

PARTIAL DECARBOXYLATION OF COAL AROMATIC ACIDS BY TRANSITION METAL COMPLEXES

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INTRODUCTION

Not too many years ago, most of our organic chemical industry depended on coal tar as a source of raw material. Today, petroleum serves this role, and relatively few chemicals are produced from coal. In the foreseeable future, this situation may be again reversed, as petroleum becomes less accessible, and the American energy companies turn to coal as a source of liquid fuels as well as chemicals.

One potential preparation of specific chemicals, directly from coal or coal tar, or from the chars and asphaltenes produced during coal liquefaction, is the result of a combination of two steps, one from traditional coal chemistry, the other from a novel reaction discovered at the Bureau of Mines. This process allows the direct conversion of coal to a mixture of isophthalic and terephthalic acids.

EXPERIMENTAL PROCEDURES

Preparation of Tributylphosphine Complexes of Dicobalt Octacarbonyl. - Addition of 2 moles of tributylphosphine per mole of $\text{Co}_2(\text{CO})_8$ in petroleum ether results in evolution of carbon monoxide and precipitation of a yellow solid, $\text{Co}_2(\text{CO})_7 \cdot 2\text{P}(\text{C}_4\text{H}_9)_3$, mp 120-121 (dec.) (from CH_3OH). This compound appears to be stable to air at room temperature when in crystalline form. When in solution, however, decomposition occurs slowly, as evidenced by the formation of a light brown precipitate.

A sample of this catalyst, stored in a refrigerator for 6 months, exhibited no decrease in catalytic activity.

Conversion of $\text{Co}_2(\text{CO})_7 \cdot 2\text{P}(\text{C}_4\text{H}_9)_3$ to $\text{Co}_2(\text{CO})_6 \cdot 2\text{P}(\text{C}_4\text{H}_9)_3$ (1). - A solution of 10 g. of yellow $\text{Co}_2(\text{CO})_7 \cdot 2\text{P}(\text{C}_4\text{H}_9)_3$ in 110 ml. of isooctane was heated to reflux (97°C) under a stream of nitrogen for 3 hours. The solution changed from yellow to dark red-brown in color. The hot solution was filtered, and much of the solvent evaporated from the filtrate under nitrogen. Red-brown crystals appeared upon cooling. These were filtered off to yield 7.7 g. of $\text{Co}_2(\text{CO})_6 \cdot 2\text{P}(\text{C}_4\text{H}_9)_3$, mp 120-121 $^\circ\text{C}$.

Decarboxylation of Benzene Polycarboxylic Acids. - The procedure for carrying out decarboxylations is illustrated by the following example.

A solution of 5 g. of pyromellitic acid and 1 g. of $\text{Co}_2(\text{CO})_7 \cdot 2\text{P}(\text{C}_4\text{H}_9)_3$ in 110 ml. of dioxane was heated to 220° for 5 hours in a magnetically stirred autoclave under an initial pressure of 2000 psig of 1:1 synthesis gas. The autoclave cooled to room temperature overnight and was vented. The reaction mixture was removed and solvent evaporated under vacuum. The residue was treated with sufficient HCl to convert resulting cobalt salts to free acids. An aliquot was

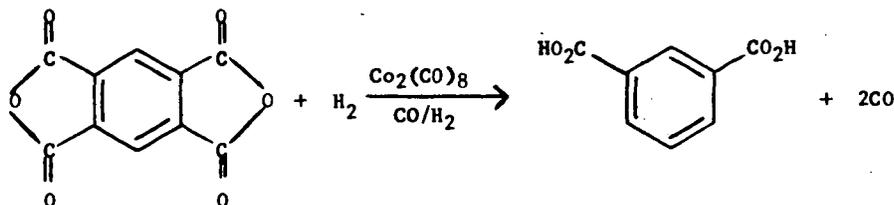
converted to trimethylsilyl esters (2) and analyzed by gas chromatography on a 6 ft. by 1/8-inch-o.d. stainless steel column packed with 3% SE-52* on 80-100 mesh AW-DMCS Chromosorb G.

