solvents used to elute the column are tabulated in Table 5.

TABLE 5

Fraction	Solvent	Volume, ml.
1	Carbon tetrachloride	225
2	" "	500
3	Acetonitrile	225
4	"	500
5	"	100
6	95% ethanol	250
7	"	450

The first part of the solvent was removed on a steam bath under reduced pressure and the remaining solvent removed by means of a jet of air at room temperature. Fractions 1 and 2 were not taken to dryness to avoid losing the more volatile components. The fractions were examined by means of a 200° inlet mass spectrometer. The first two fractions contained only biphenyl and naphthalene. Fraction 3 contained a mixture of small amounts of many components while the later fractions contained almost exclusively mass 196. This mass 196 was shown to be the lactone of 2-hydroxy-2'-biphenyl carboxylic acid by its infrared spectrum. The total weights of the various components of these fractions based on the total weight of the residue rather than the 9.60 g. actually chromatographed are tabulated in Table 6.

TABLE 6

Component	Weight, g.
Mass 232 (phenylnaphthylketone)	0.05
Pyrene	0.09
Lactone of 2-hydroxy-2'-biphenylcarboxylic acid	0.4
Biphenyl	3.0
Naphthalene	3.1
Mass 149 (fragment)	0.08

Very small amounts of the following components were also found: Mass 220, mass 208, mass 182 (benzophenone), mass 180 (fluorenone), Mass 168 (biphenylene oxide), and possibly Mass 280. The pyrene was identified by its mass and ultraviolet spectra.

RESULTS

The amounts of the various nuclei found using each of these decarboxylation methods are tabulated and compared with calculated amounts in Table 7. The amounts found using the copper-quinoline method generally agreed very well with the calculated amounts. This agreement would probably be even better if a larger amount of the mixture had been decarboxylated. The amounts of the most volatile components, benzene and furan, that were obtained were substantially below the calculated amounts. This was doubtless due to the long reaction time that was used. Low yields of benzene were also obtained when the acids obtained by the controlled oxidation of bituminous coal were decarboxylated using this method and a long reaction time.² It is interesting to note that the furan nucleus survived the decarboxylation. This indicates that since no furan was found in the decarboxylation products of the coal acids, the furan ring is probably not present in the coal acids. Neither pyrene nor any derivative of pyrene was found in the neutral decarboxylation products indicating that α -(1-pyrene) butyric acid was not decarboxylated. This is not unexpected since it is an aliphatic acid and not an aromatic acid as are the others.

An unexpected product of the copper-quinoline decarboxylation of the model mixture was methylnaphthalene. Apparently about six per cent of the naphthalene was converted to methylnaphthalene during the decarboxylation. This presence of methylnaphthalene where there should be none casts doubt on the large amounts of methylnaphthalene obtained from the coal acids and reported in our earlier paper.² The amounts of methylnaphthalene found in the decarboxylation products of the coal acids have been much more variable than have the amounts of any other nucleus. It is likely that some of the methylnaphthalene that was found in the decarboxylation products was actually present as naphthalene in the original acid mixture.

TABLE 7
Copper-Quinoline Method Thermal Decomposition Method

Component	Calc. Amount, g.		Amt. found, g.		Amt. found, %		Amt. found, g.		Amt. found, %	
	9.3	0.27	5.4	0.26	58	96	0.65	7.	---	---
Benzene										
Toluene										
Isopropylbenzene										
Naphthalene										
Biphenyl										
Furan										
n-propylpyrene										
Methylnaphthalene										
Pyrene										
Mass 232 (phenylnaphthylketone)										
The lactone of 2-hydroxy-2'-biphenylcarboxylic acid										
	0.0	0.0	0.0	0.0	---	---	0.40	---	---	---

In addition to the above components, very small amounts of phenols were found in the products of the copper-quinoline method and probably were also present in the products of the thermal decomposition method. Complex, oxygenated nuclei were also found in the products of the thermal decomposition method.

Very small amounts of phenols were also found in the copper-quinoline decarboxylation products of the model mixture. Because of this, it is doubtful if much can be concluded from the small amounts of phenols found in decarboxylation products of the coal acids.

The thermal decomposition of the copper salts of the model mixture resulted in a much less complete decarboxylation. No furan and no propylpyrene were found in the products although a small amount of pyrene itself was detected. A significant amount of the lactone of 2-hydroxy-2'-biphenylcarboxylic acid was found doubtless arising from the diphenic acid. Small amounts of mass 232, probably phenylanthrylketone, and other oxygenated products were also obtained by using this decarboxylation method. Therefore, the lactone of 2-hydroxy-2'-biphenylcarboxylic acid and probably the 9-fluorenone and the biphenylene oxide reported by Entel³ and by us in a previous paper⁴ are artifacts of the decarboxylation method and not present as such in the coal acids. These nuclei were found by using the thermal decarboxylation method but not by using the copper-quinoline method. Larger amounts of benzophenone were also found by using the thermal decomposition of the copper salts and so probably some of this oxygenated nucleus is also an artifact of the method. Small amounts of phenols are probably also present in the decarboxylation products as they were when the copper-quinoline method was used but they were masked by the large amounts of undecarboxylated and partially decarboxylated acids recovered.

CONCLUSION

The copper-quinoline decarboxylation method seems to be quite reliable and to provide a good estimate of the amounts of the various nuclei present. Significant amounts of methyl-naphthalene, however, were found where only naphthalene should have been found. Therefore, some of the methyl-naphthalene and perhaps some of the other methyl substituted aromatics reported in the previous papers^{1,2} as occurring in the acids obtained by the controlled oxidation of bituminous coal may be artifacts and not actually present. The thermal decomposition of the copper salts resulted in a much less complete decarboxylation of the model mixture and, in addition, resulted in the formulation of oxygenated nuclei. The lactone of 2-hydroxy-2'-biphenylcarboxylic acid which is present in the thermal decarboxylation products of the coal acids^{3,4} is probably obtained from a diphenic acid type precursor since it was also found in the decarboxylation products of the model mixture. It also seems likely that the 9-fluorenone and the biphenylene oxide and some of the benzophenone that was found when this decarboxylation method was used are also artifacts of the method.

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