[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Catalytic Hydrogenation of Carbon Dioxide to Higher Hydrocarbons[1]

BY W. WALKER RUSSELL AND GLENN H. MILLER[2]

It is known that carbon dioxide can be catalytically converted to higher hydrocarbons at atmospheric pressure by reaction with hydrogen, and that the products are qualitatively similar to those obtained from the Fischer–Tropsch synthesis using carbon monoxide.

A series of iron and cobalt catalysts active for liquid hydrocarbon synthesis have been studied by Küster[3] who obtained, using alkalized catalysts, small oil yields of short duration followed by wax formation. He obtained, however, only methane from an alkalized, kieselguhr–supported Fischer–Tropsch catalyst.

Ruthenium catalysts when properly alkalized with rubidium or potassium carbonate, but not with sodium or lithium carbonate, have also been found active for higher hydrocarbon synthesis from carbon dioxide and hydrogen.[4]

The present work was undertaken in an endeavor to obtain more information about the synthesis of higher hydrocarbons from carbon dioxide and hydrogen which, compared to the synthesis of higher hydrocarbons from carbon monoxide and hydrogen, has received relatively little attention. Because reported yields of liquid hydrocarbons from the carbon dioxide synthesis are small and the catalysts employed soon lost their activity, it appeared of interest to seek the critical factors. For example, what part does the water gas shift play as a limiting or controlling factor in the synthesis, inasmuch as this shift has been considered by some[5] to be critical, and also what is the effect of catalyst composition including such factors as supports, promoters, and alkalies? In this connection, it is to be noted that whereas Fischer–Tropsch cobalt catalysts do not require alkalizing and are more effective when supported on kieselguhr, catalysts for the carbon dioxide synthesis have been found to require alkalizing and heretofore[3,4] have proved to be inactive when supported. Since earlier work with this synthesis[3] indicated that the catalysts lost activity rapidly, yet deliberate poisoning of Fischer–Tropsch catalysts with limited amounts of hydrogen sulfide produced improved oil yields,[6] it appeared desirable to study the poisoning, both deliberate and non-deliberate, of these catalysts as well as methods for their stabilization.

Experimental

Apparatus.—Electrolytic hydrogen, and carbon dioxide containing less than 0.5% impurities (mostly nitrogen) were passed from cylinders through calcium chloride to their respective calibrated flowmeters containing high grade diffusion pump oil. The metered hydrogen was then purified by passage over reduced copper at 400°, through an active, alkalized, copper-promoted, cobalt scrubbing catalyst at room temperature, then through ascarite, calcium chloride, and phosphorus pentoxide, respectively. The metered carbon dioxide was purified by passage over reduced copper and copper oxide at 400°, through the same type of scrubbing catalyst used for the hydrogen, and then through calcium chloride and phosphorus pentoxide. The so purified hydrogen and carbon dioxide were mixed in a large phosphorus pentoxide tube before entering the catalyst.

The catalyst chamber, unless otherwise noted, consisted of a vertical Pyrex tube of 22 mm. i. d. in which was axially sealed a 7-mm. o. d. thermocouple well which extended the entire length of the catalyst bed. The catalyst rested on a plug of glass cotton, and was heated in an electric tube furnace having a length of 75 cm., a core diameter of 3.7 cm., and an o. d. of 17.5 cm. The furnace windings were divided into end sections 22.5 cm. in length and a middle section 30 cm. long. Using a thermometer in the top furnace section, and a thermocouple in the catalyst chamber well, this section was controlled manually with a variac. This was found necessary in order to prevent a hot spot from occurring near where the reacting gases first contacted the catalyst. The two lower sections of the furnace were controlled by means of a Brown potentiometric controller–recorder activated by a thermocouple placed in a well just outside of the catalyst tube, and midway between the top and bottom of the furnace, and near the middle of the catalyst bed. The furnace temperature at this point and the temperature of the movable thermocouple in the catalyst bed were continuously recorded by the Brown instrument. With the controls so placed it was possible to maintain a uniform temperature throughout the furnace except for about 15 cm. at each furnace end. The catalyst bed was centered in the uniform temperature zone which was about 45 cm. long. The temperature in most cases could be controlled within ±1-2°.

The reacting gases passed downward through the catalyst bed and along with the products of synthesis through two traps cooled in a Dry Ice–acetone mixture. No product ordinarily collected in the second trap. Upon removal, the trap was weighed to ascertain the total weight of condensed product, and water was then admitted from a leveling bulb through the trap side arm. After melting the ice, the water forced the oily products of synthesis up into the graduated stem of the trap for measurement.

The gaseous, uncondensed products passed to a wet test meter, except the portion periodically withdrawn for gas analysis. For analysis the gases were collected slowly in order not to disturb synthesis conditions and to secure a representative sample. Mercury was used for the collection and manipulation of the gases which were analyzed for carbon dioxide, unsaturated hydrocarbons, oxygen, carbon monoxide, hydrogen, and saturated hydrocarbons. The various hydrocarbons were not further separated.

Preparation of Catalysts.—The catalysts were numbered from 7 to 23, inclusive. Chemicals of analytical reagent grade were used in the preparation unless otherwise stated. All catalysts contained cobalt and copper.

Unsupported Catalysts.—In the case of these catalysts, to a boiling solution of the metal nitrates which contained a cobalt ion concentration between 0.85 and 1.55 *M*, a solution containing a potassium carbonate concentration

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[1] This paper is based on a portion of a thesis presented by G. H. Miller in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, October, 1948.

[2] University Research Fellow, Brown University, 1947-1948.

[3] Küster, *Brennstoff-Chem.*, **17**, 221 (1936).

[4] Fischer, Bahr and Meusel, *ibid.*, **16**, 466 (1935).

[5] Küster, *ibid.*, **17**, 203 (1936).

[6] Herrington and Woodward, *Trans. Faraday Soc.*, **35**, 958 (1939).

