

[CONTRIBUTION FROM THE CENTRAL EXPERIMENT STATION, BUREAU OF MINES]

Kinetics of Carbiding and Hydrocarbon Synthesis with Cobalt Fischer-Tropsch Catalysts¹BY SOL WELLER²

This paper presents some of the first results obtained in a study of the Fischer-Tropsch hydrocarbon synthesis. The synthesis involves formation of hydrocarbons by the passage of carbon monoxide-hydrogen mixtures over metallic catalysts at elevated temperatures; with cobalt catalysts, the equation for the reaction may be written as $x\text{CO} + 2x\text{H}_2 = (\text{CH}_2)_x + x\text{H}_2\text{O}$. In the course of this study, it is hoped to elucidate somewhat the mechanism by which the synthesis occurs.

For the production of liquid hydrocarbons, cobalt or iron catalysts are ordinarily used at temperatures of 170–300°. Straight-chain hydrocarbons are produced almost exclusively, the relative proportions of saturated and unsaturated constituents varying with the catalyst and conditions.

Fischer and Tropsch³ first suggested, in 1926, that the synthesis proceeded through the formation of a metallic carbide which was hydrogenated to form methylene groups whose subsequent polymerization resulted in the formation of hydrocarbons. On the whole, this has remained the most popular theory. If it is correct and if metal carbide is an intermediate in the synthesis, one should expect that the rate of formation of carbide in carbon monoxide would be at least as great as the rate of the synthesis. Comparisons of these rates have been published by Craxford and Rideal⁴ and by Eïdus and Zelinskiï.⁵ Both sets of investigators used catalysts containing cobalt, thoria, and kieselguhr in the ratios 100:18:100.

Craxford and Rideal found that the initial rate of carbiding in carbon monoxide was considerably slower than the synthesis rate and that the steady carbiding rate reached after a few hours was one two-hundredth of the synthesis rate (at 200°). The value of their data is doubtful, however, since they used a static system. Carbon dioxide is evolved in the course of the carbiding, according to the equation $2\text{Co} + 2\text{CO} = \text{Co}_2\text{C} + \text{CO}_2$; if the carbon dioxide is not removed by positive circulation, its accumulation tends to limit the reaction rate by preventing diffusion of carbon monoxide to the catalyst surface and also possibly by a direct inhibition because of carbon dioxide adsorption.

Eïdus and Zelinskiï employed a flowing system. They found that the rate of carbiding was about one-tenth of the synthesis rate. Because the reaction rate was followed by a weight-gain

method, however, it was not possible to determine the initial rate; the first point was obtained after five hours of carbiding. Eïdus and Zelinskiï reported that the carbiding rate was constant for fifteen to twenty hours and then dropped to a lower constant value. It is not known to what extent their data under given conditions were reproducible.

Experimental

The results reported here were obtained by use of a closed all-glass apparatus (Fig. 1) in which the reaction gases were continuously circulated through the sample bed by means of an all-glass reciprocating piston pump, P, operated by a solenoid.⁶ The space velocity was about 2 liters gas/cc. catalyst/hour.

The catalyst was contained in S, a U-shaped 3-mm. i. d. tube surrounded by an oil-bath held at constant temperature by means of a boiling tetralin bath. Temperature drift during an experiment was usually less than several tenths of 1°. The sample tube was equipped with a special 4-way stopcock⁷ for convenience in making surface area measurements and in permitting gas circulation. Reaction products were frozen continuously in trap T, kept immersed in liquid nitrogen. All reactions were carried out at constant pressure with the use of a Taylor-Strother manostat,⁸ M and N. A small lamp, L, indicated the make and break of electrical contact in N. The volume decrease during a reaction was followed by means of a mercury-filled gas buret, B. The apparatus "dead space" was measured with helium.

The sample used here was a precipitated cobalt-thoria-kieselguhr (100:18:100) catalyst containing 34% cobalt on an unreduced basis.⁹ The catalyst was pelleted before use, and a sample weight of 0.4 to 0.6 g. was customarily employed.

