of bulk carbide in the synthesis must therefore be considered to be still undetermined.

Noteworthily, however, the *initial* rate of carbon monoxide pickup is at least comparable with the synthesis rate. The processes occurring during the first few minutes of carbiding, identified as "surface carbiding" by Craxford and Rideal, may be closely related to the synthesis. Very little can be said about them at present, and their nature must be studied further.

Acknowledgment.—Thanks are due to Dr. L. J. E. Hofer for many helpful discussions of the problems considered here.

Summary

1. Rates of carbiding, of hydrogenation of carbide, and of hydrocarbon synthesis from carbon monoxide–hydrogen mixtures have been measured for a cobalt–thoria–kieselguhr catalyst (100:18:100) with the use of a circulating gas system.

2. The initial carbiding rate is comparable with the synthesis rate, but the steady rate of bulk carbiding is about one-tenth as large.

3. The apparent activation energies for bulk carbiding and for the synthesis are 31 and 26 kcal./mole, respectively.

4. Within the pressure range 8 to 45 cm. the pressure dependence of the carbiding rate can be expressed as Rate = kp^n, where n is 0.20–0.26.

5. Some of the implications of the experimental results for the mechanism of the carbiding and synthesis are discussed.

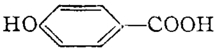
PITTSBURGH, PA. RECEIVED NOVEMBER 25, 1946

[CONTRIBUTION FROM THE RESEARCH DIVISION, THE UPJOHN COMPANY]

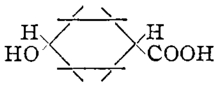
The Hydrogenation of *m*- and *p*-Hydroxybenzoic Acid[1]

BY ROBERT H. LEVIN AND JANET HALL PENDERGRASS

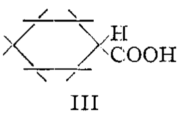
When *p*-hydroxybenzoic acid (I) is reduced, the hydrogenation–hydrogenolysis products cyclohexanecarboxylic acid (III), or cyclohexanol (IV), may be formed, frequently to the exclusion of the expected 4-hydroxycyclohexanecarboxylic acid (II). Low pressure catalytic hydrogenation of *p*-hydroxybenzoic acid has yielded mostly cyclohexanecarboxylic acid.[1a-4] Balas and Kosik[1a] obtained only this hydrogenolysis product, using a platinum black catalyst in water. Balas and Srol[2] isolated some of the *cis*-4-hydroxycyclohexanecarboxylic acid and a small amount of the *trans* form by carrying out the reduction in alcohol. Edson[3] used platinum oxide catalyst in water and obtained the *trans*-4-hydroxycyclohexanecarboxylic acid in 20% yields. The remainder of his product was cyclohexanecarboxylic acid. Recently Hardegger and co-workers[4] reported that hydrogenolysis was the main reaction in a series of low pressure experiments. It is of interest that Long and Burger[5] could only obtain the hydrogenolysis product (VI) by the reduction of 6-hydroxy-1-naphtholic acid (V) using platinum oxide as the catalyst; and recently[6] Price and coworkers reported that all procedures leading to hydrogenation of 6-hydroxy-1,2,3,4 tetrahydro-1-naphthoic acid always resulted in the simultaneous removal of the oxygen at carbon 6.



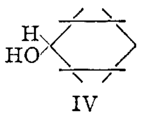
I



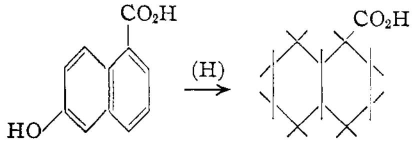
II
cis and *trans* isomers



III

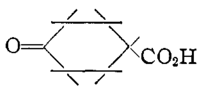


IV



V VI

In 1905 Lumsden[7] reported that the sodium and alcohol reduction of anisic acid gave 70% of cyclohexanecarboxylic acid and 10% of the unexpected δ-ketocyclohexanecarboxylic acid VII. Under the same conditions *p*-hydroxybenzoic acid did not react.



VII

Poor yields of 4-hydroxycyclohexanecarboxylic acid and the formation of cyclohexanol have been reported[8,9,10] in the high pressure reduction of

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(1) Presented before the Division of Organic Chemistry at the 111th A. C. S. meeting, Atlantic City, April, 1947.

(1a) Balas and Kosik, *Časopis Českoslov. Lekárnistva*, **7**, 105 (1927).

(2) Balas and Srol, *Collection Czechoslov. Chem. Commun.*, **1**, 658 (1929).