TABLE I

COMPOSITION AND CHARACTERISTICS OF COBALT–COPPER CATALYSTS[a]

		Additional catalyst components					Twenty-four hour period of maximum oil yield					Before oil yield dropped below 0.5 ml. per 24 hr.		
No.	K_2CO_3, %	CeO_2, %	Support type[b]	Reduction conditions, °C.	Init. cat. bulk density, g./ml.	Catalyst shrinkage, %	Temp., °C.	Ml. of oil	Total l. CO_2 passed[c]	% CO_2 reacting	% Gas contraction	Total synth. hr.	Total ml. oil	Final 24 hr. oil yield, ml.
7	0	0	—	S. M.,[d] 200	0.56	63	200	trace	24[e]	..	56	..	...	0
8	2	0	—	S. M., 200	.55	21	225	1.72	48[e]	49	46	218	8.25	1.24
9	2	0	—	S. M., 175	.56	..	225	4.07	48[e]	56	55	290	22.83	0.79
10	2	0	—	S. M., 200	.43	33	200	2.40	48[e]	40	40	144	6.81	.50
11	2	0	—	S. M., 200	.43	14	225	1.94	48[e]	22	21	118	5.68	.79
12	2	0	—	H_2,[f] 275	.42	27	200	0.06	48[e]	10	4	..	...	..
13	2	0	—	S. M., 175	.41	6	200	2.19	48[e]	44	48	144	5.16	1.01
14	2	5	—	S. M., 175	.42	44	225	2.42	48[e]	54	54	1122	45.46	0.57
15	2	1	—	S. M., 175	.43	34	225	2.82[g]	60	34	46	885	50.68	1.25
16	0	1	—	S. M., 200	.40	50	225	0.16[g]	60	40	55	..	...	..
17	3[h]	1	—	S. M., 200	.41	17	225	1.78	48[e]	40	39	252	7.45	1.14
18	4.5	1	MgO	H_2,[i] 400	.35	24	240	0.48	120	21	25	..	...	..
19	4.5	1	MgO	S. M., 200	.35	23	225	0.16[g]	60	8	8	..	...	..
20	6	1	H. S. C.	H_2,[i] 400	.50	14	245	2.02[g]	60	19	26	819	29.76	0.88
21	7	100	CeO_2	H_2,[i] 400	.35	70	250	1.45[j]	60	23	33	492	12.86	1.06
22	4.5	1	F. C.	H_2,[i] 400	.96	25	240	0.22[g]	60	23	32	..	...	..
23	3.8	1	H. S. C.	H_2,[i] 400	.49	..	225	1.64	60	22	30	386	13.89	0.74

[a] All catalysts were prepared from 100 parts cobalt and 5 parts copper, with percentages of additional components based on cobalt. All supported catalysts contained 100 parts of support, except Catalyst 23, which contained 50 parts of support. The unreduced weights of all catalysts were 50 g., except Catalysts 7, 22, and 23 which weighed 20, 100, and 62.5 g., respectively. [b] H. S. C. = Johns–Manville Hyflo Super-Cel (flux-calcined); F. C. = Johns–Manville Filter-Cel. [c] Synthesis gas ratio 1:2 = CO_2:H_2 unless otherwise noted. [d] S. M. = synthesis gas mixture of 2 l. carbon dioxide and 6 l. of hydrogen per hour. [e] Synthesis gas ratio 1:3 = CO_2:H_2. [f] Reduced with 6 l. of hydrogen per hour. [g] Catalyst previously activated by synthesis gas at a higher temperature. [h] In Catalyst 17, potassium phosphate was substituted for potassium carbonate. [i] Reduced with 60 l. of hydrogen per hour. [j] Catalyst previously activated with steam.

between 2.0 and 3.6 *M* was added slowly with rapid stirring in 10% excess of that required for complete precipitation of the metal nitrates. For the ceria promoted catalysts $Ce(NO_3)_3 \cdot 6H_2O$ was also dissolved along with the above metal nitrates before precipitation with potassium carbonate. The carbonate precipitate was washed repeatedly with boiling water until the filtrate was neutral, then the precipitate was dried at 100–110°, powdered, and bottled. The unsupported catalysts were alkalized by stirring the desired weight of the prepared metal carbonate mixture into a watery paste with the desired weight of dissolved potassium carbonate, or in the case of Catalyst 17, potassium phosphate, then evaporating on a steam-bath to an extrudable consistency. After extrusion through a glass syringe of 3 mm. bore onto glass plates the catalyst was dried at 100–110°, then cut into 3 mm. lengths with a sharp stainless steel spatula, and finally sieved to pass a no. 6 mesh but to be retained by a no. 12 mesh sieve.

Supported Catalysts.—Various supporting materials were used including C. P. reagent grade magnesium oxide "low in sulfur," and also several commercial kieselguhrs sold by Johns-Manville Co. For Catalysts 18, 19, 20, 22, and 23, the support was suspended in the hot potassium carbonate solution and after digesting for an hour the well-agitated mixture was used for the precipitation of the metal nitrate solution. The alkalizing of the supported catalysts was not carried out as a separate step upon the previously dried carbonates, rather the potassium carbonate solution was thoroughly mixed into the wet but well washed support-carbonate precipitate, whereupon the catalyst mass was extruded, and after the single drying was ready for reduction. In the case of Catalysts 18, 19 and 20, the amounts of potassium carbonate in the catalysts were estimated from the weights of water lost in drying the alkalized, extruded catalysts, and a knowledge of the concentrations of the potassium carbonate solutions used to finally impregnate the well washed support-carbonate precipitates just before extrusion. The alkalizing of Catalysts 21, 22 and 23 involved washing the metal carbonate-support mixture free from alkali and nitrate ion, then suspending in a solution containing a known amount of potassium carbonate, filtering and sucking down to an extrudable consistency, and then determining the amount of potassium carbonate retained in the catalyst by titrating the alkali in the filtrate. For Catalysts 20 and 23 a flux-calcined kieselguhr "Hyflo Super Cel," which was slightly basic, was used without additional purification. For Catalyst 22 a natural, uncalcined kieselguhr "Filter Cel," was used after nitric acid extraction, thorough washing, and extraction with hot potassium carbonate solution.

Catalyst 21, in which cerium oxide was incorporated as a support, was precipitated with potassium carbonate solution at a temperature below 10° and washed at room temperature.

Reduction of Catalysts.—The unsupported catalysts, except Catalyst 12, were reduced in synthesis gas as shown in Table I. During reduction the temperature was raised slowly from room temperature to 150° and held there for eighteen hours, then slowly raised until synthesis set in, usually in the range of 175 to 200°. Thereafter the temperature was raised as the conditions of synthesis required.

Supported Catalyst 19 was reduced like the unsupported catalysts but at temperatures up to 250°. The remainder of the supported catalysts were reduced in a fast flow of hydrogen for two hours, as shown in Table I.

