Experimental

Reagents.—All solutions were prepared using doubly distilled water. The second distillation was from an alkaline permanganate solution in a Barnstead still. The perchloric acid used was Reagent Grade (Merck, G. F. Smith or Baker). The sodium perchlorate was from two sources: some was prepared from Reagent-grade sodium carbonate and perchloric acid while other batches were prepared by recrystallizing G. F. Smith sodium perchlorate. Most of the experiments were performed using G. F. Smith Reagent Grade "Perchloratoceric Acid" in perchloric acid. Some were performed, however, using a solution prepared by electrolytic oxidation of a cerium(III) perchlorate solution. This cerium(III) perchlorate was prepared by conversion of cerium(III) chloride which had been recrystallized from concentrated hydrochloric acid. The spectra of solutions prepared using this cerium(IV) perchlorate were the same as those of similar concentrations using the other source of cerium(IV) perchlorate. Stock solutions of perchloric acid were analyzed by conventional volumetric procedures. The primary standard upon which the concentrations were based was mercuric oxide. The stock solutions of sodium perchlorate were analyzed by evaporating measured volumes of the solution, drying the solid salt at 120° and weighing.[14] The cerium(IV) concentration in each solution used in a spectral study was determined at the time of the spectrum determination by titration with a solution of iron(II) sulfate in sulfuric acid. The iron(II) sulfate solution was standardized at the same time by a similar titration with a standard cerium(IV) solution in sulfuric acid. Ferrous orthophenanthroline was used as the indicator. The acidity of those solutions which were relatively concentrated in perchloric acid was reduced by adding sodium sulfate before the cerium(IV) determinations were carried out.

Spectrophotometric Studies.—The spectra were determined using a Model DU Beckman spectrophotometer. Measurements were made using both one cm. and ten cm. cells. Light path lengths of 0.302 and 0.102 cm. were also realized by using quartz inserts for the one cm. cells; these were obtained from the Pyrocell Manufacturing Co. In the case of the ten cm. cells, a special thermostatic compartment, which was constructed in the shop of this Chemistry Department, was used. The temperature of the one cm. cells was controlled by use of the "Thermospacer" arrangement manufactured by the National Technical Laboratories. Temperature control was within several tenths of a degree of 25.4°. The blank cell in each case contained a solution of perchloric acid and sodium perchlorate. The optical density of each solution was determined at least twice.

Discussion

Cerium(IV), in forming polymeric species in acidic solution, is not exhibiting a unique behavior. Studies on bismuth(III) by Graner and Sillen,[15] on zirconium(IV) by Connick and Reas,[8] and on uranium(VI) by Sutton,[16] have demonstrated the existence of polymeric species of these metal ions in acidic solution. It is generally believed that the binding of the metal ions in these polymeric species is by oxide or hydroxide bridging. The species existing in cerium(IV) solutions are probably similarly constituted. A comparison of the fraction of the metal ion present in monomeric forms in the case of cerium(IV) and zirconium(IV)[8] indicates a greater tendency on the part of zirconium(IV) toward polymerization. This is particularly interesting since existing data indicate that the equilibrium quotient $(\mathrm{MOH}^{+++})(\mathrm{H}^{+})/(\mathrm{M}^{+4})$ is greater in the case of cerium(IV) than in the case of zirconium (IV).[8] It would appear that the factors which determine the tendency for simple hydrolysis are not identical with those which determine the tendency for polymer formation.

The value of the dimerization equilibrium quotient calculated by Heidt and Smith[4] ($k_2 = 50$ at 1.00 molar perchloric acid) is in agreement with those derived from this research This is support for the mechanism of the photochemical oxidation of water by cerium(IV) proposed by these authors as opposed to that proposed by Evans and Uri.[5]

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[14] Walton, "Inorganic Preparations," Prentice-Hall, Inc., New York, N. Y., 1948, p. 73.

[15] F. Graner and L. G. Sillen, *Acta Chem. Scand.*, 1, 631 (1947).