(3) Edson, *J. Soc. Chem. Ind.*, **53**, 138T (1934).

(4) Hardegger, Plattner and Blank, *Helv. Chim. Acta*, **27**, 793 (1944).

(5) Long and Burger, *J. Org. Chem.*, **6**, 852 (1941).

(6) Price, Enos and Kaplan, Abstracts 111th A. C. S. meeting, April, 1947, p. 23M.

(7) Lumsden, *J. Chem. Soc.*, **87**, 87 (1905).

(8) Ipatiew and Rasuvajew, *Ber.*, **58B**, 306 (1926).

(9) Mitsuii, *Mem. Coll. Sci. Kyoto Imp. Univ.*, **A18**, 329 (1935).

(10) Martin and Robinson, *J. Chem. Soc.*, 491 (1943).

p-hydroxybenzoic acid with various nickel catalysts. However, Martin and Robinson[10] obtained quantitative conversion of the ethyl ester to *trans*-ethyl 4-hydroxycyclohexanecarboxylate by the novel use of palladium-on-strontium carbonate. This has been repeated by Hardegger, *et al.*,[11] and in our laboratory.

Edson[3] has suggested that the *cis* acid formed by the hydrogenation of *p*-hydroxybenzoic acid is easily lactonized; and hydrogenolysis of the lactone then gives cyclohexanecarboxylic acid. This corresponds to the mechanism proposed by Adkins, Wojcik and Covert[12] for the catalytic reduction of *o*-benzoylbenzoic ester to *o*-benzylbenzoic acid. If this mechanism holds for *p*-hydroxybenzoic acid, then acidic conditions should promote lactonization and increase the formation of cyclohexanecarboxylic acid, while basic media should tend to prevent lactonization and thereby produce more 4-hydroxycyclohexanecarboxylic acid. The experiments carried out to evaluate this theory are summarized in Table I. The reaction was stopped after hydrogen uptake had leveled off at 80% or more. It is apparent that acidic reagents do increase the amount of hydrogenolysis product while the use of alkali gives better yields of 4-hydroxycyclohexanecarboxylic acid. Greater amounts of alkali slow down the reduction, and the sodium salt of *p*-hydroxybenzoic acid could not be reduced under these conditions. The best yield, 49%, was obtained using just a few drops of alkali. This yield, calculated on the basis of *p*-hydroxybenzoic acid utilized, is greater than 60%.

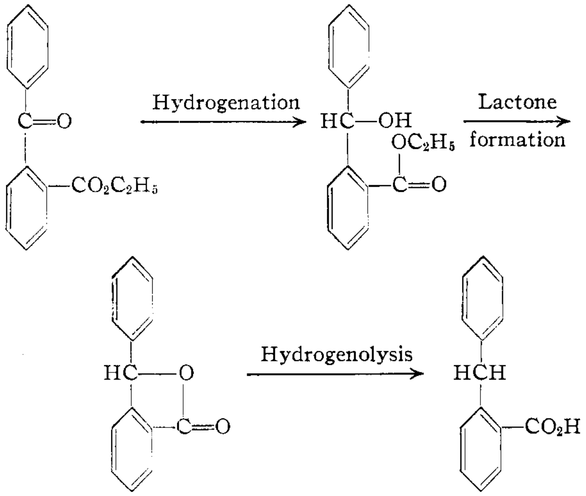


TABLE I

HYDROGENATION OF 0.1 MOLE OF *p*-HYDROXYBENZOIC ACID USING 0.6 G. OF PLATINUM OXIDE

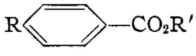
Solvent	Time of hydrogenation, hours	% Yield 4-Hydroxycyclohexanecarboxylic acid[a]	Cyclohexanecarboxylic acid	Starting material recovered
HOAc	1	9	47	20
EtOH	4	28	38	22
EtOH + 1 drop HCl[b]	4	3	47	30
EtOH + 5 drops KOH[c]	8	49	27	20
EtOH + 10 drops KOH	20	38	22	27
EtOH + 20 drops KOH	24	35	22	27
EtOH + *p*-OHC_6H_4COONa	10	..	..	100

[a] *cis* and *trans* mixture. [b] Concentrated hydrochloric acid. [c] 10% potassium hydroxide.