Catalyst compositions are given in Table I and are designated in terms of starting materials, thus for example if the cobalt in the cobalt nitrate used for Catalyst 22 represented 100 parts by weight, the copper in the copper nitrate was 5 parts, the alkalizing potassium carbonate was 4.5 parts, the kieselguhr was 100 parts, and the cerous nitrate was sufficient to yield 1 part of CeO_2. The completeness of reduction of cobalt and copper carbonates or oxides to the metal in the reduced catalysts was not determined. Also, the cerium probably does not exist in the active catalyst entirely as CeO_2 but rather as a mixture of cerous and ceric oxides and carbonates.

Method of Catalyst Evaluation.—The volume and composition were known for the entering synthesis gas and also for the exit gas after passage through Dry Ice cooled traps. Thus the contraction and also the hydrogen and carbon dioxide participating in synthesis could be easily determined, as well as carbon monoxide and hydrocarbons in the exit gas. Only traces of oxygen or unsaturated gaseous hydrocarbons ever appeared in the exit gases. The amount of oil, or liquid hydrocarbons defined as hydrocarbons[7] condensed by Dry Ice and not vaporized at room temperature, was determined volumetrically. From a pycnometric density determination[8] the weight of oil was calculated. The density of the oil increased as synthesis temperature was raised as the catalyst aged and as the wax content of the oil increased. The density at 25° ranged from 0.652 to 0.725 for the various oils synthesized. Any gases synthesized which were vaporized from the Dry Ice trap during the measurement of an oil sample at room temperature were negligibly small in amount, and were not evaluated. Oil samples were usually collected over twelve to twenty-four hour periods. The total number of synthesis hours per catalyst varied from about two hundred to eleven hundred hours.

Analysis of Oils.—Representative oil samples were analyzed further by distilling 1 ml. samples in a micro still. A sample whose initial density was 0.690 gave 85% by weight distilling below 150° with a distillate density of 0.681, the higher temperature distillate being a heavy oil having a density of 0.814. Another sample whose initial density was 0.730 gave 69% distilling below 150° with a distillate density of 0.722, and a higher temperature distillate which consisted principally of a yellowish-white wax melting at about 30°.

A number of oil samples were also analyzed by a standard method[9] for olefins plus aromatics, and showed such unsaturation to vary from 1 to 26% with the average at about 10%. In general unsaturation in the oil increased with temperature and increasing catalyst age. Unsaturation also increased as the partial pressure of hydrogen decreased and/or the gas flow was increased. Catalyst composition as a variable appeared to make little difference for the yield of unsaturates.

Several oil samples were also analyzed for carbon and hydrogen by a semimicro combustion method. These analyses showed that carbon and hydrogen accounted for at least about 99% of the liquid hydrocarbon yield. The average carbon hydrogen ratio was 5.24, corresponding to a hypothetical hydrocarbon $CH_{2.26}$ or approximately to the saturated hydrocarbon C_7H_{16}.

Results and Discussion

Preliminary Work.—Catalysts up to and including Catalyst 13 were employed particularly to study the conditions for and the nature of the synthesis. Considering Catalysts 8, 9, 10, 11 and 13, each had the same initial composition, as shown in Table I, but the batch of precipitated carbonates used for the last three catalysts was dried for sixty hours instead of a week, as for the first two catalysts, prior to the reduction which was the same for each of the five catalysts. As is evident from Table I, these catalysts differed in their characteristics. During their first forty-eight hours of synthesis at 225° Catalysts 8 and 9 showed a gradual linear decrease in gaseous contraction with the oil yield at first increasing. However, Catalysts 10, 11 and 13 showed an exponential and more rapid decrease in contraction with the oil yield decreasing throughout the period.

Catalyst 9 produced a maximum yield of 2.28 ml. of oil during the twelve-hour period following the first eight hours of synthesis at 225°. This was the largest yield per hour obtained from any of the catalysts studied in this work and corresponds to 95 ml. (65 g.) of liquid hydrocarbons per cubic meter of carbon dioxide passed, or 170 ml. (116 g.) per cubic meter of carbon dioxide converted. This is almost three times the maximum yield reported earlier.[3] This was not a sustained yield, however, as the following twelve-hour period produced only 1.58 ml. Catalyst 13 which was an attempt to duplicate Catalyst 9 gave a maximum oil yield at 200°, namely 1.23 ml. in twelve hours. For these five catalysts the condensed product first synthesized was a colorless oil from which no wax separated, but as the catalysts aged and the synthesis was carried to higher temperatures, the wax content of the oil increased until finally only wax condensed. While the wax first synthesized was odorless and white, the final waxy products were yellow and of unpleasant odor. This sequence of condensed product changes was not materially altered by varying the bed length of the 50-g. charge of catalyst from 3.8 to 80.0 cm. However, the best efficiency was obtained with a bed length of about 25 cm. employed in the catalyst chamber already described.

Ceria Additions to Alkalized Catalysts.—It was found by dissolving small amounts of cerous nitrate in the cobalt and copper nitrate solution prior to precipitation with potassium carbonate, that a much more stable catalyst resulted and that a greatly increased amount of liquid hydrocarbons could be synthesized over the catalyst during its useful life. Catalysts 14 and 15 which contained 5 and 1% of ceria, respectively, were reduced like Catalysts 8–11 and 13 and were otherwise of the same composition. Catalyst 21 contained a hundred times more ceria than Catalyst 15 and will be considered with the supported catalysts. Fig. 1 presents the history of the first six hundred hours of operation of Catalyst 15, each point on a curve representing the average for a twenty-four hour run. Solid lines connect runs at the same temperature, ratio, and rate of synthesis gas flow, and these runs are successive unless off curve points intervene. The lower or contraction curve measures the over-all activity of the catalyst, the middle curve its activity in oil synthesis, while the top curve gives the catalyst's efficiency in converting the reacting carbon dioxide into oil. How these factors are influenced by variations in temperature, rate of flow and composition of synthesis gas, and catalyst age is evident from Fig. 1.

While raising or lowering the temperature produced a simultaneous increase or decrease in contraction, the effect upon the oil yield and efficiency of converting carbon dioxide to oil was less simple. Thus raising the temperature of synthe-

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[7] In this paper the terms *oil* and *liquid hydrocarbons* are used interchangeably, and as above defined.