[16] J. Sutton, *J. Chem. Soc.*, suppl. issue No. 2, S 275 (1949).

MADISON, WISCONSIN RECEIVED JULY 23, 1951

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Catalytic Hydrogenation of the Oxides of Carbon to Higher Hydrocarbons[1]

BY ROBERT N. R. MULFORD AND W. WALKER RUSSELL

The effects of carbonate, chloride, sulfate, thiosulfate and sulfide, added singly as potassium or sodium salts prior to catalyst precipitation, upon ceria promoted, copper containing cobalt catalysts in the syntheses of hydrocarbons from the oxides of carbon at atmospheric pressure have been studied. All of these cobalt catalysts produced oil when the initial carbon dioxide-hydrogen mixture was first passed over a supported iron, water gas catalyst, but with no water gas catalyst present only the cobalt catalysts containing potassium carbonate or sulfate produced oil. In general the effects of certain of these catalyst additives were to alter the distribution between liquid and gaseous synthesis products, to increase oil yields, and to shift the temperature range of maximum oil yields. The effects of the additives are attributed to selective activation and/or beneficial poisoning of the cobalt catalysts.

Introduction

The problem of producing higher hydrocarbons from the oxides of carbon may be considered one of controlled or partial reduction followed by polymerization. The complete reduction of either oxide produces methane when polymerization does not intrude. More specifically the problem becomes that of stopping the reduction process short of methane when polymerizable intermediates are present. A previous study[2] indicated that by the proper selective activation and/or poisoning of cobalt catalysts some control over the reduction and polymerization processes occurring on the catalyst surface could be obtained. In the present work the effects of certain additives upon the catalytic behavior of cobalt in producing oil from the reduction of the oxides of carbon have been studied. These additives included substances containing sulfur or chlorine which are usually considered

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[1] This paper is based on a portion of a thesis presented by R. N. R. Mulford in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, October 1950.

[2] W. W. Russell and G. H. Miller, THIS JOURNAL, 72, 2446 (1950).

undesirable poisons for metal hydrogenation catalysts. The study has been confined to the effects of such additives upon the distribution between gaseous products and liquid hydrocarbons, and related phenomena. No attempts have been made in this work to analyze the oils formed so that no information as to the effects of catalyst composition upon the distribution in the liquid phase is available.

Supported Fischer–Tropsch cobalt catalysts have been beneficially poisoned by others[3] who placed limited amounts of hydrogen sulfide in the feed gas. Because poisoning by such a technique can be very non-selective,[4] it was sought in the present work to disperse the additive thoroughly in the carbonate precipitate and then to produce the actual catalyst by later reduction so that the additive might be selectively allocated to surface sites which adsorbed most strongly.

Experimental

Apparatus.—The reactant gases, carbon dioxide and hydrogen, of the same grade, and metered and purified as described elsewhere,[2] after thorough mixing could be passed through either the hydrocarbon catalyst alone, or first through the water gas catalyst and then through the hydrocarbon catalyst. The gases were in an all glass system after metering and until they had passed through one or both catalysts in Runs 34, 35 and 36, but in the later runs in which a Vycor water gas catalyst chamber was used, short heavy rubber connections attached the latter catalyst chamber to the hydrocarbon catalyst tube.