In the next series of experiments (Table II), a number of derivatives of *p*-hydroxybenzoic acid were reduced under similar conditions. It may be concluded that the lactone mechanism for hydrogenolysis, which seemed to be supported by the experiments of Table I, is not entirely tenable. Indeed, the formation of the esters of cyclohexanecarboxylic acid in good yields indicates that hydrogenolysis must occur by some other mechanism, probably before hydrogenation takes place. A direct displacement of the *p*-hydroxyl or the OR group by hydrogen is quite possible.[13]

TABLE II

HYDROGENATION OF *p*-HYDROXYBENZOIC ACID AND DERIVATIVES USING



0.1 MOLE OF COMPOUND AND 0.6 G. OF PLATINUM OXIDE IN ALCOHOL

Compound R	R'	Hydrogenation addition %	Hydrogenation -olysis[a] %	Starting material recovered, %
OH	H	29	38	22
AcO	H	1	70	10
OH	C_2H_5	14[b]	50[c]	29
CH_3O	H	..	74[d]	13

[a] Hydrogenolysis of R group. [b] *Anal.* Calcd. for $C_9H_{16}O_3$: C, 62.76; H, 9.37. Found: C, 63.12; H, 9.22. [c] *Anal.* Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.33. Found: C, 69.68; H, 11.29. [d] Further identified as the amide, m. p. 183. *Anal.* Calcd. for $C_7H_{13}ON$: C, 66.10; H, 10.30; N, 11.02. Found: C, 66.58; H, 10.17; N, 10.79.

A comparison was made of low and high pressure reductions of ethyl *p*-hydroxybenzoate in ethyl acetate using palladium-on-strontium carbonate as catalyst.[10] At low pressure 80% of the theoretical hydrogen was finally absorbed after seven hours, giving 44% of ethyl-4-hydroxycyclohexanecarboxylate, 16% of ethyl cyclohexanecarboxylate and 27% of unchanged starting material. At high pressure hydrogenation was complete in one hour, giving a quantitative yield of the desired product. These experiments indicate that hydrogenation and hydrogenolysis are competing reactions, and that under pressure hydrogenation is favored.

High pressure hydrogenations of *p*-hydroxy-

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(11) Hardegger, Heusser and Blank, *Helv. Chim. Acta*, **29**, 477–483 (1946).

(12) Adkins, Wojcik and Covert, THIS JOURNAL, **55**, 1669 (1933).

(13) Schwenk, Papa, Whitman and Ginsberg, *J. Org. Chem.*, **9**, 1 (1944), have recently reported on the lability of the *o*- and *p*- (but not *m*-)methoxy group in the methoxybenzoic acids to displacement by hydrogen in the presence of aqueous alkali and nickel–aluminum alloy.

benzoic acid and its sodium salt were carried out using Raney nickel catalyst[14] and temperatures of 200–250°. The mixture of products was fractionated through a modified Widmer column. From reduction of the sodium salt was isolated cyclohexanol in 47% yield, 4-hydroxycyclohexanecarboxylic acid in 3% yield, and unchanged starting material. Reduction of the free acid in alcohol produced 27% of cyclohexanol, 4% of cyclohexanecarboxylic acid, 15% of 4-hydroxycyclohexanecarboxylic acid, some *p*-hydroxybenzoic ester, and some starting material.

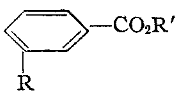
The sodium and alcohol reduction of *m*-hydroxybenzoic acid has been reported to give 3-hydroxycyclohexanecarboxylic acid in yields up to 65%.[15]

Catalytically, Edson[3] obtained a *cis* and *trans* mixture of the desired 3-hydroxy acid in 40% yield, and 60% of cyclohexanecarboxylic acid. Balas and Srol[2] obtained only the *cis*-3-hydroxycyclohexanecarboxylic acid, but reported no yield.

In our hands hydrogenation of *m*-hydroxybenzoic acid and derivatives was analogous to the *p*-hydroxy compound (Table III). Alkali again retarded the amount of hydrogenolysis. As further evidence against the lactone mechanism of hydrogenolysis, *cis*-3-hydroxycyclohexanecarboxylic acid was subjected to hydrogenation over platinum oxide catalyst for eight hours and was recovered unchanged.

TABLE III

HYDROGENATION OF 0.15 MOLE OF *m*-HYDROXYBENZOIC ACID AND DERIVATIVES WITH PLATINUM OXIDE CATALYST IN ETHYL ALCOHOL



Compound R	Compound R′	Catalyst g.	Time, hours	% Yields of products: *cis* and *trans* 3-hydroxy-cyclohexane-carboxylic acid	% Yields of products: Cyclohexane-carboxylic acid	% Yields of products: Starting material recovered
OH	H[a]	1.0	20	64	31	..
HO	H[b]	0.9	6	57	11	29
HO	CH_3	1.0	70	70 (as ester)	15 (as ester)	..
AcO	H	0.5	36	..	66	10

[a] 0.19 mole used. [b] 0.5 ml. of 10% potassium hydroxide added to solution.