[8] A. S. T. M. Standards, Vol. III, 1944, p. 1097.

[9] Mills, Kurtz, Heyn and Lipkin, *Anal. Chem.*, **20**, 333 (1948).

sis on Catalyst 15 from 200 to 225° initially decreased the oil yield and the catalyst's oil producing efficiency. Later raising the temperature from 215 to 220°, and from 220 to 225° produced substantially equivalent behavior. Again considering the initial temperature rise from 200 to 225° it is evident that during the next seventy-two hours at 225°, while the contraction fell slightly, the oil yield increased 36% due to the increase in catalyst efficiency. Reducing the temperature from 225 to 220° and then to 215° extended the oil yield upward in a nearly linear manner with corresponding increases in catalyst efficiency, the initial oil yield at 215° being by 81% larger than the initial oil yield at 225°.

The runs on Catalyst 15 in which the ratio of carbon dioxide to hydrogen was varied from 1:2 to 1:3 while the total flow varied only from 7.5 to 8 l. per hour, and in which the ratio was varied from 1:1.5 to 1:2 to 1:3 while the carbon dioxide rate remained at 2.5 l. per hour, indicated the best catalyst efficiency at the ratio of 2.5:5 l. per hour. This was confirmed by similar tests upon Catalyst 14.

Although Catalysts 14 and 15 did not equal Catalyst 9 in maximum oil yield per twenty-four hours, yielding 2.42 and 2.27 ml. respectively *vs.* 4.07 ml., the cerium-containing catalysts possessed markedly greater stability and showed little tendency to yield waxy hydrocarbons and therefore a much longer life. The stability of these catalysts is best illustrated by the lengths of time they were active in actual synthesis. After ten hundred and fifty hours Catalyst 14 was yielding 1 ml. of oil, while after eight hundred and eighty-five hours Catalyst 15 was yielding 1.25 ml. of oil per twenty-four hours, whereas Catalyst 9 produced only 0.46 ml. of oily, yellow wax per twenty-four hours after only three hundred and fourteen hours of synthesis.

The Over-all Apparent Activation Energy.—The stability of Catalyst 14 was so good that, after some twelve hundred hours of synthesis, it was considered justified to determine the temperature coefficient of the over-all reaction, *i. e.*, total reaction, employing a constant degree of conversion method,[10] in which the reaction rate is measured as the total amount of synthesis gas reacting in unit time. It was found possible to maintain a constant degree of gaseous contraction, using either 4.5 or 7.5 l. per hour of 1:2 synthesis gas, by adjusting the catalyst temperatures to a suitable value in the range of 235 to 250°. Ten apparent activation energies so obtained ranged from 20.3 to 25.3 kcal. giving an average value of 23.1 kcal.

Variations in Alkalizing Catalysts.—In order to assess the importance of alkalinity, Catalysts 7, 16 and 17 were prepared. Catalyst 7 was prepared from the same metal carbonate batch as Catalyst 8 and reduced in like manner, but no alkalizing alkali was present. Unlike Catalyst 8, however, Catalyst 7 yielded scarcely a trace of oil at 200° although the gaseous contraction was 56%, and no trace of oil at 225° although the contraction rose to 60%. At the latter temperature all of the carbon dioxide reacting appeared in the exit gases as methane.

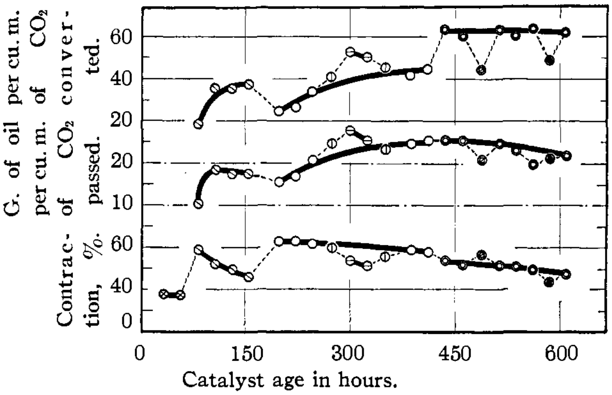

Fig. 1.—Effect of several variables upon synthesis of oil over Catalyst 15 (Co:Cu:CeO_2:K_2CO_3, 100:5:1:2) at temperatures: ⊗, 175°; ⦸, 200°; ⊖, 215°; ⦶, 220°; O, 225°; ⊘, 230°. Input velocity of synthesis gas given as ratio of liters per hour of CO_2 to H_2: O, 2:6; ◎, 2.5:5; **O**, 2.5:3.75; ⊙, 2.5:7.5.

Catalyst 16 was prepared from the same dried metal carbonate batch as Catalyst 15 except no alkalizing alkali was used. Initial runs at 200, 220 and 225° produced no trace of oil, and although the gaseous contraction reached 68% all the reacting carbon dioxide was converted to methane.

Catalyst 17 was similar to Catalyst 15 except that 3% potassium phosphate replaced the 2% of potassium carbonate. Oil synthesis started on Catalyst 17 at 200° and reached a maximum of 1.78 ml. per twenty-four hours at 225°. Although, compared to Catalyst 15, the phosphate alkalized catalyst was less stable, the gaseous contraction initially 48% at 225° dropping to 24% after forty-eight hours of synthesis, the relatively good yields of liquid hydrocarbons with Catalyst 17 appears to eliminate the possibility that a carbonate–bicarbonate mechanism is essential in explaining the behavior of the alkali.

Thus the importance of having excess alkali present in the catalysts if liquid hydrocarbons are to be produced is substantiated by the present work. The amounts of potassium carbonate used for alkalizing covered the range of 2 to 7%, within which limits, the activities of the resulting catalysts appeared to be practically independent of alkali concentration.