The hydrocarbon catalyst chamber consisted of a vertical Pyrex tube of 22 mm. i.d. having an axial thermocouple well, placed in an electrically heated furnace and controlled by a potentiometric controller-recorder all as earlier described.[2] The water gas catalysts during Runs 34 through 36 were placed in tubes similar to those used for the hydrocarbon catalysts. After Run 36 the water gas catalysts were placed in Vycor tubes having no thermocouple well. The catalyst was supported upon a perforated steel disc in the Vycor tube which was attached to the system with a graded seal. The water gas catalyst furnace which could be operated at temperatures up to 800° was also automatically controlled. The products from the water gas catalyst first passed through two traps in series. The first trap was iced to remove most of the water, the remainder being removed in the second trap which was cooled in a Dry Ice–acetone mixture. The products from the hydrocarbon catalyst likewise passed first through two traps in series but both were cooled with the Dry Ice mixture. In a graduated arm of the first trap the volume of oily products synthesized during a run could be measured as already described.[2] The gaseous, uncondensed products passed to a wet test meter, except the portions periodically withdrawn for gas analysis. Such withdrawals which could be made simultaneously and separately from the water gas catalyst and from the hydrocarbon catalyst, were done slowly in order not to disturb synthesis conditions and to secure representative samples. Mercury was used for the collection and manipulation of the gases which could be analyzed for carbon dioxide, unsaturated hydrocarbons, hydrogen, carbon monoxide and methane. The term methane as used in this work includes also small amounts of other gaseous saturated hydrocarbons.

Preparation of Water Gas Catalysts.—These catalysts were iron supported on kieselguhr and promoted with ceria, and in two cases also with potassium carbonate. Chemicals of analytical reagent grade were used, the cerous nitrate being the purified grade from G. Frederick Smith Co. Calculated amounts of $Fe(NO_3)_3 \cdot 9H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ were dissolved in water to make a solution about 0.23 *M* in ferric nitrate. The kieselguhr was then added and the mixture mechanically, rapidly stirred at room temperature while a slight excess of 15 *N* ammonium hydroxide was slowly added. The precipitate was washed by decantation and filtration with boiling water until the diphenylamine test for nitrate was negative, and further until the precipitate started to peptize. If potassium carbonate were to be added, the desired amount was dissolved in sufficient water to make a slurry with the filter cake. After evaporation on a steam-bath to a paste, the precipitate either with or without the carbonate was extruded onto a glass plate with a glass syringe. After drying at 105° for two hours the extruded material was cut to form pellets about 5 mm. long and 3 mm. thick which after sieving to remove dust were placed in the catalyst tube. All water gas catalysts were reduced in pure hydrogen flowing at six liters per hour at temperatures up to the maximum at which they were to be used. The water gas catalysts were designated by prefixing a W before the number of the run in which they were used. All water gas catalysts were prepared separately except W34 and W35 which were portions of the same batch. The compositions of the various water gas catalysts are given in Table I.

Preparation of Hydrocarbon Catalysts.—These catalysts were prepared by dissolving the calculated amounts of analytical reagent grade $Co(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and also $Ce(NO_3)_3 \cdot 6H_2O$ (the latter being Mallinckrodt No. 4380) in boiling water to produce a cobalt ion concentration of 1.55 *M*. The mixed metal nitrates were precipitated by adding slowly with vigorous stirring a 10% excess of boiling 3.55 *M* potassium carbonate solution. Washing with boiling water was carried out as for the water gas catalysts. After the washings, the precipitate filter cake was broken up into small pieces and dried at 110°. All catalysts were dried between 60 and 70 hours, except Catalysts 39 and 40, which were dried one week. Varying the drying period within these limits appeared to make no difference. The dried catalyst lumps were powdered, bottled and then analyzed for metallic content. On the basis of the analysis the desired amount of additive was calculated. The additives, which were used singly, were the following analytical reagent grade salts: K_2CO_3, K_2SO_4, KCl, $K_2S_2O_3 \cdot xH_2O$, $Na_2S \cdot 9H_2O$. The additive was dissolved in enough water so that when thoroughly mixed with the dry powdered carbonate precipitate a thin paste was formed. After evaporation the precipitate was extruded similarly to the water gas catalysts and dried for a few hours at 105°. It was then cut into pellets about 3 × 5 mm. with a sharpened stainless steel spatula. In the cases of the catalysts containing thiosulfate or sulfide the evaporation and drying steps were carried out in an atmosphere of carbon dioxide in order to prevent sulfate formation. The hydrocarbon catalysts were reduced in a flow of 2 l. of carbon dioxide and 6 l. of hydrogen per hour. The catalyst temperature was raised slowly to 150°, held there for 18 hours, then raised to 175° over a 2-hour period preceding the first test at 175°. On Catalysts 37 to 40 inclusive a series of runs employing just carbon dioxide and hydrogen in the temperature range of 175 to 230° was first made. Following these runs, the water gas catalyst was placed in series, and runs with the carbon monoxide enriched gas were made in the temperature range of 175 to 250°. With Catalysts 35 and 36 the initial carbon dioxide hydrogen runs covered the temperature region of 175 to 195°, and the succeeding runs with carbon monoxide the temperature region of 180 to 210°, then more runs were made with the initial feed gas mixture at 210° and above. On Catalyst 34 after initial runs with carbon dioxide and hydrogen in the temperature region of 175 to 210°, runs with and without carbon monoxide in the feed gas were repeatedly alternated at 210°, and later at 220°.

