50.56; H, 5.71; N, 13.80). When the anil in a 27% solution of sodium carbonate was heated under reflux until ammonia was no longer evolved, the keto acid VIII was isolated on neutralizing the reaction mixture with acetic acid. The keto acid melted with decomposition at 175°.

Anal. Calcd. for $C_{16}H_{20}N_2O_7$: C, 54.54; H, 5.68. Found: C, 54.30; H, 5.91.

Ethyl 1-D-Ribityl-2-oxo-6,7-dimethyl-1,2-dihydro-3-quinoxalinecarboxylate, IX.—A mixture of 5 g. of the diamine, III, 3 g. of ethyl oxomalonate in 35 cc. of ethanol was refluxed for thirty minutes. The product crystallized after storage in the refrigerator for twelve hours. The product was recrystallized from ethanol from which it separated as pale yellow, microscopic needles melting at 167–168°. The yield was 5 g.

Anal. Calcd. for $C_{18}H_{24}O_7N_2$: C, 56.85; H, 6.32; N, 7.38. Found: C, 56.60; H, 6.26; N, 7.27.

The above keto ester was hydrolyzed by dissolving in absolute methanol containing 1 equivalent of sodium methylate and adding a few drops of water. The sodium salt of the free acid precipitated shortly. The salt was dissolved in a minimum amount of water and was treated with a small excess of acetic acid. The keto acid, which separated, melted at 174–176° (dec.) and when mixed with a sample of the keto acid obtained by the exhaustive hydrolysis of the anil, VI, the melting point was not depressed.

Acknowledgment.—We are indebted to Drs. R. T. Major and J. R. Stevens[18] for their interest and suggestions. We are also indebted to Dr. J. L. Stokes for the microbiological assays and to Mr. R. N. Boos for the microanalyses.

Summary

A new synthesis of alloxazines and isoalloxazines from orthophenylenediamines and halobarbituric acids has been described. Pyridine is an outstanding solvent for the reaction. Evidence has been presented to indicate that the reaction does not depend on the hydrolysis of the halobarbituric acids to alloxan.

RAHWAY, N. J. RECEIVED SEPTEMBER 27, 1945

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[18] At present Director of Research of J. T. Baker Co., Phillipsburg, N. J.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES OF UNIVERSAL OIL PRODUCTS COMPANY]

Synthesis of Methanol from Carbon Dioxide and Hydrogen over Copper–Alumina Catalysts. Mechanism of Reaction

BY V. N. IPATIEFF AND G. S. MONROE

The reactions of hydrogen and carbon monoxide over a great range of experimental conditions have been studied and reported by various investigators. However, the literature on the reactions of hydrogen and carbon dioxide, especially under high pressure, is relatively scant. The subject is usually dismissed by the statement that the carbon dioxide reduces to the monoxide and from this point follows the usual behavior of hydrogen and carbon monoxide.

This paper deals, for the most part, with the reactions of carbon dioxide and hydrogen over copper–alumina catalysts at pressures of about 410 atm. at which pressure the effects of change in catalyst composition, hydrogen:carbon dioxide ratio, and temperature were investigated. A few experiments, however, were made at 117–410 atm. to study the influence of pressure on the reaction. Some experiments were also made with carbon monoxide and hydrogen and with carbon monoxide–carbon dioxide mixtures and hydrogen to obtain parallel data for comparison.

Experimental

Materials.—The carbon dioxide and hydrogen for these experiments were of commercial grade. The carbon monoxide was prepared by the dehydration of 85% commercial formic acid with concentrated phosphoric acid (85%). The purity of the carbon monoxide was 98+%. Formalin was used for the experiments with formaldehyde and water.

Catalysts.—The copper–alumina catalysts were prepared by the precipitation at 60° of basic copper carbonate on alumina (hydroxide calcined at 350°) by the addition of ammonium carbonate solution to cupric nitrate solution containing the alumina held in suspension by vigorous agitation. After thorough washing, the precipitate was dried (final temperature 240°), ground to 40-mesh, mixed with 4% rosin, and pilled to 1/8" × 1/8" size (cylindrical). After burning out the rosin with air at 220°, the pills were reduced in hydrogen at 250°. The catalyst containing copper alone was prepared by the same method employed for the copper–alumina catalysts, precipitating the copper in the absence of alumina. The catalyst consisting only of alumina was made by pilling 40-mesh alumina (calcined at 350°) according to the procedure previously described.