Tank hydrogen was passed over palladized asbestos at 300°, then through magnesium perchlorate and a trap cooled to -78°. Carbon monoxide, prepared by the action of 96% sulfuric acid on 90% formic acid (C. P.), was passed through soda lime, magnesium perchlorate, and a trap at -78°; it was shown to be mass-spectroscopically pure. Tank helium was passed through a bed of activated charcoal cooled to -195°; this product was also mass-spectroscopically pure. The synthesis gas used contained 64.6% hydrogen, 34.9% carbon monoxide, 0.4% nitrogen, 0.1% methane, and less than 0.1% oxygen (by volume).

Before each series of runs, each sample of the air-dried catalyst was reduced in a rapid stream of hydrogen for two hours at 400°. (After reduction, samples were found by low-temperature nitrogen adsorption to have surface areas of 27–28 sq. m./g.) The sample was then evacuated at 200° for an hour and exposed to pure carbon monoxide for the first carbiding run. Successive carbiding experiments on a given sample were separated by a hydrogenation, usually at 200°; such a hydrogenation has been shown by Bahr and Jessen¹⁰ to quantitatively remove carbidic carbon, primarily as methane.

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(3) Fischer and Tropsch, *Brenn. Chem.*, **7**, 97 (1926).

(4) Craxford and Rideal, *J. Chem. Soc.*, 1604 (1939).

(5) Eïdus and Zelinskiï, *Bull. Acad. Sci. U. R. S. S.*, **45**, 190 (1942).

(6) Porter, Bardwell and Lind, *Ind. Eng. Chem.*, **18**, 1086 (1926).

(7) Anderson, *Ind. Eng. Chem., Anal. Ed.*, **18**, 156 (1946).

(8) Taylor and Strother, *THIS JOURNAL*, **56**, 586 (1934).

(9) Catalyst 108B. Its preparation is described in a U. S. Bureau of Mines Technical Paper, in preparation; H. H. Storch, *et al.*, Synthetic Liquid Fuel Processes. Hydrogenation of Carbon Monoxide. Part I.

(10) Bahr and Jessen, *Ber.*, **63**, 2226 (1930).

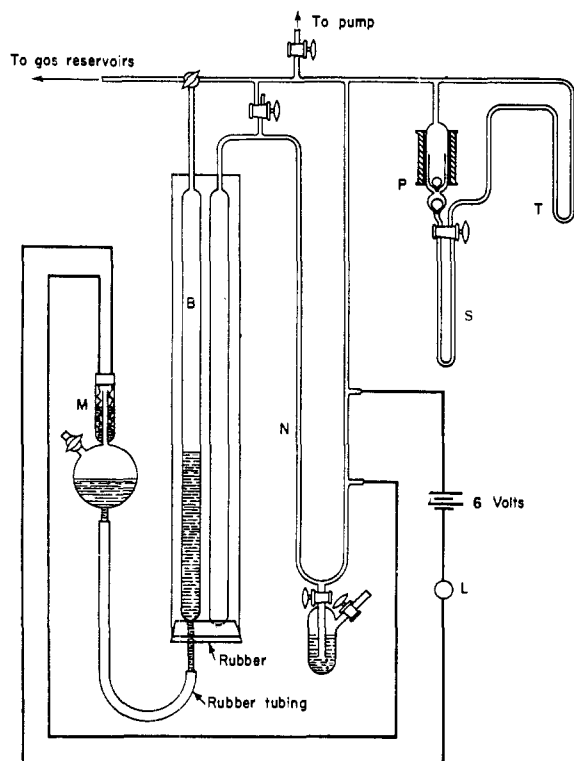


Fig. 1.—Apparatus.

The influence of gas flow rate on reaction rates was not considered in this study. Even for the synthesis, consideration of the flow rate indicates that there was always less than 3% conversion of gas per pass through the catalyst bed. The assumption has been made, therefore, that in these experiments the limiting reaction rate was measured, that is, that change in flow rate would have had no effect on the reaction rate.