Method of Catalyst Evaluation.—The volume and composition were known from meter readings for the carbon dioxide–hydrogen mixture entering the water gas catalyst also entering the hydrocarbon catalyst when used alone. The exit gases from each of these catalysts first passed through Dry Ice cooled traps, which in the case of the water gas catalysts removed water from the gases before they passed over the hydrocarbon catalyst. In the case of the hydrocarbon catalysts the oil yield consisted of liquid hydrocarbons condensed by Dry Ice and not vaporized when measured at room temperature. Tests showed that any hydrocarbons so vaporized were insignificant in amount and had average carbon numbers not much larger than the gaseous mixture which passed through the traps uncondensed, *e.g.*, 1.3 to 1.6 *vs.* 1.1 for the latter mixture. The composition of the dried gas passing from the water gas cata-

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(3) E. F. G. Herrington and L. A. Woodward, *Trans. Faraday Soc.*, **35**, 958 (1939).

(4) W. W. Russell and L. G. Ghering, THIS JOURNAL, **57**, 2544 (1935).

TABLE I

COMPOSITION AND CHARACTERISTICS OF WATER GAS CATALYSTS[a] AND HYDROCARBON CATALYSTS[b] 12 HOUR PERIOD OF MAXIMUM OIL YIELD[c]

	Water gas catalysts						Hydrocarbon catalysts										
							Additive					% CO_2 reacting[e]			Ml. oil per cu. m. of		
No.	% wt. K_2CO_3	Temp., °C.	% CO_2 converted to CO	% CO_2 reacting, converted to CO	W.G. cat. in series	Wt. unreduced cat. g.	Substance	M.mole substance/ mole Co.	% wt.	Temp., °C.	Ml. of oil	Total converted	Total converted[f] to CH_4	Gas %[g] contraction	Total CO_2 Passed	Total CO_2 Converted	CO Passed[h]
34	0	450			No	50.0	K_2CO_3	8.6	2.0	220	0.60	40.4	32.8	52	22.6	55.8	
					Yes					210	3.34	40.0	9.2		125.5	313.9	
35	0	450	(25.5)	(51.0)	No	49.3	K_2SO_4	8.6	2.5	235	0.19	36.0	26.8	46	7.1	19.8	
			26.5	65.4	Yes[d]					180	2.33	54.0	21.0	37	109.4	202.6	413.4
36	2.5	450	(32.2)	(83.3)	No	46.9	K_2CO_3	8.6	2.0	235	0.22	44.8	39.2	53	8.3	18.5	
			31.0	67.4	Yes[d]					205	3.14	38.5	16.5	27	147.4	300.8	437.9
37	2.5	750	(38.4)	(85.7)	No	45.3	KCl	8.6	1.1	250	0.00	32.4	32.4	51	0.0	0.0	
			27.6	71.1	Yes					240	2.00	34.8	10.8	19	75.2	268.5	273.1
38	0	750	(32.4)	(88.0)	No	41.2	None			230	0.00	44.4	41.6	63	0.0	0.0	
			23.2	89.2	Yes					200	1.90	35.2		33	71.4	202.9	251.7
39	0	600	(42.7)	(77.5)	No	46.4	Na_2S	8.6	1.1	230	0.00	48.8	49.2	63	0.0	0.0	
			39.6	71.2	Yes					220	3.60	48.0	25.2	42	135.3	281.9	331.8
40	0	600	(43.2)	(93.1)	No	46.5	$K_2S_2O_3$	8.6	2.8	230	0.00	47.6	44.0	63	0.0	0.0	
			40.8	82.9	Yes					235	3.15	50.8	20.4	38	118.4	204.5	284.4