DISCUSSION AND RESULTS

When coal is carefully air oxidized in the presence of alkali, a mixture consisting largely of aromatic acids is produced (3). This work was originally carried out to obtain product information which could be useful in deducing structure of coal. The product proved to be of sufficient interest in itself for a large chemical company to do bench scale work on oxidizing coal to coal acids (4,5). Unfortunately, the mixed acids, as obtained, found no large markets, largely because of the complexity of the product. Though commercialization did not occur, interest in coal acids has increased, and workers in laboratories scattered around the world have published on this topic in recent years (6-10). Analyses of these fragmentary results indicate that these coal acid mixtures may contain up to 95% (7) benzenepolycarboxylic acid (BPCA), ranging all the way from phthalic acid to mellitic acid.

If it were possible to convert this complex mixture to one with but a few separable components, the oxidation of coal and its derivatives might again become promising. This second step in the process, the conversion of the coal acids to a simple mixture rich in isophthalic and terephthalic acids, is now feasible as a result of a reaction developed at the Bureau of Mines (11,12). In this reaction, a selective decarboxylation of BPCA is effected by $\text{Co}_2(\text{CO})_8$ and certain of its derivatives.

The reaction was initially carried out on anhydrides, rather than acids, and used $\text{Co}_2(\text{CO})_8$ as a decarboxylation catalyst. In a typical example, pyromellitic anhydride is decarboxylated to isophthalic acid in 90% yield at 220°C.



This reaction is unique in that a partial, selective decarboxylation occurs. Generally, decarboxylations of aromatic acids are non-specific and drastic (13-15), the products being the parent hydrocarbon.

The reaction has been applied to a number of benzenepolycarboxylic acids and anhydrides, with results shown in tables 1 and 2. For decarboxylation to occur, there must be 2 adjacent carboxyl groups, as in phthalic acid or anhydride, only one of which is eliminated. In anhydrides, the carboxyl which is retained predominantly (12) is the one meta to a ring substituent, such as $-\text{COOH}$, which is normally meta-directing in electrophilic substitution. Similarly, ortho-para directing groups ($-\text{Cl}$, $-\text{CH}_3$) result in retention predominantly of a para

* Reference to a company or product name is made to facilitate understanding and does not imply endorsement by the U. S. Bureau of Mines.

carboxyl. These directional effects are not observed if the substituent is ortho to the two carboxyl groups, when apparently steric effects become important. When both ortho positions are occupied by large groups, as in 3,6-dimethylphthalic anhydride, no decarboxylation takes place. The free acids show less specificity than do the anhydrides. This is illustrated by pyromellitic anhydride, which gives almost exclusively isophthalic acid, while pyromellitic acid goes to a 2:1 mixture of isophthalic and terephthalic acids.

TABLE 1. - Decarboxylation of benzenepolycarboxylic anhydrides with synthesis gas and $\text{Co}_2(\text{CO})_8^a$

Anhydride	Quantity, μmoles	$\text{Co}_2(\text{CO})_8$ μmoles	Product acid or anhydride	Yield, %
Phthalic ^b	176	13	Benzoic	91
Hemimellitic (1,2,3)	26	3	Benzoic	65
			Isophthalic	15
Trimellitic (1,2,4)	26	6	Isophthalic	~ 100
Pyromellitic (1,2,4,5)	23	12	Isophthalic	90
Mellitic (1,2,3,4,5,6)	10	2	Mellitic	80

^a Standard reaction conditions: 85 ml. toluene, 3500 psig 1 H_2 :1 CO, 5 hours at 200°C.

^b Solvent was 175 ml. toluene.