Results and Discussion

Change of Carbiding Rate with Time.—In Fig. 2 is presented the variation of the carbon monoxide consumption with time for a typical carbiding run, IVj. The initial rate of carbon monoxide pickup (average rate during the first minute) by a reduced sample was very high, but difficultly reproducible. (On successive experiments with one sample this initial carbiding rate at 200° ranged from 0.10 to 0.22 g. carbon fixed as carbide/g. cobalt/hour; see Table 1.) The rate decreased rapidly from the high initial value but leveled off after fifteen to twenty minutes to a value, in the case of Run IVj, of 63×10^{-4} g. carbon/g. cobalt/hour (given by the slope of the straight line in Fig. 2) and remained constant over a period of two to two and one-half hours, following which it gradually decreased. At the conclusion of Run IVj the sample was 41% carbided, this figure being based on the assumption that carbiding proceeds only to the formation of cobalt carbide. As yet no simple rate law has been found which satisfactorily represents the carbiding process over an extended range.

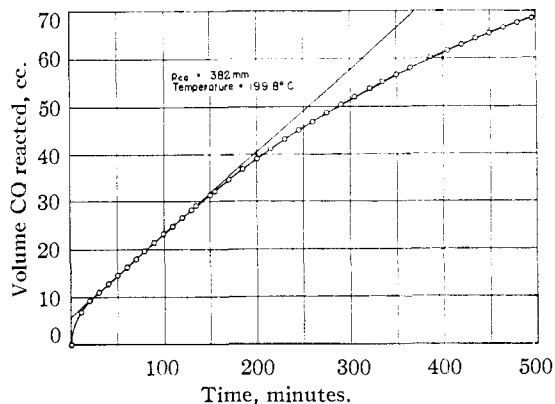


Fig. 2.—Carbiding of 108B, run IVj.

In Table I are summarized carbiding and synthesis rates (see discussion of synthesis below) for a number of runs with Sample IV. The high, poorly reproducible initial carbiding rates may be

TABLE I
RATES OF CARBIDING AND SYNTHESIS WITH SAMPLE IV,
CATALYST 108B

Run	Gas	Pres. sure, mm.	Temp., °C.	Dur. ation of expt., minutes	Time interval, minutes ^a	Rate of carbiding or synthesis, g. C/g. Co/hr. $\times 10^{4b}$
IVa1	CO	377	200.0	85	0-1	2160
					25-85	66.0
IVd1	CO	382	199.2	85	0-1	1800
					20-85	62.9
IVg	CO	382	199.5	385	0-1	1660
					15-120	63.2
					100-140	59.9
					225-260	46.8
IVj	CO	382	199.8	510	340-385	34.8
					0-1	1260
					20-150	63.0
					435-510	24.4
IV11	CO	382	190.0	80	0-1	1030
					35-80	29.6
IV12	CO	382	200.0	65	0-65	61.8
IV13	CO	382	190.0	60	0-35	30.6
IVn1	CO	378	200.0	70	0-1	1120
					40-70	57.1
IVp2	CO	455	199.5	60	10-60	44.9
IVr1	CO	380	199.8	65	0-1	1060
					25-65	42.7
IVr2	CO	98	199.8	40	0-40	31.8
IVr3	CO	380	199.8	265	0-35	43.7
IVs	S. G. ^c	757	175.5	385	30-100	160
					140-245	126
IVw1	S. G.	763	174.8	60	5-60	120
IVw2	S. G.	763	185.8	50	0-40	238
IVw3	S. G.	763	174.8	30	0-30	115
IVw4	S. G.	763	185.8	80	5-50	228

^a This is the time interval during which the given rate was observed. ^b Carbiding rates are on the basis of carbon fixed as carbide; synthesis rates are based on the assumption that the only reaction occurring is $x\text{CO} + 2x\text{H}_2 = (\text{CH}_2)_x + x\text{H}_2\text{O}$. ^c S. G. means synthesis gas of composition 64.6% H_2 , 34.9% CO , 0.4% N_2 , and 0.1% CH_4 .

noted. The steady carbiding rates (between, say, twenty and one hundred and fifty minutes) ran around 60 to 65×10^{-4} g. carbon/g. cobalt/hour.

Unsuccessful efforts were made to reproduce the observation of Craxford and Rideal⁴ that evacuation of the sample at any time during the "second slow stage" of carbiding and introduction of fresh carbon monoxide does not lead to repetition of the initial rapid reaction. If this were true, it would permit an important discrimination to be made between possible reaction mechanisms for the carbiding process. It was always observed, however, that evacuation (at 200°) after several hours of carbiding, followed by re-introduction of carbon monoxide, resulted in a large increase in the carbon monoxide pickup (though the rate was still only a fraction of the original initial rate), and the carbiding rate decreased only after fifteen to twenty minutes to a continuation of that observed prior to the evacuation. Unfortunately, this behavior is compatible with a number of quite divergent reaction mechanisms.