[a] All water gas catalysts were prepared from 100 parts of iron, 1 part of ceria and 100 parts of kieselguhr, with percentages of potassium carbonate based on iron. Water gas catalysts W38, W39 and W40 were supported on Johns–Manville Filter-Cel, and the other water gas catalysts were supported on Johns–Manville Hyflo Super-Cel, a flux-calcined kieselguhr. The unreduced water gas catalysts each weighed 50.0 g., except W36 which weighed 65 g.

[b] All hydrocarbon catalysts were prepared from 100 parts of cobalt, 5 parts of copper, 1 part of ceria, with the percentages of additive based on cobalt.

[c] Synthesis gas ratio was 2.2 l. CO_2 to 4.4 l. H_2 per hour, unless otherwise noted.

[d] Synthesis gas ratio was 1.75 l. CO_2 to 5.25 l. H_2 per hour.

[e] By total carbon dioxide converted is meant the carbon dioxide converted on the water gas catalyst plus that reacting over the hydrocarbon catalyst.

[f] This column also includes any carbon monoxide which reacted to form methane. This is evidenced when this column plus % CO_2 converted to CO is greater than total % of CO_2 converted.

[g] The gas contraction is that which occurred over the hydrocarbon catalyst only.

[h] Ml. of oil per cu. m. of CO converted was the same as for CO passed, except for Catalyst 37 for which the former figure was 325.1.

lyst to the hydrocarbon catalyst could be readily obtained by analysis but the determination of the rate of exit gas flow from the water gas catalyst required that the hydrocarbon catalyst be temporarily dead ended. Oil samples were usually collected over periods of 12 hours. The total number of synthesis hours per hydrocarbon catalyst varied from three hundred to over five hundred. All gas volumes are at S.T.P.

Results and Discussion

Water Gas Catalysts.—The water gas catalysts were iron supported on kieselguhr, promoted with 1% of ceria, and in two cases (W36, W37) also with potassium carbonate. The abilities of these catalysts to produce carbon monoxide from mixtures of carbon dioxide and hydrogen containing one- or twofold excesses of hydrogen are shown in Table I. In the table the figures in parentheses in columns 4 and 5 give average figures while the other figures in these columns refer to that particular run which gave a maximum oil yield. The catalysts operated at 450° became choked with carbon at the entering end after 139 and 121 hours, respectively, for Catalysts W34 and W35. Catalyst W36 which contained an axial glass wool wick was still not plugged after 236 hours of operation. Such local carbon deposition, however, caused little or no observable loss in catalyst activity. The effect of carbonate in the catalyst at 450° was increased activity and efficiency in forming carbon monoxide with less methane production. Alkali appeared to distil from the catalyst during use at 750°, but at this temperature no carbon appeared whether or not potassium carbonate was added to the catalyst. After use at 750° the iron catalysts were nearly white in color, and the steady loss in activity which catalysts W37 and W38 suffered during more than 400 hours of use was further evidence of sintering. The fact that these catalysts showed no appreciable loss in activity during their first 40 hours gives evidence for the time factor in the sintering. Catalyst W39 which was employed exclusively at 600° maintained its activity well throughout a 300-hour run and when removed was free from carbon and possessed a dark gray color. Catalyst W40 was used at 600° except for 40 hours at 750° at the end of the run. At 600° the dried exit gases from Catalyst W40 averaged 19.3% carbon monoxide and this figure rose to 23% while at 750°, but fell to 10.5% when the temperature was reduced to 600°. The nearly white color of this catalyst when removed was further evidence of sintering. Thus, although sintering of the kieselguhr supported iron catalysts appeared not to be serious below 600°, it became so at 750°, and 600° is probably near the upper limit for catalyst stability. The high temperatures were favorable also for suppressing methane formation. Catalyst W40 operated at 600° gave the best all around performance.