Apparatus and Procedure.—All experiments were made in a flow-type apparatus. This equipment consisted essentially of four parts: a high-pressure gas charger for hydrogen and hydrogen–carbon monoxide mixture; a high-pressure liquid charger with feed pump for charging liquid carbon dioxide; a high-pressure vertical reaction tube with a copper liner heated by an electric furnace; and a pressure regulator attached to the exit end of the reaction tube.

The hydrogen or hydrogen–carbon monoxide mixture from the high-pressure gas charger was discharged into the preheater section of the reaction tube with water displacement by means of a hydraulic pump. From the amount of water pumped from graduated cylinders into the chargers, the amount of gas discharged into the reaction tube could be determined.

The carbon dioxide was pumped as liquid from a charger with a calibrated gage glass into the top preheater section of the reaction tube, where it contacted and mixed with the hydrogen from the gas charger before reaching the catalyst zone.

The reaction tube, made from stainless steel, was 86 cm. long and had an inside diameter of 2.38 cm. with the liner inserted. The top section (first 38 cm. filled with copper punchings) served as a preheater. The middle section (25.4 cm.), with a capacity of 100 cc., served as the catalyst zone. The lower section (22.6 cm.) contained a loose-fitting copper bar or filler to serve as a support for the catalyst and at the same time to hasten the exit of the products from the reaction tube. A thermocouple pocket

TABLE I

SYNTHESIS OF METHANOL FROM CARBON DIOXIDE AND HYDROGEN OVER COPPER–ALUMINA CATALYSTS

Expt.	Catalyst[a] Cu	Catalyst[a] Al_2O_3	Temp., °C. Furn.	Temp., °C. Cat.	Press., atm.	Mole ratio, H_2/CO_2	H. G. S. V.[b]	% CO_2 converted to CH_3OH	% CO_2 converted to C_2H_5OH	% CO_2 converted to CH_4	% CO_2 converted to CO	% CO_2 recov.
1	100	0	300	273	412	5.8	1075	0.0	0.0	11.2	0.0	88.0
2	88	12	300	271	413	2.6	1295	3.5	0.0	6.0	1.8	92.2
Effect of Temperature												
3	62	38	300	286	412	5.0	1145	84.5	2.7	1.3	0.1	5.1
4	62	38	350	335	414	4.8	1080	52.7	0.0	1.0	0.6	5.2
5	62	38	400	389	412	6.1	955	34.5	1.7	27.6	2.9	15.5
6	62	38	475	467	412	3.9	1225	1.8	0.0	44.2	13.6	38.6
Effect of H_2/CO_2 Ratio												
7	28	72	300	287	409	3.9	1185	93.6	6.5	2.7	0.0	4.9
8	28	72	300	291	409	1.6	1280	26.7	0.0	1.5	3.5	64.6
9	28	72	300	275	409	0.6	1380	9.6	0.0	0.0	3.7	85.5
Effect of Pressure												
10	8	92	300	282	409	4.3	1170	94.3	2.5	2.0	0.0	3.3
11	8	92	300	263	235	4.3	985	27.1	0.0	2.1	8.3	54.0
12	8	92	300	263	117	5.3	1075	12.6	0.0	1.7	16.7	58.1
13	0	100	300	272	414	4.1	1145	0.0	0.0	2.0	1.9	90.5

[a] Composition expressed as weight %. [b] Houry gas space velocity, volume of gas charged per unit volume of catalyst per hour.

TABLE II

SYNTHESIS OF METHANOL FROM CARBON MONOXIDE AND HYDROGEN AT 409 ATM. OVER COPPER–ALUMINA CATALYSTS. EFFECT OF CARBON DIOXIDE

Expt.	Temp., °C. Furn.	Temp., °C. Cat.	Mole ratio H_2/CO	Mole ratio H_2:CO:CO_2	H. G. S. V.	% CO or (CO + CO_2) converted to CH_3OH	% CO or (CO + CO_2) converted to C_2H_5OH	% CO or (CO + CO_2) converted to $(CH_3)_2O$	% CO or (CO + CO_2) converted to CO_2	% CO or (CO + CO_2) converted to CH_4	% Recovered CO	% Recovered CO_2
14[a]	300	326	2.0	....	1775	40.4	0.6	41.0	3.4	10.0	0.8	...
15[b]	300	322	2.2	....	1695	42.9	1.6	32.0	1.6	14.8	0.4	...
16[c]	300	335	2.2	....	1690	39.1	0.9	33.7	1.9	10.2	0.6	...
17[b]	300	299	...	15.3:3.1:1.0	1175	64.0	0.4	1.8	...	5.6	2.1	5.2
18[b]	300	302	...	8.5:1.1:1.0	1080	90.5	0.2	0.2	...	0.0	1.1	3.2

[a] Catalyst: 62% Cu + 38% Al_2O_3. [b] Catalyst: 28% Cu + 72% Al_2O_3. [c] Catalyst: 8% Cu + 92% Al_2O_3.