Temperature and Pressure Dependence of Carbiding.—The temperature and pressure coefficients of the steady state carbiding process were determined by a change of the temperature or pressure during a single run, followed by a return to the initial condition to verify the fact that the rate had not changed; if the determinations were carried out rapidly, it proved possible to return to a rate very close to the original. Runs IVI (Table I) and IVa (data not given), performed in this way, gave values of 31.2 and 30.8, respectively, with an average of 31.0 kcal./mole, for the apparent activation energy of the steady state (that is, that between twenty and one hundred and fifty minutes) carbiding process. This figure

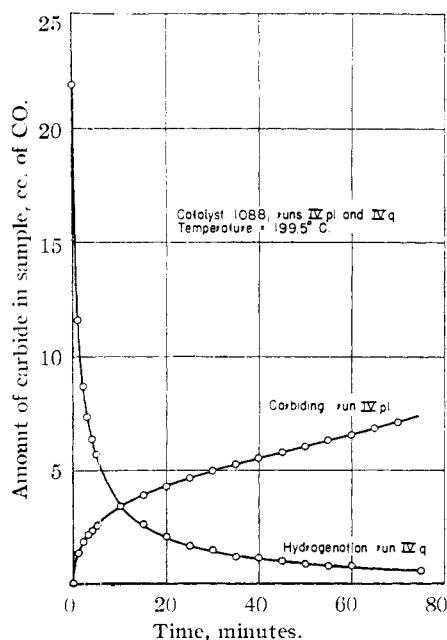


Fig. 3.—Carbiding or hydrogenation of carbide.

is compared in the latter portion of Table III with values given by Craxford and Rideal⁴ and calculated from the data of Efdus and Zelinskiĭ.⁵ The earlier values are much lower. This may be due to the error involved in using integral values when the rate is changing with time (Efdus and Zelinskiĭ), and, in the case of Craxford and Rideal, perhaps to the fact that a different limiting step in the mechanism was being measured.

The pressure dependence of the carbiding process was measured in a comparable way. Run IVr, Table I, was a typical experiment. If the steady carbiding rate is expressed as rate = kp^n , over the range investigated (8–45 cm.) n was found in several experiments to have values of 0.20 to 0.26. This may be compared with the statement of Craxford and Rideal⁴ that the rate of the slow second stage is independent of pressure above 30 cm. but decreases below that pressure. The low dependence of the steady carbiding process on pressure indicates that the rate-determining step during this process is not one involving the impact of gaseous carbon monoxide molecules with the surface (for example, to form a layer of adsorbed carbon monoxide or to react with such a layer to produce carbon dioxide); if this were true, one would expect the pressure dependence of the rate to be at least linear.

Hydrogenation of Carbide.—The hydrogenation of a carbided sample proceeded at a much faster rate than did the carbiding of a reduced sample, in agreement with the observation of Craxford and Rideal.⁴ This behavior is illustrated (Fig. 3) by the successive runs IVp, a carbiding experiment, and IVq, a hydrogenation, both carried out at 200° . A time of two and one-half hours was required to introduce 2.8 mg. carbon into the sample during Run IVp; this was one-half the total amount of carbide produced during the run (only a part of which is shown in Fig. 3). By contrast, approximately one minute was required to remove this amount of carbon from the sample in Run IVq. In fact, it seemed to be generally true for catalyst 108B that at 200° about one minute was sufficient to remove half the carbide in a carbided sample, even for samples carbided as much as 50%; approximately complete removal of carbide by hydrogen was effected in two to three hours at 200° .

The velocity of the hydrogenation reaction has an important implication for the mechanism of the carbiding reaction. Both the formation of bulk carbide and its removal by hydrogenation probably proceed by the diffusion of carbon atoms through the interior of the metal. Since the hydrogenation occurs at a rate so much more rapid than does the carbiding, the diffusion of carbon through the interior is probably not the rate-determining step for the carbiding. Presumably some reaction occurring at the surface is limiting.