Supported Catalysts.—The widespread use of supported catalysts in the synthesis of liquid hydrocarbons from hydrogen and carbon monoxide made it appear of interest to investigate

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[10] Anderson, Krieg, Seligman and O'Neill, *Ind. Eng. Chem.*, **39**, 1548 (1947).

supported catalysts for the synthesis using carbon dioxide, even though earlier attempts[4] to support alkalized ruthenium catalysts for the latter synthesis had failed, presumably due to reaction of the free alkali with the silicate of the support. Because of its slightly basic character and successful use in Fischer–Tropsch catalysts[11] magnesia suggested itself as a possible support. Catalysts 18 and 19 had the same composition, each containing 100 parts of magnesia but differed in that the former was reduced at 400° with hydrogen, while the latter was reduced with synthesis gas like the unsupported catalysts. Since the maximum oil yield between 175 and 240° on Catalyst 18 was small, as is shown in Table I, it appears that the magnesia used proved to be a poor catalyst support. No oil was synthesized over Catalyst 19 at 200, 225 or 250°, although at the latter temperature much methane was formed. The behavior of these two catalysts indicated the necessity of using a higher reduction temperature for supported catalysts, and all catalysts following Catalyst 19 were reduced in a fast flow of hydrogen at 400°.

Catalyst 21 contained 100 parts of ceria but it underwent excessive shrinkage, losing nearly 70% in volume after five hundred hours of synthesis. In the temperature range of 200–245° the best oil yield was 1.09 ml. per twenty-four hours at 245°. It, therefore, appears that while ceria acts as an effective stabilizer and promoter, it is not effective as a catalyst support in preventing loss of catalyst bulk volume at higher temperatures, *e. g.*, 400°. Actually Catalyst 21 was less active in oil synthesis than the catalysts containing only a few per cent. of ceria.

Kieselguhrs have large surfaces[12] and have been extensively used to support Fischer–Tropsch catalysts, and although siliceous in nature appeared to warrant investigation. Catalysts 20, 22, and 23 were supported on kieselguhr. Catalyst 22 employed acid-extracted "Filter Cel," a natural kieselguhr which is reported to have a surface area of nearly 23 sq.m. per gram,[12] however, only methane and water, and no oil were obtained between 200 and 225° although at the latter temperature the contraction reached 53%. Catalysts 20 and 23 were supported on "Hyflo Super Cel," a flux-calcined kieselguhr reported to have a surface area less than a tenth of that of the natural kieselguhr.[12] Both Catalyst 20 and 23 produced oil. The largest twenty-four hour oil yield from the former between 175 and 240° being 1.16 ml. at 220°, and from the latter 1.64 ml. at 225°.

Thus neither of these two supported catalysts gave quite as large or any better sustained oil yields than comparable unsupported Catalysts 14 or 15. The better performance of Catalysts 20 and 23 as compared to Catalyst 22 is attributed to the prior flux-calcination of the kieselguhr used in the first two catalysts which appears to have sufficiently neutralized the silica so that the alkalizing potassium carbonate remained effective.

In comparing the unsupported and supported catalysts here studied, it should be noted that the former were reduced with synthesis gas while the temperature was slowly raised to a point at which considerable synthesis occurred. An exception was unsupported Catalyst 12 which was reduced in hydrogen alone at 275°. This catalyst produced only very small amounts of oil, and after a few days only wax in small quantities.

Additional information pertaining to the catalysts studied is presented in the compilation of data shown in Table I which is believed to be self-explanatory.

Selective Poisoning and Activation of Catalysts.—Upon several occasions at the end of a run on Catalysts 14, 15, 16, 19, 20 and 22 the catalyst temperature was raised for several hours while a mixture of hydrogen and carbon dioxide passed over the catalyst, or in the case of Catalyst 16 while this catalyst was left in contact with a static atmosphere of the mixed gases. The temperature was then immediately reduced to synthesis temperature, and another run made from which any products synthesized at the higher temperature and during approximately the first hour at synthesis temperature were excluded. A comparison of synthesis at 220° on Catalyst 14 before and after heating the catalyst, for four hours at 320° in a 1:1 mixture of hydrogen and carbon dioxide at a flow of 4 l. per hour, showed a 54% increase in oil yield accompanied by a 22% decrease in contraction and a corresponding improvement in catalyst efficiency. This is shown graphically in Fig. 2. After six hundred and twenty-two hours of synthesis and again after six hundred and ninety-one hours, Catalyst 15 was heated for fifteen to sixteen hours at 250° in a 2:1 mixture of hydrogen and carbon dioxide at a flow of 7.5 l. per hour. These treatments caused increases in oil yields at 225° during subsequent twenty-four hour periods of 0.90 ml. and 0.28 ml., *i. e.*, increases of 47 and 13%.

Three, four to six hour heatings of the non-alkalized Catalyst 16 in a 1:1 static mixture of carbon dioxide and hydrogen, each preceding a twenty-four hour run at 225°, initiated during the latter small but definite oil formations of 0.07, 0.10, and 0.16 ml., respectively. In a twenty-four hour run at 225° following heating the magnesia-supported Catalyst 19 for two hours at 400° in a 1:2 carbon dioxide–hydrogen flow of 7.5 l. per hour, a definite oil yield of 0.16 ml. was obtained. Two similar treatments of the natural kieselguhr-supported Catalyst 22 at 300° and one at 350°, the first one followed by a twenty-four hour run at 225° and the two latter at 240°, initiated oil formations of 0.10, 0.09 and 0.22 ml., respectively. A similar treatment of supported Catalyst 20 at 300° caused, as is shown in Fig. 3, considerable in-

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[11] Craxford, *Fuel*, **26**, 119 (1947).

[12] Anderson, McCartney, Hall and Hofer, *Ind. Eng. Chem.*, **39**, 1618 (1947).

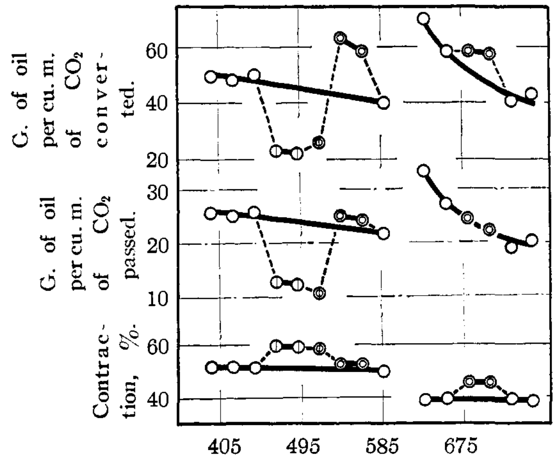

Fig. 2.—Effect of several variables including an activation on Catalyst 14 (Co:Cu:CeO$_2$:K$_2$CO$_3$, 100:5:5:2) at temperatures: O, 220°; ⦶, 230°. Input velocity of synthesis gas given as ratio of liters per hour of CO$_2$ to H$_2$: single circles, 2:6; double circles, 2:4. Break between solid curves indicates treatment at 320° at a ratio of 2:2.

creases in oil yield and catalyst efficiency accompanied by decreased contraction. These effects persisted for the next seventy hours of synthesis and until the catalyst was activated with hydrogen. Further similar treatments of Catalyst 20 produced smaller effects.