TABLE III

EFFECT OF COPPER–ALUMINA CATALYSTS ON 40% AQUEOUS FORMALDEHYDE SOLUTION (FORMALIN) IN THE PRESENCE AND ABSENCE OF HYDROGEN

Expt.	Catalyst Cu	Catalyst Al_2O_3	Temp., °C. Furn.	Temp., °C. Cat.	Press., atm.	Mole ratio H_2/HCHO	H. G. S. V. H_2	H. L. S. V. Formalin	Products/mole HCHO chgd. CH_3OH	Products/mole HCHO chgd. CO	Products/mole HCHO chgd. CO_2	Products/mole HCHO chgd. H_2	Moles consumed H_2	Moles consumed H_2O
19	28	72	300	283	26	1.0	165	0.57	0.73	0.02	0.18	...	0.21	0.24
20	28	72	350	334	26	1.0	165	.57	.60	.09	.26	...	.00	.34
21	62	38	305	272	410	1.2	272	.70	.87	.00	.22	...	.62	.36
22	62	38	303	263	410	...	...	.57	.79	.00	.13	0.20	...	.62

sheathed with duronze extended downward through the center of the tube through the preheater section into the catalyst zone. This arrangement made possible the installation of fixed thermocouples at the top, middle and bottom of the catalyst zone to determine the catalyst temperature.

The products after release to atmospheric pressure were passed into a gas separator or receiver where most of the liquid product separated. The gaseous products from the gas separator were led through a Dry Ice–acetone trap and finally through a wet-test meter. Any of the normally liquid products carried along by the gas were retained in the Dry Ice–acetone trap.

Analytical Methods.—The composition of the gaseous products was determined by absorption and combustion methods, and that of the liquid products by fractional distillation, the methanol and ethanol contents of the fractions being evaluated by density and refractometer determinations.

Discussion of Results

Effect of Catalyst Composition.—The effect of catalyst composition on conversion (Table I, expts. 1, 2, 3, 7, 10, 13) was investigated with catalysts with copper content ranging from 0–100%. Copper and alumina, separately, did not catalyze methanol formation from carbon dioxide and hydrogen, the mixture of the two being necessary. The highest conversion was obtained with catalysts of compositions in the range of 8–28% Cu + 92–72% Al_2O_3.

Effect of Temperature.—The effect of increase in temperature (expts. 3–6), studied with a catalyst containing 62% Cu, was to lower the conversion from 85 to about 2% and at the same time to increase conversion to methane and carbon monoxide from about 1% to 44 and 14%, respectively.

Effect of Hydrogen: Carbon Dioxide Ratio.—Change in the hydrogen: carbon dioxide ratio (expts. 7–9) did not materially influence the type of reaction products obtained. The methanol yield, however, fell off due to decrease in the limiting reactant–hydrogen.

Effect of Pressure.—Lowering the pressure (expts. 10–12) from 409 to 117 atm. reduced the conversions from 94 to about 13%, the reaction at the lower pressures tending to stop with the reduction of the dioxide to the monoxide.

Carbon Monoxide and Hydrogen.—Experiments made with carbon monoxide and hydrogen over copper–alumina catalysts (Table II, expts. 14–16), under conditions similar to those employed with carbon dioxide and hydrogen, gave unexpected results. The methanol conversion was only 39–43%, and at the same time 10–15% and 32–41%, respectively, of the carbon monoxide charged reacted to give methane and dimethyl ether. Formation of dimethyl ether from carbon monoxide and hydrogen has also been observed with other catalysts.[1]

The question arises, why is it that in the action of hydrogen upon carbon dioxide no dimethyl ether was formed? It might be supposed that the presence of water formed upon the reduction of carbon dioxide or the carbon dioxide itself, hindered the formation of methyl ether. In order to throw light on this question some experiments were made to determine the effect of hydrogen upon carbon monoxide in the presence of water and carbon dioxide, separately.

The experiments with water, not tabulated, were inconclusive in that though ether formation was eliminated, the methanol conversion was reduced to about 4 and 62% of the carbon monoxide charged reacted with water to form carbon dioxide. The results with carbon dioxide (Table II, expts. 17, 18) show almost complete elimination of ether formation even when only 25% of the carbon monoxide was replaced with carbon dioxide.