Synthesis.—At the conclusion of carbiding Run IVr, when the sample was 42% carbided,

it was exposed to synthesis gas having a hydrogen to carbon monoxide ratio of 1.85. Data for typical synthesis experiments, Runs IVs and IVw, are also presented in Table I.

The temperature dependence of the synthesis was measured in Runs IVw (Table I) and IVu (data not given). The corresponding values for the apparent activation energy of the synthesis were 26.1 and 26.9 kcal./mole, respectively, with an average of 26.5 kcal./mole. This agrees well with the value of 26.2 kcal./mole found by an identical technique with a cobalt-thoria-magnesia-kieselguhr (100:6:12:200) catalyst¹¹ and with that of 25 kcal./mole found by Dr. R. B. Anderson in a Bureau of Mines catalyst testing run with a cobalt-thoria-magnesia-kieselguhr catalyst.¹² The value of 9.5 kcal./mole given by Craxford and Rideal⁴ (Table III) seems quite low.

In Table II are presented mass spectrometric analyses of the gaseous products from several syn-

thesis runs. These analyses closely resemble those obtained with larger-scale testing units; this demonstrates that true synthesis was being measured in these studies. It is noteworthy that no extended induction period for the synthesis was observed. The gas sample at the conclusion of Run IVs, when synthesis had been carried on only six and one-half hours, contained as much higher hydrocarbons and as little methane as samples obtained after longer times of synthesis. Mass balances indicated that one-half to three-fourths of the hydrogen and carbon monoxide that reacted formed liquid and solid products which did not appear in the gas phase.

At the conclusion of Run IVz sample IV was removed from the apparatus and exposed to air. X-Ray analysis¹³ showed primarily cubic cobalt to be present, with indications, however, of an appreciable amount of material believed to be cobalt carbide.¹⁴ Since the sample was about 40 per cent. carbided before the synthesis was begun, this result does not prove that carbide is formed during the synthesis. It does demonstrate, however, that under the conditions of the synthesis and for a total time of forty hours of synthesis, cobalt carbide is stable. (In pure hydrogen, the carbide would have been removed in a few hours.)

General Discussion.—A comparison has been made in the upper portion of Table III of typical carbiding and synthesis rates observed in these experiments (column 3) with those calculated from curves in the paper of Craxford and Rideal⁴ (column 1) and from data given by Eïdus and Zelinskiï⁵ (column 2). All rates are for a temperature of 200°. The carbiding rate of Eïdus and Zelinskiï was interpolated from those at 192° and 212° with the assumption that the activation energy was 14.8 kcal./mole. The synthesis rate in column 3 was corrected from that at 185° with the use of 26.5 kcal./mole as the activation energy. The synthesis rate of Craxford and Rideal is for the first minute of synthesis (the rate thereafter decreasing); the other two are steady synthesis rates. The rates in this paper are in reasonable agreement with those of Eïdus and Zelinskiï; those of Craxford and Rideal are much lower. It seems established that the steady carbiding rate, which is associated with the formation of bulk carbide, is about one-tenth as fast as the synthesis rate. As was pointed out by Craxford and Rideal, therefore, bulk carbide cannot be a necessary intermediate in the Fischer-Tropsch process unless its formation is much faster in the presence of hydrogen than it is in pure carbon monoxide. At present the possibility cannot be ruled out that oxygen removal may be the rate-limiting step, and that oxygen may be removed more rapidly by hydrogen to form water during the synthesis than it is by carbon monoxide to form carbon dioxide during carbiding in carbon monoxide. The role

TABLE II
MASS SPECTROMETRIC ANALYSES OF GASEOUS SYNTHESIS PRODUCTS

Gas	Run IVs, ^a %	Run IVu, ^b %	Run IVv, ^b %	Run IVy, ^a %
CO ₂	...	3.05	4.4	...
H ₂	33.25	27.4	25.4	40.4
CO	36.3	20.8	40.9	37.3
N ₂	0.7	0.9	0.8	0.6
CH ₄	18.6	21.8	23.2	15.1
C ₂ H ₆	2.75	2.95	3.2	2.2
C ₃ H ₈	0.6	0.4	0.5	0.2
C ₃ H ₆	1.4	.85	1.1	.6
C ₃ H ₄	2.4	2.5	2.5	1.6
C ₄ H ₁₀	0.85	0.65	0.5	0.4
C ₄ H ₈	1.5	1.0	1.1	.85
C ₅ H ₁₂	0.5	0.45	0.2	.2
C ₅ H ₁₀	.8	.2	.4	.4
C ₆ H ₁₄	.2	.1	.1	.05
C ₆ H ₁₂	.15	.1	.1	.1

