

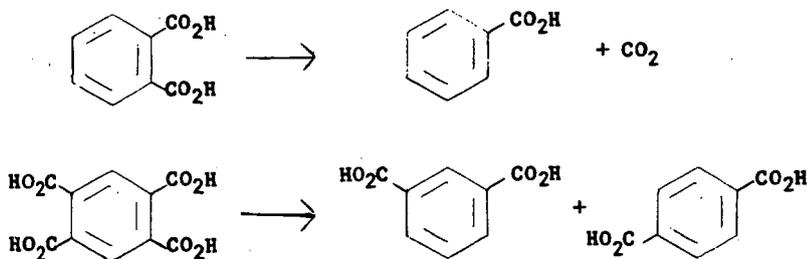
GAS CHROMATOGRAPHIC SEPARATIONS OF BENZENECARBOXYLIC ACIDS DERIVED FROM COAL

Marvin L. Kaufman, Sidney Friedman, and Irving Wender

U. S. Bureau of Mines, Pittsburgh Coal Research Center,
4800 Forbes Avenue, Pittsburgh, Pennsylvania 15213

INTRODUCTION

When benzenepolycarboxylic acids are treated with hydrogen and carbon monoxide at elevated temperatures and pressures in the presence of dicobalt octacarbonyl, a reductive decarboxylation reaction occurs^{2/}



The products of the reaction are carboxylic acids containing fewer carboxyl groups than are present in the starting acid. In most cases mixtures of benzenecarboxylic acids are obtained.

Alkaline oxidation of coal produces a mixture containing relatively large amounts of benzenecarboxylic acids.^{2,7/} If these "coal acids" can be decarboxylated by the above reaction, commercially useful products such as isophthalic and terephthalic acids might be obtained. In studying the feasibility of this decarboxylation reaction, it is necessary to have an analytical procedure by which the benzenecarboxylic acids can be separated and analyzed quantitatively. Several chromatographic procedures, including thin layer, column, and paper chromatography, for the separation of this type of acids appear in the literature.^{2,3,6/} All of these procedures, however, are deficient in some respects. The visualization and quantitative estimation of the separated acids is difficult. Moreover, the separation of isophthalic and terephthalic acids was not reported.

The free acids cannot be analyzed by gas liquid chromatography (g.l.c.) because they are not volatile enough and they tend to decarboxylate or form anhydrides at high temperatures. In order to chromatograph acids, derivatives are usually prepared; esters are the most common. Schnitzer and Desjardins^{8/} have described a g.l.c. procedure utilizing methyl esters to separate benzenecarboxylic acids. Complete esterification of all of the acids required the use of diazomethane, a reagent with some undesirable properties. In addition, isophthalic and terephthalic acids were not separated sufficiently for quantitative analysis and tailing of the peaks was noticeable. Trimethylsilyl esters of amino acids,^{1/} phosphonic acids^{5/} and carboxylic acids^{4/} have been prepared and analyzed by g.l.c. Symmetrical peaks are obtained and separations were usually adequate. The preparation of trimethylsilyl esters is also relatively simple experimentally. For these reasons, the preparation and gas chromatographic behavior of the trimethylsilyl esters of benzenecarboxylic acids was investigated and is the subject of this paper.

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DISCUSSION

Several methods have been used for the preparation of trimethylsilyl derivatives.^{1,4,5/} All of the reagents investigated for the preparation of trimethylsilyl esters of benzenecarboxylic acids were successful in silylating the acids that contained up to four carboxyl groups. However, the esters of the pentacarboxylic acid and the hexacarboxylic (mellitic) acids either did not form or their formation was not reproducible. A procedure that was found to give consistent results was to reflux the acids with equal volumes of hexamethyldisilazane, trimethylchlorosilane and toluene until the resulting ammonium chloride sublimed and the acids were completely solubilized. This procedure was used to obtain the esters used in this paper.

To carry out a quantitative analysis on benzenecarboxylic acids and on the coal acids, flame ionization detector response factors for each of the acids were determined relative to *m*-toluic acid as a standard. Synthetic mixtures of ten benzenecarboxylic acids plus *m*-toluic acid were prepared, silylated and chromatographed. Figure 1 shows the separation of this synthetic mixture. Once the response factors were determined, other mixtures of the acids containing different weights of each acid were prepared and analyzed using the appropriate response factors. Table 1 compares the known and found values of a sample mixture and shows that the analysis can be made satisfactorily.