TABLE 2. - Decarboxylation of benzenecarboxylic acids

Acid	Quantity, μmoles	Catalyst, μmoles	Product acid	Yield, %
Phthalic	60	3 ^a	Benzoic	95
Hemimellitic	19	6 ^a	Benzoic	40
			Isophthalic	38
Hemimellitic	25	1.5 ^b	Benzoic	56
			Isophthalic	12
Trimesic (1,2,3)	25	1.5 ^b	Trimesic	90
Pyromellitic	12	6 ^c	Terephthalic	15
			Isophthalic	30
			Pyromellitic	55
Pyromellitic	25	1.5 ^c	Terephthalic	35
			Isophthalic	65
Prehnitic (1,2,3,5)	8	3 ^c	Terephthalic	4
			Isophthalic	13
			Trimesic	25
			Prehnitic	58

^a Reaction conditions: $\text{Co}_2(\text{CO})_8$, 85 ml. dioxane, 3500 psig 1 H_2 :1 CO, 5 hours at 200°C.

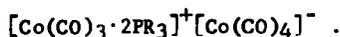
^b Reaction conditions $\text{Co}_2(\text{CO})_7 \cdot 2\text{P}(\text{C}_4\text{H}_9)_3$, 110 ml. dioxane, 2000 psig 1 H_2 :1 CO, 5 hours at 220°C.

^c Reaction conditions: $\text{Co}_2(\text{CO})_8$, 110 ml. dioxane, 2000 psig 1 H_2 :1 CO, 5 hours at 220°C.

In the decarboxylation of anhydrides, $\text{Co}_2(\text{CO})_8$ functions in catalytic amounts; the same is true for phthalic acid. But in reactions involving pyromellitic acid, the $\text{Co}_2(\text{CO})_8$ is consumed in the course of the decarboxylation, resulting in a mole of product per mole of $\text{Co}_2(\text{CO})_8$. Since neither of the products of this reaction, isophthalic and terephthalic acids, react with $\text{Co}_2(\text{CO})_8$ under normal decarboxylation conditions, deactivation of the catalyst must be the result of direct reaction between it and pyromellitic acid.

It has been found that if one or two of the carbon monoxide groups of $\text{Co}_2(\text{CO})_8$ are substituted by certain tertiary phosphine ligands, the resulting complexes are excellent decarboxylation catalysts and are no longer destroyed by pyromellitic acid. Though the complex with triphenylphosphine shows no decarboxylative activity, the complex formed by ethyldiphenylphosphine is an active catalyst, as is one from diethylphenylphosphine. Other phosphines which impart catalytic activity are diphenylphosphinoethane and the trialkylphosphines: triethyl-, tripropyl-, tributyl-, trihexyl-, tricyclohexyl-, and trioctylphosphine.

The reaction of $\text{Co}_2(\text{CO})_8$ with phosphines results in two principal series of complexes. At room temperature, or lower, the usual product is the result of loss of one carbon monoxide and the formation of a yellow, ionic crystalline product insoluble in petroleum ether and soluble in dioxane and acetone. These complexes have the ionic structure (16)



If these complexes are heated, or if the preparation is carried out at elevated temperature, a second carbon monoxide is lost, and a non-ionic complex $\text{Co}(\text{CO})_6 \cdot 2\text{PR}_3$, is formed (1). These complexes are red or red-brown and very soluble in petroleum ether.

Either series of complexes may be used for decarboxylation. While the yellow salts appear to be more stable toward long term storage, the red-brown complexes are the stable ones at 220° in the reaction, and are presumed to form in situ from the yellow salts. It is possible to form the complexes themselves in situ, though most of the work reported here was carried out using preformed catalyst.

Solvent plays a critical role in the decarboxylation. Many solvents are too reactive under the conditions used, reacting either by themselves (dimethylsulfoxide, amines) or with the acids or anhydrides (amides, alcohols). The anhydrides are readily decarboxylated in toluene, as well as in other suitable, inert solvents. The acids, being insoluble in toluene, can be reacted in dioxane, acetone, or methyl ethyl ketone. This last solvent is especially convenient, since it is proposed as an extraction solvent for separation of the coal acids (4).