Effect of Carbon Monoxide upon Synthesis.—Catalyst 34, which contained potassium carbonate as an additive, started to yield oil from carbon dioxide and hydrogen first at 205° and reached at 220° a maximum oil yield of 0.60 ml. per 12 hours. To study the effect of first converting to carbon monoxide part of the carbon dioxide in the carbon dioxide hydrogen feed gas, water gas Catalyst W34 operated at 450°, was repeatedly cut in ahead of Catalyst 34. When the water gas catalyst was in series, its exit gases were first dried at Dry Ice temperature inasmuch as tests showed water removal to be desirable because of carbon monoxide lost when water vapor was present, presumably due to some reversal of the water gas equilibrium at the lower temperature of the hydrocarbon catalyst. The effect of prior conversion of carbon dioxide to carbon monoxide was always to increase sharply the oil yield, actually from 5- to 35-fold on Catalyst 34. The presence of carbon monoxide in the synthesis gas also produced other effects such as increases of up to 11% in the total amount of carbon dioxide reacting over the hydrocarbon and the water gas catalysts when the initial synthesis gas contained carbon dioxide to hydrogen in the ratio of 1.75 to 5.25, but decreases of up to 32% in the total amounts of carbon dioxide so reacting when the synthesis gas ratio was 2.2 to 4.4. However, the presence of carbon monoxide in the synthesis gas always sharply decreased the total amount of methane formed even though the occurrence of the water gas reaction increased the ratio of hydrogen to carbon dioxide in the synthesis gas. These decreases in methane formation were as large as 72%, but averaged about 55%.

Effect of Catalyst Additives.—Catalysts 34 to 40 inclusive were prepared in order to study the effects of certain additives. In order to disperse the additive uniformly throughout the catalyst mass, the dissolved additive was intimately mixed with the precipitated catalyst before reduction. The behavior of this group of catalysts during the 12 hours when each catalyst produced a maximum of oil is shown in Table I. The ability (solid lines) and efficiency (dotted lines) of these catalysts, except the first, in producing oil from carbon monoxide in successive runs are shown in Fig. 1 plotted against temperature. The jaggedness of these curves indicates an important characteristic of these hydrocarbon catalysts, namely, that of self poisoning during, and as a result of, synthesis occurring on their surfaces. When such self poisoning had occurred to a sufficient extent, raising the catalyst temperature increased the oil yield, but if not to a sufficient extent the oil yield fell. In the latter case methane formation increased but also the rate of self poisoning and eventually oil formation again increased. Similar self poisoning was also found in the hydrogenation of carbon dioxide to oil.[2]