In this connection, it is important to note that the energy released during the reduction of carbon monoxide (Table II, expts. 14–16), caused the catalyst temperatures to average about 30° above that of the furnace. This energy caused the dehydration of methanol (in nascent state) to dimethyl ether. No such comparable release of energy was observed in the formation of methanol from hydrogen and carbon dioxide (Table I), due to the endothermic nature of the reaction involved in the reduction of carbon dioxide to the monoxide.

The experimental results obtained lead to a hypothesis concerning the formation of methanol from carbon dioxide and hydrogen. The first reaction is that of hydrogen with carbon monoxide (carbon dioxide being initially reduced to carbon monoxide with the formation of water) to produce formaldehyde. The formaldehyde in the presence of the amphoteric aluminum oxide by means of intermolecular oxidation and reduction may give methanol and formic acid (Cannizzaro reaction) in the sense of the equation

$$2HCHO + H_2O \longrightarrow CH_3OH + HCOOH$$

The water produced in the reduction of the carbon dioxide would be in excess of that required for the reaction. The formic acid produced under these conditions can decompose in two ways.

$$(1)\quad HCOOH \longrightarrow H_2 + CO_2$$
$$(2)\quad HCOOH \longrightarrow H_2O + CO$$

Ipatieff[2] and Freitag have shown that water and carbon monoxide at high temperatures and pressures form formic acid, the latter decomposing at still higher temperatures almost quantitatively into hydrogen and carbon dioxide.

In the two experiments at 26 atm. in the presence of hydrogen (Table III, expts. 19, 20) with aqueous formaldehyde over copper–alumina catalysts, methanol was formed with the consumption of water, some of the hydrogen reacting in the experiment at 283° and none at 334°. At 410 atm. and 299° in the presence of hydrogen (expt. 21) the simultaneous consumption of both hydrogen and water indicates that methanol produced could probably be attributed to two sources, the direct hydrogenation of the formaldehyde and to the Cannizzaro reaction. Methanol formation was also observed when aqueous formaldehyde solution reacted in the absence of hydrogen over copper–alumina catalyst (expt. 22). It is likewise probable that the formation of methanol from carbon dioxide and hydrogen under pressure could be produced in the same way—reduction of the carbon dioxide through carbon monoxide to formaldehyde, the formaldehyde being converted to methanol by direct hydrogenation and by the Cannizzaro reaction.

Acknowledgment.—The authors wish to express their appreciation to Mr. Lee Fischer and to Mr. E. J. Maxfield for valuable assistance in making these experiments and to Dr. Herman Pines for supplying the carbon monoxide.

Summary

The synthesis of methanol from carbon dioxide and hydrogen over copper alumina catalysts was investigated over a catalyst temperature range of 282–487° and a pressure range of 117–410 atm.

Copper alone and alumina alone had no catalytic effect. The most active catalyst had a copper content of 8–28%, giving conversions of 94% at 410 atm. and catalyst temperature of 285°.

Similar experiments with carbon monoxide and

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[1] R. F. Brown and A. E. Galloway, *Ind. Eng. Chem.*, **21**, 310 (1929).

[2] Ipatieff "Catalytic Reactions at High Pressures and Temperatures," The Macmillan Co., New York, N. Y., p. 238.

hydrogen gave conversions of 39–43%, with as much as 15 and 41% of the carbon monoxide charge reacting to give methane and dimethyl ether, respectively. When carbon dioxide was added to the carbon monoxide (mole ratio, CO: CO_2 = 3.1:1.0) the methanol conversion was raised to 64% and the formation of dimethyl ether reduced to about 1%.

Results obtained with aqueous formaldehyde solutions indicate that the formation of methanol from carbon dioxide and hydrogen under pressure may proceed along two paths. After reduction of the carbon dioxide to the formaldehyde stage, part of the methanol is formed by direct hydrogenation of the formaldehyde and part by the Cannizzaro reaction.

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(3) Original manuscript received May 19, 1943.