To study the effect of synthesis temperature upon the stability of selective poisoning, synthesis temperature was reduced in steps on Catalyst 20 after a twenty-four hour high temperature synthesis gas treatment at 300° during which 0.32 ml. of oil was formed, and the contraction averaged 48%. Reducing the synthesis temperature to 275° increased the above oil yield four-fold during the subsequent forty-eight hours, and although the contraction and the amount of carbon dioxide reacting remained almost constant, gaseous hydrocarbon formation increased at the expense of the oil yield during this period. Even though the over-all catalyst activity appeared to remain almost constant, yet the distribution of hydrocarbon products was changing due to poison removal from the methane producing areas of the catalyst. Lowering synthesis temperature to 260° again initially produced a larger oil yield accompanied by a slowly increasing contraction and gaseous hydrocarbon formation, indicating that catalyst poison was still being removed. These phenomena were repeated upon further lowering synthesis temperature to its initial value of 245°, except that the oil yield was now diminished. Thus no temperature was found at which the selective poisoning was completely stable.

The effects of passing hydrogen over Catalysts 15, 20, 21 and 23 for several hours at or above synthesis temperature were also studied. After seven hundred and sixty hours of synthesis, passing hydrogen for twenty-four hours over Catalyst 15 at 5 l. per hour at 225° caused the oil yield in twenty-four hours subsequent synthesis at this temperature to rise 0.55 ml. or 37%. A similar hydrogen treatment but at 300° for ten hours on Catalyst 20, Fig. 3, produced in a subsequent twenty-four hour run at 225°, an increase of 0.34 ml. or of 24% in oil yield at an average contraction which had increased from 21 to 28%. An immediate additional hydrogen treatment at 400° on this catalyst produced little effect. A similar hydrogen treatment on Catalyst 21 at 300° for twelve hours, preceded and followed by a twenty-four hour run at 240°, gave an increase in oil yield of 0.14 ml. or 13% and an initial increase in contraction of 39%. A similar hydrogen treatment for ten hours at 300° on Catalyst 23, preceded and followed by a twenty-four hour run at 225°, produced an increase in oil yield of 0.22 ml. or 27% and an initial increase in contraction of 101%.

Treatments with carbon dioxide, water vapor or methane either at or above synthesis temperature were carried out on Catalysts 21 and 23. Passing 2.5 l. per hour of carbon dioxide over Catalyst 23, for six hours at 300° after seventy-four hours of synthesis, caused a slight decrease in the oil yield subsequently obtained at 225°. A similar treatment of Catalyst 21, for seven hours after three hundred and sixty-four hours of synthesis, caused in a subsequent twenty-four hour run at 250° a loss in oil yield of 0.35 ml. or 35%. Immediately following this run, treating Catalyst 21 similarly but with the carbon dioxide saturated at room temperature with water vapor restored the oil yield at 250° from 0.65 to 0.89 ml. Immediately following this run, treating Catalyst 21 in a current of steam followed by a twenty-four hour run at 250° gave an increase in oil yield of 0.56 ml. or 63%.

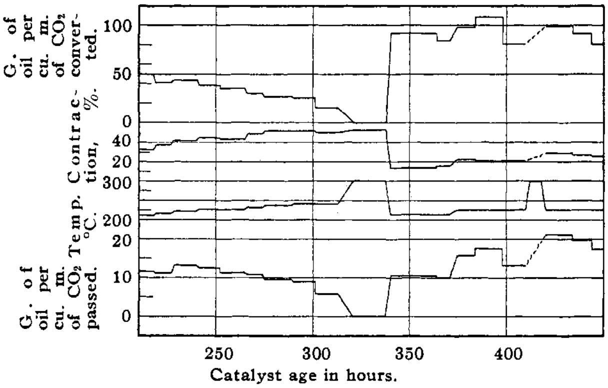

Fig. 3.—Effect of temperature and time upon synthesis of oil over Catalyst 20 (Co:Cu:CeO$_2$:K$_2$CO$_3$:Kg, 100:5:1:6:100). Synthesis gas input velocity given as ratio of liters per hour of CO$_2$ to H$_2$:2.5:5. Broken curve indicates hydrogen treatment at a flow of 5 liters per hour.

After one hundred and ninety-five hours of synthesis, steam was passed over Catalyst 23 at 300° for three hours, and a subsequent twenty-four hour synthesis at 225° showed an increase in oil yield of 0.09 ml. or 12%, while the average contraction had decreased from 23 to 18%. After three hundred and forty hours of synthesis, Catalyst 23 was heated at 325° for six hours in a flow of 2.5 l. per hour of a methane-rich gas (77.4% CH_4, 4.7% CO_2, 17.9% H_2). A subsequent twenty-four hour run at 260° produced an increase in oil yield of 0.14 ml. or 16%.

Discussion and Conclusions

All of the catalysts studied contained 5% copper which is itself a mild hydrogenation catalyst, and its presence in cobalt catalysts has been found to lower the temperature of catalyst reduction.[13] Furthermore, copper-containing catalysts have been found to be very active in the water gas reaction[14] without synthesizing significant quantities of methane. With such catalysts used under the experimental conditions of the present work, a synthesis gas containing a 1 to 2 ratio of carbon dioxide to hydrogen gave a greater conversion of the former to oil with less methane formation than the theoretical 1 to 3 ratio, required to reduce carbon dioxide to methylene radicals.

During continued use in synthesis, all of the catalysts studied showed a loss in activity which was slowest in catalysts containing ceria. Such non-deliberate poisoning is common in hydrocarbon synthesis and can be more or less compensated for a time by small increases in synthesis temperature. Raising the temperature too rapidly produced an increased gaseous contraction accompanied by a diminished oil yield. However, by again lowering the temperature somewhat the oil synthesis increased, or by continued synthesis at the higher temperature the oil yield slowly increased. Such an effect of lowering the synthesis temperature is shown in Fig. 2, and the changes in the reaction product distribution on continued synthesis at the higher temperature is also illustrated in Fig. 1. Figure 4 shows the non-deliberate but beneficial poisoning of Catalyst 17 produced by continuous synthesis at 215°.