Table 1. Analysis of synthetic mixture of benzenecarboxylic acids

Component	Position of carboxyl groups	Composition, percent by weight	
		Known	Found
Benzoic	1	6.5	6.3
Phthalic	1,2	4.3	4.0
Isophthalic	1,3	8.4	8.6
Terephthalic	1,4	6.6	7.1
Hemimellitic	1,2,3	5.5	5.1
Trimellitic	1,2,4	14.2	15.8
Trimesic	1,3,5	12.8	13.4
Pyromellitic ^{1/}	1,2,4,5	20.5	21.4
Pentacarboxylic	1,2,3,4,5	8.6	6.3
Mellitic	1,2,3,4,5,6	12.6	12.0

^{1/} The other tetracarboxylic acids [prehnitic (1,2,3,5) and mellophanic (1,2,3,4)] were not available. From comparison between the chromatograms of the methyl and trimethylsilyl esters, the authors feel that these should also be separable as trimethylsilyl esters.

The newly developed analytical method was then used for determining the nature of the products from the decarboxylation of pure acids. It was found that polycarboxylic acids containing carboxyl groups ortho to each other decarboxylated giving mixtures of acids containing fewer carboxyl groups than were present in the original acid. For example, in aqueous dioxane, pyromellitic acid yields a 2:1 mixture of isophthalic and terephthalic acids while hemimellitic acid yields a 1:1 mixture of benzoic and isophthalic acids. In general, yields are 70 to 90%.

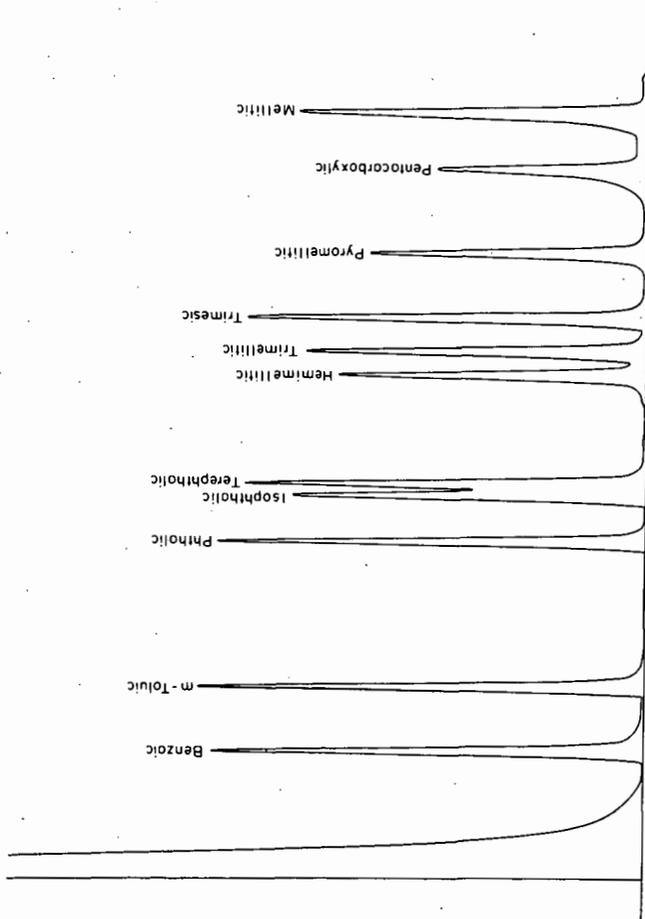


Figure 1. — Separation of benzenecarboxylic acid trimethylsilyl esters.

The coal acids, a mixture obtained from the Dow Chemical Company, and the decarboxylated acids containing a known amount of m-toluic acid were then silylated and chromatographed. Figures 2 and 3 show the type of chromatogram obtained. Using the correction factors which were determined previously, the analysis of the coal acids was carried out. Table 2 summarizes the results. It can be seen that the starting acids contain fairly large amounts of phthalic, hemimellitic, trimellitic, pyromellitic and pentacarboxylic acids. The decarboxylated acids contain large amounts of benzoic, isophthalic and terephthalic acids with only traces of higher acids. Thus it was shown that the decarboxylation reaction essentially converts almost all of the tri-, tetra-, and pentacarboxylic acids to iso- and terephthalic acids and that the benzoic acid results primarily from decarboxylation of phthalic acid. By use of the analytical method described, it was shown that the coal acids were upgraded and converted into valuable products, i.e., benzoic, isophthalic and terephthalic acids, upon undergoing the decarboxylation reaction.

Table 2. Analysis of coal acids

Component	Coal acids, weight percent	
	Before decarboxylation	After decarboxylation
Benzoic	-	4
Phthalic	3.3	Trace
Isophthalic	} 0.4	10
Terephthalic		3
Hemimellitic	2.8	-
Trimellitic	5.5	-
Trimesic	-	> 0.5
Pyromellitic	10.1	Trace
Mellophanic	-	1/
Prehnitic	-	1/
Pentacarboxylic	3.4	Trace
Mellitic	Trace	Trace
Total	25.5	17.5

1/ Traces possibly present; no standards available.