Several complexes of other transition metals have been investigated as decarboxylation catalysts. These include rhodium oxide, iron carbonyl and several phosphine derivatives, manganese carbonyl, bis(triphenylphosphino)palladium dichloride, and chloro-tris(triphenylphosphino)rhodium. Each has been reported to show activity in hydroformylation or carbonylation-decarbonylation reactions. Only rhodium oxide (presumably converted to a rhodium carbonyl) has shown any activity toward decarboxylation, and that activity was poor.

The decarboxylation has been applied to a mixture of acids obtained by oxidation of coal (4). The results of this decarboxylation are shown in the GC analysis of the acids before and after the reaction (table 3). The initial mixture is rich in tri-, tetra-, and pentacarboxylic acids, while the product is mostly

isophthalic and terephthalic acids. Using some of the data scattered in the literature concerning both yields and composition of coal acids, it is possible to speculate on a process that can turn a ton of coal into about 400 lb. of isophthalic and terephthalic acid with a value of five to ten times that of the original coal at today's market price.

TABLE 3. - 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 (1,2,3,4)	--	a
Prehnitic (1,2,3,5)	--	a
Pentacarboxylic	3.4	Trace
Mellitic	Trace	Trace
Total	25.5	17.5

^a Traces possibly present; not completely separated from pyromellitic acid.

While the oxidation reaction has been applied only to coal and coke in the past, it is believed that other suitable aromatic sources can be used. These include coal tar, and the chars and asphaltenes currently being produced by the various coal liquefaction processes being investigated. A bench-scale unit to optimize yields of BPCA from various coals and chars is now in operation.

As an alternative to decarboxylation of the total product, a portion of the pyromellitic acid present in the coal acids could be recovered by sublimation before decarboxylation. While this would decrease the overall yields of isophthalic and terephthalic acids, it would furnish a product with considerably higher value.

CONCLUSIONS

Controlled air oxidation of coal yields a mixture consisting largely of benzene-polycarboxylic acids. These acids can be partially and selectively decarboxylated to yield a product rich in isophthalic and terephthalic acids by means of catalysts derived from $\text{Co}_2(\text{CO})_8$ by replacement of carbon monoxide groups by certain tertiary phosphine ligands.

REFERENCES

1. F. Piacenti, M. Bianchi, and E. Benedetti, *Chim. Ind. (Milan)*, **49**, 245 (1967).
2. M. L. Kaufman, S. Friedman, and I. Wender, *Anal. Chem.*, **39**, 1011 (1967).
3. R. C. Smith, R. C. Tomarelli, and H. C. Howard, *J. Am. Chem. Soc.*, **61**, 2398 (1939).

4. R. S. Montgomery and R. McMurtrie, Symposium on Technology and Use of Lignite. BuMines Inf. Circ. 8234, pp. 74-98 (1964).
5. W. L. Archer, R. S. Montgomery, K. B. Bozer, and J. B. Louch, Ind. Eng. Chem., 52, 849 (1960).
6. N. W. Franke, M. W. Kiebler, C. H. Ruof, T. R. Savich, and H. C. Howard, Ind. Eng. Chem., 44, 1784 (1952).
7. J. E. Germain and F. Valadon, Bull. Soc. Chim. France 1960, 11.
8. Y. Kamiya, Fuel, 40, 149 (1961).
9. V. Gomez Aranda and F. Gomez Beltran, Combustibles, 22, 147 (1962).
10. A. Benning, Brennstoff-Chemie, 36, 38 (1965).
11. I. Wender, S. Friedman, W. A. Steiner, and R. B. Anderson, Chem. and Ind., 1958, 1694.
12. S. Friedman, M. L. Kaufman, and I. Wender, Ann. N. Y. Acad. Sci., 145, 141 (1967).
13. Y. Kamiya, Fuel, 42, 347 (1963).
14. A. C. McKinnis, U. S. Pat. 2,729,674 (1956).
15. A. C. McKinnis, U. S. Pat. 2,864,854 (1958).
16. L. H. Slaugh and R. D. Mullineaux, J. Organometal Chem., 13, 469 (1968).