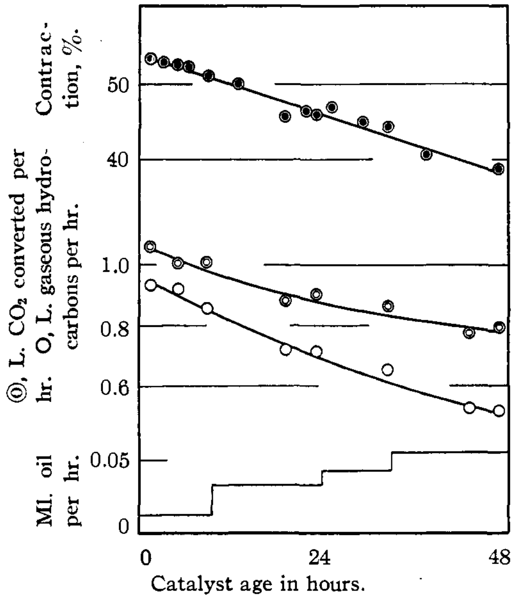

Fig. 4.—Non-deliberate poisoning on Catalyst 17 ($Co:Cu:CeO_2:K_3PO_4$, 100:5:1:3) at temperature 215°. Input velocity of synthesis gas given as ratio of liters per hour of CO_2 to H_2:2:6.

It appears that when synthesis temperature is raised the hydrogenation steps are initially accelerated increasing the carbon dioxide consumed, the gaseous contraction, and the formation of methane; however, this is accompanied by a rather selective poisoning of the hydrogenation centers on the catalyst surface, which eventually allows a greater fraction of the methylene radicals synthesized to form liquid hydrocarbons on the polymerization centers of the catalyst. Thus it appears that a certain degree of selective poisoning of the catalyst is necessary before a maximum yield of liquid hydrocarbons can be obtained at a given temperature.

A study of the conditioning of catalysts for synthesis by treatment with various interactants, usually at an elevated temperature, was undertaken after it was accidentally found that a selective poisoning, accompanied by catalyst activation for oil synthesis, could be produced by raising the temperature of synthesis 25 to 100° for several hours, then resuming synthesis at the initial temperature. At the elevated temperature mostly gaseous hydrocarbons, principally methane, and little or no oil were formed. Upon resuming synthesis at the lower temperatures prevailing before the high temperature treatments, the liquid hydrocarbon yields were up to 50% higher, although the amount of carbon dioxide reacting had dropped by as much as 15%, indicating a highly selective and beneficial poisoning effect. Examples of such a high temperature treatment are shown in Figs. 2 and 3. High temperature synthesis gas treatments were made on eight different catalysts, six of which produced their maximum oil yields following such treatments. Catalysts which contained no potassium carbonate or other alkali were able to produce small amounts of oil only after being selectively poisoned by a high temperature treatment. Catalyst 22, which probably had its alkali content neutralized by the silica of the natural kieselguhr support, also produced some oil, but only after such a treatment. These facts strongly suggest that one function of the alkali in the catalyst is to produce a selective poisoning of the methane producing areas of the catalysts, and thus promote polymerization of methylene radicals by a repression of the competitive hydrogenation reaction.

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[13] Fischer and Koch, *Brennstoff Chemie*, **13**, 61 (1932).

[14] White and Shultz, *Ind. Eng. Chem.*, **26**, 95 (1934).

The experiments with various gases carried out in an endeavor to obtain more information about the selective activation produced by the high temperature synthesis gas treatments showed activation to occur with hydrogen, water vapor, or methane, and only carbon dioxide produced no activation. The effects of a hydrogen activation, which was more selective on the unsupported catalysts, usually lasted about twelve hours during which the enhanced contraction decreased, and after which the oil yield had diminished to about its former value. This hydrogen activation may be attributed to a somewhat selective removal of inhibitors which left the catalyst with more active surface which then became poisoned again by certain synthesis products. In the high temperature treatments, the mode of action of the methane and also that of the water vapor appears to be much the same as that of the hydrogen.

The beneficial, selective poisoning which occurred during the treatments of the catalysts at higher than synthesis temperature with the carbon dioxide–hydrogen mixtures is believed due to the synthesis and cracking of small amounts of higher hydrocarbons, with subsequent strong adsorption of the more unsaturated cracking products largely upon the hydrogenation areas of the catalyst, presumably bare metallic centers. During subsequent synthesis at lower temperatures there is evidence of the removal of at least part of the high temperature poisoning. Thus the catalyst slowly regained some of its hydrogenating power until a maximum contraction was reached, and the slow poisoning which accompanied normal synthesis became predominant.

The phenomena of selectively poisoning supported nickel catalysts at high temperatures with a mixture of carbon dioxide and hydrogen has already been reported.[15] In this instance, the portion of the nickel surface responsible for most of the hydrogenation of carbon dioxide to methane could be poisoned without affecting the nickel surface which catalyzed the hydrogenation of nitrous oxide. Also, Fischer–Tropsch catalysts have been selectively poisoned with small amounts of hydrogen sulfide,[6] and the results are in general agreement with the results of the poisoning produced by the high temperature treatments in the present work. Such selective poisoning phenomena find most convincing explanation in terms of a nonuniform catalyst surface, *e. g.*, catalysts which have areas for polymerization distinct from those for hydrogenation, and where variations in catalytic activity probably occur within each of these two types of area.

Carbon monoxide has been considered as a possible intermediate[3] in the synthesis of higher hydrocarbons from carbon dioxide and hydrogen. In the present work little or no carbon monoxide appeared in the exit gases when the catalysts were most active for oil synthesis. As the catalysts lost activity and the synthesis temperature was raised the carbon monoxide content of the exit gases increased, in some cases up to 1–2%. When synthesis was interrupted by raising the temperature, as in the high temperature synthesis gas treatments, the carbon monoxide content of the exit gases decreased. Since raising the temperature should increase carbon monoxide formation by the water gas reaction, it appears that on active catalysts carbon monoxide was hydrogenated about as fast as formed. On only one of the catalysts shown in Table I was there definite evidence that carbon monoxide had decomposed with the deposition of carbon. Catalyst 14 which temporarily developed a hot spot in the early stages of synthesis showed at the entering end, catalyst granules which were carbon-swollen.