EXPERIMENTAL

Reductive Decarboxylation of Hemimellitic Acid. A solution of 3.1 g. hemimellitic acid (0.0187 mole) and 2.1 g. dicobalt octacarbonyl in 70 ml. dioxane and 15 ml. of water was placed in a 150 ml. Aminco rocking autoclave and pressured to 3500 p.s.i.g. with 1:1 synthesis gas ($H_2:CO$). The autoclave was heated to 200°C. for 5 hr. and allowed to cool overnight. The gases were vented and the reaction mixture taken to dryness under vacuum. The residue was refluxed with dilute hydrochloric acid and again taken to dryness. Most of the product was crystalline, but some gummy material was still present. The product was refluxed with water, cooled, and filtered to yield 3.0 g. of pale, purple solid. A further 0.54 g. of product was extracted from the filtrate with ether.

Gas Chromatographic Analyses. The gas chromatographic analyses were performed on a Micro Tek GC 2000R dual column, programmed-temperature chromatograph equipped with a dual hydrogen flame ionization detector. A 3 foot by 1/8 inch OD stainless steel column packed with 3% Apiezon L on 60 to 80 mesh AW-DMCS treated Chromosorb G was used. Helium at a flow rate of approximately 55 ml. per min. was the carrier gas. Runs were temperature programmed from 90° to 260° at a rate of 7.5° per min. The analysis takes less than one-half hr. under these conditions.

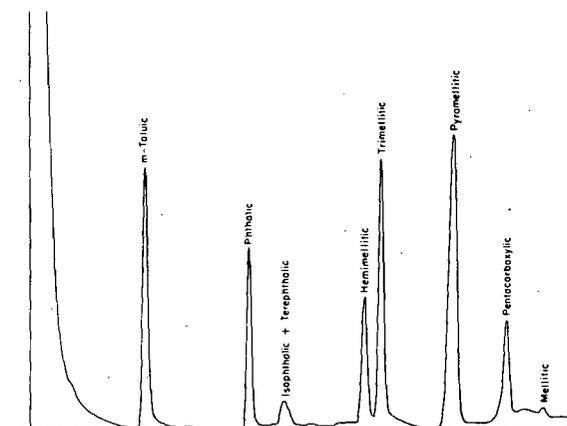


Figure 2 - Cool acids before decarboxylation.

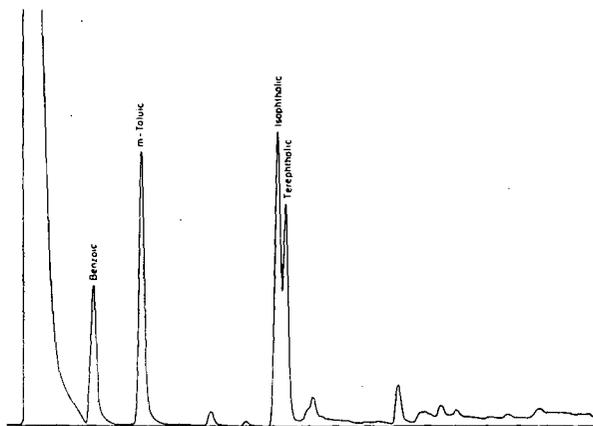


Figure 3 - Cool acids after decarboxylation.

The trimethylsilyl esters were prepared by refluxing the acids with a 1:1:1 mixture of hexamethyldisilazane:trimethylchlorosilane:toluene until the acids were completely solubilized and the resulting ammonium chloride had sublimed. This takes one to two hr. The reaction mixture is kept in a vial sealed with a serum cap to keep out moisture. The fact that the trimethylsilyl ester derivatives are readily hydrolyzable back to the original acid is a useful property of these esters. For example, upon elution from the chromatograph, the ester is trapped out in a capillary tube and exposed to the atmosphere for a short time to affect hydrolysis to the free acid. The infrared spectrum of the acid can then be obtained for positive identification. This has proved extremely helpful for identification since retention times are not reproducible to the degree necessary for identification.

CONCLUSION

By using a g.l.c. separation based on trimethylsilyl esters, it has been possible to rapidly analyze mixtures of carboxylic acids and show that benzenecarboxylic acids undergo a reductive decarboxylation in the presence of hydrogen and carbon monoxide at elevated temperatures and pressures with dicobalt octacarbonyl as a catalyst. The advantages of the trimethylsilyl esters over the methyl esters are that they are easily prepared, chromatograph without tailing, are better separated and are easily converted to the original acid for positive identification. Additionally, with the use of this procedure it has been shown that coal acids undergo this reaction and that valuable products are obtained.

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Manufacturers and products named only to identify the materials used; no endorsement by the Bureau of Mines is implied.

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