^a Volume per cent. on CO₂- and air-free basis. ^b Volume per cent. on air-free basis.

TABLE III
RATES AND ACTIVATION ENERGIES OF CARBIDING AND SYNTHESIS

	Craxford and Rideal	Eïdus and Zelinskiï	This paper
Rates (g. C/g. Co/hr. × 10 ⁴) at 200°			
Carbiding			
1st stage	35 ^a	1000-2200 ^a
2nd stage	0.8 ^b	42 ^c	60-65 ^c
Synthesis	280	~430	560
Apparent Activation Energies (kcal./mole)			
Carbiding			
1st stage	10.0 ^d
2nd stage	18.0 ^b	14.8 ^c	31.0 ^e
Synthesis	9.5	26.5

^a First minute. ^b After two to three hours. ^c First five hours. ^d First few minutes. ^e Twenty to one hundred and fifty minutes.

(11) Unpublished data.

(12) Anderson, Krieg, Seligman and O'Neill, *Ind. Eng. Chem.*, to be published.

(13) The X-ray analysis was obtained through the courtesy of Dr. L. J. E. Hofer.

(14) Hofer and Peebles, *THIS JOURNAL*, **69**, 893 (1947).

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

Noteworthy, 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 $\text{Rate} = kp^n$, 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.

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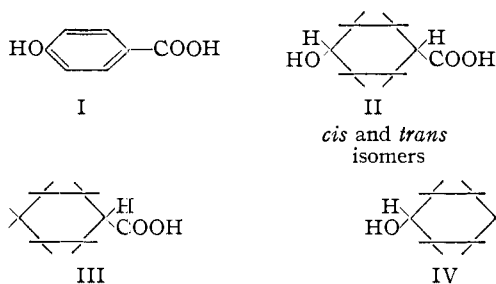
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[CONTRIBUTION FROM THE RESEARCH DIVISION, THE UPJOHN COMPANY]

The Hydrogenation of *m*- and *p*-Hydroxybenzoic Acid¹

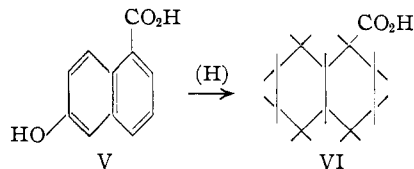
BY ROBERT H. LEVIN AND JANET HALL PENDERGRASS

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

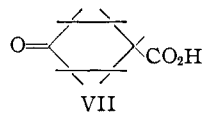


p-hydroxybenzoic acid has yielded mostly cyclohexanecarboxylic acid.^{1a-4} Balas and Kosik^{1a} obtained only this hydrogenolysis product, using a platinum black catalyst in water. Balas and Srol² isolated some of the *cis*-4-hydroxycyclohexanecarboxylic acid and a small amount of the *trans* form by carrying out the reduction in alcohol. Edson³ 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-workers⁴ re-

ported that hydrogenolysis was the main reaction in a series of low pressure experiments. It is of interest that Long and Burger⁵ could only obtain the hydrogenolysis product (VI) by the reduction of 6-hydroxy-1-naphtholic acid (V) using platinum oxide as the catalyst; and recently⁶ Price and co-workers reported that all procedures leading to hydrogenation of 6-hydroxy-1,2,3,4 tetrahydro-1-naphtholic acid always resulted in the simultaneous removal of the oxygen at carbon 6.



In 1905 Lumsden⁷ 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.



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

(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. Lékárnictva*, **7**, 105 (1927).

(2) Balas and Srol, *Collection Českoslov. 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) Mitsui, *Mem. Coll. Sci. Kyoto Imp. Univ.*, **A18**, 329 (1935).

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