Using the water gas equilibrium constant[16] and assuming no disturbing side reactions, it is calculated that at most 13.8% carbon dioxide would be converted to gaseous carbon monoxide at 225° from a 1:3 carbon dioxide–hydrogen mixture. Were this carbon monoxide completely converted to a liquid of assumed composition $(CH_2)_x$, a yield of 2.1 g. would be obtained in twelve hours from an input of 8 liters per hour. No oil yield exceeding this figure was obtained. Unsupported, unpromoted Catalyst 9 produced under the above experimental conditions a maximum yield of 1.6 g. of liquid hydrocarbons. However, it cannot be excluded that at some time during the twelve hours the instantaneous yield of liquid hydrocarbons was relatively greater.

On the average, 56% of the carbon dioxide reacted during the above twelve-hour period. The excess of carbon dioxide reacting can be explained by at least two mechanisms: first, by the favorable factor of carbon monoxide removal by hydrogenation outweighing such unfavorable factors of this hydrogenation as hydrogen consumption and water formation in influencing the water gas equilibrium and, second, by a conversion of carbon dioxide to methane which does not involve carbon monoxide as an intermediate. In support of the latter, experience with the Fischer–Tropsch synthesis indicates that the hydrogenation mechanism for carbon dioxide[17] differs from that for carbon monoxide. In any event, the formation of methane from carbon dioxide need involve no polymerization step.

In the present work the water gas equilibrium, assuming no interference by other reactions, can provide sufficient carbon monoxide to account for all the hydrocarbons higher than methane formed in all cases. However, one or both of the two mechanisms just discussed appear to be required to account for the considerable amounts of methane always simultaneously formed, which varied from one to three times such equilibrium volumes of carbon monoxide.

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[15] Russell and Loebenstein, THIS JOURNAL, **62**, 2573 (1940).

[16] Emmett and Shultz, *ibid.*, **52**, 4268 (1930).

[17] Pichler, *Brennstoff-Chem.*, **24**, 39 (1943).

While the optimum temperature for liquid hydrocarbon synthesis depended most upon the history and age of the catalyst, and upon whether or not the catalyst was supported, maximum liquid hydrocarbon yields were usually obtained near 225° which is at least 30° above that generally found best for Fischer–Tropsch synthesis.[18] This appears consistent with the participation of the endothermic water gas shift.

The values of the apparent activation energy for the over-all, or total reaction, found in the present work to lie between 20.3 and 25.3 with an average of 23.1 kcal., compare closely with the values of 23.8 and 26.4 kcal.[10] found for the synthesis from carbon monoxide on a cobalt–thoria–magnesia–kieselguhr catalyst. This indicates that a similar rate controlling mechanism, which is clearly not diffusion, may be involved in both syntheses.

The authors are tentatively inclined to attribute the much smaller oil yields produced in the hydrogenation of carbon dioxide, in comparison with carbon monoxide, to limitations imposed by the water gas equilibrium.

Acknowledgment.—The authors are indebted to Mr. R. N. R. Mulford for several analyses on the liquid hydrocarbons synthesized.

Summary

The present work comprised a study of several types of copper-activated, cobalt catalysts for the synthesis of higher hydrocarbons from carbon dioxide and hydrogen at atmospheric pressure, and in a temperature range from 175 to 300°.

Catalysts containing no alkali produced no liquid hydrocarbons or only traces, but did yield small amounts of liquid hydrocarbons after a suitable poisoning. Alkalizing with potassium carbonate or phosphate was necessary in order to produce catalysts active for liquid hydrocarbon synthesis, and it appears that the alkali can act as a selective poison for methane-forming catalyst centers.

Small additions of cerium oxides to the alkalized catalysts were very effective in increasing synthesis life and catalyst stability.

Although an alkalized, ceria-containing catalyst supported on a natural kieselguhr produced only methane, when a flux-calcined kieselguhr was substituted as a support, a catalyst was obtained which synthesized nearly as much liquid hydrocarbons as unsupported catalysts of about the same composition.

The optimum synthesis temperature was near 225°, but depended on catalyst composition and activity. Raising synthesis temperature some 25 to 100° for several hours produced a selective poisoning of catalyst hydrogenation centers, which caused a marked increase in liquid hydrocarbon formation upon resumption of synthesis at the initial temperature.

While the carbon monoxide theoretically available from the water gas reaction (assuming no complicating reactions) is in all cases ample to account for all of the higher hydrocarbons formed, it is entirely inadequate to account also for the amounts of methane formed. The maximum liquid hydrocarbon yield obtained was 95 ml. per cubic meter of carbon dioxide passed, and was accompanied by 360 liters of gaseous hydrocarbons.

The apparent activation energy for the over-all synthesis was found to be 23.1 kcal.

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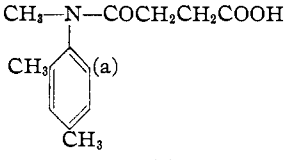
[18] Hall and Smith, *J. Soc. Chem. Ind.* (*London*), **65**, 128 (1946).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Restricted Rotation in Aryl Amines. XI. Influence of Groups Decreasing the Basicity of the Nitrogen Atom

BY ROGER ADAMS AND JOSEPH R. GORDON[1]

In a recent paper,[2] a comparison of various groups in the 6-position upon the stability of the optically active forms of compounds of type I was discussed. It was found that the methyl and methoxyl groups had the relative effectiveness on stability expected from the previously reported work on optically active biphenyl derivatives. The molecules, however, in which the bromine, iodine and nitro groups were present were much less stable than anticipated. This anomalous behavior was ascribed to the tendency for an increased double bond character of the carbon–nitrogen bond in the derivatives of amines of decreased basicity. The tendency for double bond formation will aid in forcing the substituents on the amino nitrogen into a coplanar configuration with the ring.



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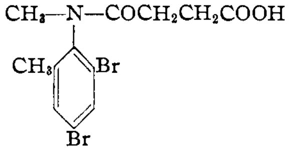

II

(a) = Br, I, NO_2, CH_3, OCH_3

This hypothesis was supported by a comparison of the stability of the bromo derivative (I) with the dibromo-*o*-toluidine derivative (II). The

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[1] An abstract of a thesis submitted by Joseph R. Gordon to the Graduate College of the University of Illinois, 1949, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Adams and Sundholm, THIS JOURNAL, **70**, 2667 (1948).