Acknowledgments.—We wish to acknowledge the technical assistance of Miss Mildred M. Wesner in certain of these experiments.

Experimental[16]

Low Pressure Hydrogenation of *p*-Hydroxybenzoic Acid.—*p*-Hydroxybenzoic acid (13.7 g., 0.1 mole) was dissolved in 50 ml. of 95% alcohol. Five drops of 10% potassium hydroxide solution and 0.6 g. of platinum oxide catalyst[17] was added and the reaction carried out on the Adams machine, starting at 43 pounds pressure. After eight hours hydrogen uptake stopped at 89% of the theoretical. The catalyst was separated by filtration and the filtrate steam distilled to remove cyclohexanecarboxylic acid. About 1.5 liters of distillate was collected. This was made alkaline, concentrated to 150 ml. on a hot-plate, acidified, and extracted with three 100-ml. portions of ether. The ether was washed, dried over anhydrous sodium sulfate, and taken to dryness to give 3.46 g. (27%) of colorless **cyclohexanecarboxylic acid** which eventually crystallized. For analysis a portion was distilled *in vacuo*, $n^{25}D$ 1.457.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.50; H, 9.18.

The residue from the steam distillation was a clear colorless solution. On cooling in ice a precipitate formed which was separated by filtration and proved to be unreacted **p-hydroxybenzoic acid**, weight 2.75 g. (20%), m. p. 206–208°.

The mother liquor from the separation of the *p*-hydroxybenzoic acid was taken to dryness *in vacuo* whereupon it solidified, giving 7.10 g. (49%) of *cis* and *trans*-**4-hydroxycyclohexanecarboxylic acid**, m. p. 96–104°. This was recrystallized once from chloroform to give material melting at 106–116°.

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.31; H, 8.39. Found: C, 58.59; H, 8.06.

Pure *cis*-4-hydroxycyclohexanecarboxylic acid melts at 152° and the *trans* isomer melts at 121°. The above mixture contained at least 50% of the *cis* modification, which could be obtained by repeated crystallization from chloroform.

Anal. Found: C, 58.58; H, 8.31.

The *trans* form could not be isolated by crystallization.

Derivatives of *p*-hydroxybenzoic acid, as indicated in Table II, were reduced under similar conditions. Hydrogen uptake was 85 to 115% of theoretical and required fifteen to twenty hours. The reaction products were separated by fractional distillation through a modified Widmer column.

We had an interesting experience with methyl anisate. We made it once by methylation of *p*-hydroxybenzoic acid with diazomethane. This product was properly characterized and on hydrogenation reacted readily to give methylcyclohexane carboxylate in 60% yield. Since then we have made numerous unsuccessful attempts to repeat this reaction, using carefully purified commercial methyl anisate and also some prepared as above, but we could obtain no hydrogen uptake.

Summary

The low pressure hydrogenation of *m*- and *p*-hydroxybenzoic acid using a platinum catalyst yields cyclohexanecarboxylic acid as the principal product and some hydroxycyclohexanecarboxylic acid.

When esters of *m*- and *p*-hydroxybenzoic acid are hydrogenated cyclohexanecarboxylic ester is obtained.

Protection of the hydroxyl group by acetylation or methylation does not change the course of the reaction.

The addition of an acid to the hydrogenation media causes rapid reaction, with almost complete hydrogenolysis. Added alkali results in a slower hydrogen uptake, whereby hydrogenolysis is diminished and hydroxycyclohexanecarboxylic acid becomes the principal product.

High pressure reduction of the acids using Raney nickel catalyst results in cyclohexanol as the major product.

KALAMAZOO, MICHIGAN RECEIVED MAY 29, 1947

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[14] Adkins, "Reactions of Hydrogen with Organic Compounds Over Copper–Chromium Oxide and Nickel Catalysts," The University of Wisconsin Press, Madison, Wis., 1937, p. 20.

[15] (a) Einhorn, *Ann.*, **291**, 297 (1896). (b) Perkin and Tattersall, *J. Chem. Soc.*, **91**, 486 (1907). (c) Boorman and Linstead, *ibid.*, 258 (1935).

[16] Microanalyses by Harold Emerson, W. A. Struck and C. Triestram of the Upjohn Microanalytical group.

[17] Obtained from the American Platinum Works, Newark, N. J.