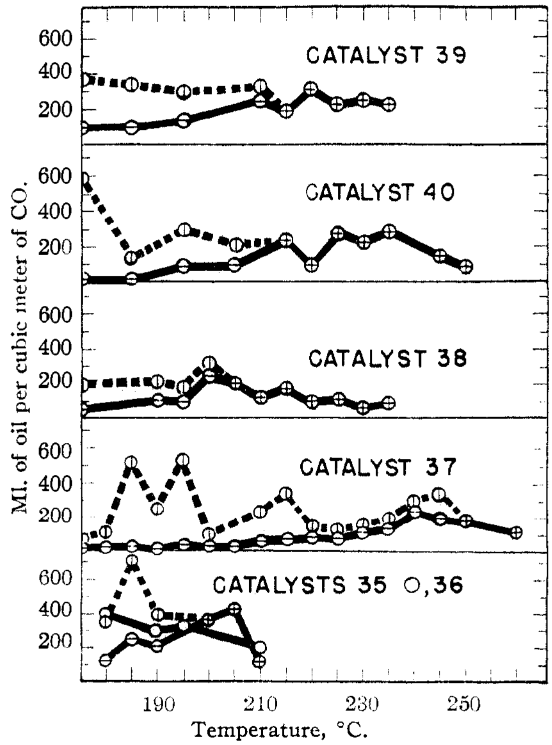

Fig. 1.—Effects of additives upon oil yields, based upon carbon monoxide passed (solid curves) and upon carbon monoxide reacted (dotted curves). Additive in catalyst ($Co:Cu:CeO_2$, 100:5:1): catalyst 35, K_2SO_4; catalyst 36, K_2CO_3; catalyst 37, KCl; catalyst 38, no additive; catalyst 39, Na_2S; catalyst 40, $K_2S_2O_3$.

All of the hydrocarbon catalysts were composed of unsupported cobalt, containing a small amount of copper and of ceria. In each, except Catalyst 38, an equal molar amount of a single additive was incorporated. Catalyst 38 which contained no additive may be considered a basis for comparison. First comparing catalyst oil yields based on the volume of carbon monoxide passed, *i.e.*, solid curves in Fig. 1 it is seen that Catalyst 38 produced a maximum oil yield of 252 ml. at 200° and somewhat less at 205°. Such a temperature region has in general proved to be close to the optimum for cobalt Fischer–Tropsch catalysts. By comparing the curves for Catalysts 36 and 38 it is seen that although the optimum temperature region remained unchanged, the oil yield increased over 70% in the presence of the additive potassium carbonate. The solid curves in Fig. 1 for the catalysts containing the other additives, except potassium sulfate, have broader maxima which occur at higher temperatures than for Catalysts 35, 36 and 38. The potassium chloride in Catalyst 37 produced a sharp poisoning effect below 230° at which temperature the oil yield first passed 100 ml. At 240°, however, Catalyst 37 yielded somewhat more oil than did Catalyst 38 at 200°. The solid curves for Catalysts 39 and 40 are roughly similar and show a temperature region for optimum oil yields intermediate to that of Catalyst 37 and Catalysts 36 and 38. Unlike the two other catalysts incorporating sulfur containing additives catalyst 35, which contained potassium sulfate, gave its maximum oil yield, which was about 64% greater than that for Catalyst 38, at the low temperature of 180°. At higher temperatures the oil yields from Catalyst 35 became progressively smaller. Catalysts 39 and 40, containing the sulfur additives sodium sulfide and potassium thiosulfate, respectively, gave maximum oil yields between 220 and 235°. These oil yields were, respectively, nearly 31 and 13% greater than the maximum yield for Catalyst 38. Catalyst 39 actually yielded the most oil per 12 hours of any catalyst studied, but appears less favorable because of the smaller amount of carbon monoxide present in the synthesis gas for example during tests on Catalyst 36.

In Fig. 1 in the dotted curves the foregoing catalysts also are compared on the basis of their efficiency in converting to oil the carbon monoxide which reacted at their surfaces. When all of the entering carbon monoxide reacted the dotted and solid curves coincide. Thus during the runs with carbon monoxide enriched synthesis gas, no carbon monoxide ever appeared in the exit gases from Catalyst 35; but was present in the exit gases from the other catalysts at temperatures below those in the vicinity of maximum oil yields, except for Catalyst 37. This catalyst, containing potassium chloride, was able to hydrogenate carbon monoxide quantitatively only above 250°.