[CONTRIBUTION FROM THE LABORATORIES OF SHELL DEVELOPMENT COMPANY, EMERYVILLE, CALIFORNIA]

Direct Catalytic Conversion of Methylcyclopentane to Benzene

BY B. S. GREENSFELDER AND D. L. FULLER[1]

Methylcyclopentane can be converted to benzene by means of the two well-known reactions

$$\mathrm{MeCyC_5H_9} \longrightarrow \mathrm{CyC_6H_{12}};\quad \Delta F^\circ = -3600 + 10T \qquad (1)$$

$$\mathrm{CyC_6H_{12}} \longrightarrow \mathrm{C_6H_6} + 3\mathrm{H_2};\quad \Delta F^\circ = 53{,}700 - 96.6T \qquad (2)$$

The free energy values[1a] correspond to the gas phase equilibria. The first reaction is promoted by catalysts such as aluminum chloride plus hydrochloric acid,[2] and molybdenum sulfide,[3] and the second by catalysts[4] such as nickel, chromic oxide and the platinum metals.

From the free energies given and the simple gas laws, it is evident that the extent of reaction (1) is independent of the pressure and decreases slowly with increasing temperature, being about 10% at 350°. Reaction (2) is hindered by pressure but favored by higher temperatures, and above 475° can go nearly to completion even with high hydrogen dilution at 25 atmospheres.

Adding (1) and (2), gives

$$\mathrm{MeCyC_5H_9} \longrightarrow \mathrm{C_6H_6} + 3\mathrm{H_2};\quad \Delta F^\circ = 50{,}100 - 86.6T \qquad (3)$$

and it is evident that the thermodynamic relationships for this reaction are very much like those for the simple dehydrogenation of cyclohexane to benzene, given above as reaction (2). It is therefore of interest to study the behavior of methylcyclopentane in the presence of a catalyst capable of converting it to benzene in a single step according to reaction (3).

Experimental Results

All experiments were performed in a continuous flow reaction system. The apparatus comprised a stainless steel catalyst tube (32 in. long × $^5/_8$ in. i. d.) supported in a vertical electrical furnace with preheat and main heat windings, the axial catalyst temperature profile being ±3°. Automatic temperature and pressure controllers and recorders were used. The hydrocarbon was fed into the top by a Hills–McCanna proportioning pump and the confluent diluent gas was measured by rotameters. The reaction product was condensed with ice water at the reaction pressure and the total liquid product was sampled hourly for analysis.

A representative summary of the data obtained in the experiments with methylcyclopentane at 490° and MoO_2/Al_2O_3 catalyst (*ca.* 14% molybdenum on "Alorco" Grade A activated alumina) is given in Table I.

In order to determine the nature of the aromatics found by specific dispersion and acid absorption, several samples were distilled. An example is given in Fig. 1 corresponding to Run 111, hours 1–2, in which about 75% wt. aromatics was found by analysis. From the curve and n^{20}_{D} values for various cuts, it will be seen that about 68% of the reported aromatics is benzene, the remainder boiling above 80° with n^{20}_{D} 1.5664. In other runs, the bottoms had n^{20}_{D} values varying from 1.51 to 1.59, and in some cases a larger fraction of the aromatics produced was benzene.

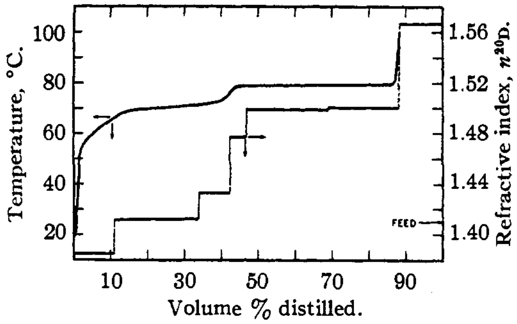

Fig. 1.—Distillation, run 111, hours 1–2.

When a suitable amount of this high boiling aromatic material was collected, it was analytically distilled under reduced pressure. The distillation curve was steep at first and then less so, but no significant plateaus were found. The distillation was stopped at 260° (corrected to 760 mm.) at which point about half the material had passed overhead. Apparently a large number of hydrocarbons was present; the high refractive index suggests that they were mainly polycyclic aromatics.

It is seen that high conversions of methylcyclopentane to benzene and other aromatics can be obtained over molybdena–alumina catalyst. The percentage conversion diminishes rapidly with the length of the process period and a beneficial effect of added hydrogen is observed.

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[1] Present address: General Aniline and Film Corporation, Easton, Penna.

(1a) A. W. Francis, "Science of Petroleum," Vol. III, Oxford University Press, London, 1938, p. 2094, and approximations based on Moore and Parks, THIS JOURNAL, **61**, 2561 (1939); Glasebrook and Lovell, *ibid.*, **61**, 1717 (1939); and Schmitt, *Compt. rend.*, **199**, 1299 (1934).

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(3) Puchkov, *J. Gen. Chem.* (*U.S.S.R.*), **8**, 1677 (1938).

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