In general the efficiency with which a catalyst converted carbon monoxide to oil decreased with increasing temperature, although Catalysts 36 and 37 showed initially sharp increases in efficiency between 180 and 195°. At temperatures between 170 and 180° where oil synthesis started, the catalysts showed a wide spread in efficiency, Catalyst 38 being about midway between the low value of 63 ml. of oil for Catalyst 37 and the remaining catalysts of which Catalyst 40 gave the largest initial efficiency of 587 ml. Only Catalyst 38 showed maximum efficiency at the temperature of maximum oil yield. Catalyst 36, containing potassium carbonate showed the highest efficiency of any of the catalysts and this at 185° well below the maximum oil yield temperature of 205°. It appears significant that in spite of differences in additives and wide differences in the efficiencies of the individual catalysts, all exhibited their highest efficiencies between 180 and 205°. Therefore, the relatively large oil yields obtained at higher temperatures with the catalysts containing potassium chloride, thiosulfate and sodium sulfide were obtained when the catalyst was not operating at best efficiency. For a comparison of actual efficiencies it may be noted that if all the carbon monoxide in a cubic meter were converted to oil of composition C_7H_{16} and density 0.7, the yield would be about 900 ml. The highest efficiency in converting carbon monoxide to oil would then be about 80% for Catalyst 36 at 185°, and the lowest about 7% for Catalyst 37 at 175°.

Discussion and Conclusions

As in the previous study[2] the initial reactants were solely carbon dioxide and hydrogen but in the present work when the water gas catalyst was in series the effect of carbon monoxide in the synthesis gas could also be ascertained. While with this arrangement the catalyst and operating conditions for the water gas reaction determined the amount of carbon monoxide produced, no new catalyst poisons were so introduced, and some opportunity to study further the water gas reaction with iron catalysts was afforded. Although in the present work considerable amounts of carbon dioxide were always present when carbon monoxide was used, the latter appeared to suppress effectively the reduction of carbon dioxide over the hydrocarbon catalysts. Thus, in the presence of carbon monoxide, the dioxide acted primarily as a diluent which action in the Fischer–Tropsch synthesis has been observed by others.[5] All of the catalysts studied produced oil when preformed carbon monoxide was present in the synthesis gas, but only those catalysts containing potassium carbonate or the less efficient potassium sulfate were able to reduce carbon dioxide to oil. Thus while these ceria promoted, copper containing cobalt catalysts when containing no additive, or when the additive sodium sulfide, potassium thiosulfate or chloride was present, produced large amounts of methane in the reduction of carbon dioxide, no oil was formed. In the hydrogenation of carbon dioxide, carbon monoxide was present in the exit gases from catalysts which synthesized oil, but no carbon monoxide was detected in the exit gases from those catalysts unable to reduce carbon dioxide to oil. Converting a portion of the carbon dioxide to monoxide prior to passage over the hydrocarbon catalyst not only increased oil formation but also sharply decreased methane formation. This phenomenon, which was reversible, was repeatedly observed. In explanation it appears probable that the more strongly adsorbed carbon monoxide actually displaced carbon dioxide from portions of the catalyst surface upon which carbon dioxide could be reduced to methane without carbon monoxide as an intermediate. While upon these portions of the surface, carbon dioxide would not be capable of being reduced to carbon monoxide, once adsorbed thereon from the gas phase, carbon monoxide would be reduced efficiently to oil.

The present work appears to confirm what was indicated in the earlier work,[2] namely, that carbon monoxide is a critical intermediate in the reduction of carbon dioxide to oil, and that methane can be produced by two mechanisms one involving, and one not involving, carbon monoxide as an intermediate.[5] Thus the synthesis of higher hydrocarbons from carbon dioxide involves one more step than the synthesis from the monoxide, namely, the water gas reaction. The production of oil from the hydrogenation of carbon dioxide appears to require that to the cobalt catalyst be added an activator for the water gas reaction and presumably for polymerization, and also a poison for methane formation. This would seem a rather difficult specification to fulfill with a single additive, but potassium carbonate and to lesser extents potassium phosphate[2] and potassium sulfate appear to meet it. The other catalyst additives here studied appear to have acted beneficially only as poisons. Thus in comparison with a ceria promoted, copper-containing cobalt catalyst containing no additive, in the presence of the additives potassium chloride, thiosulfate or sodium sulfide oil yields were increased, and the temperature range for maximum oil yields was displaced upward and broadened. That alkalinity alone in a catalyst additive is insufficient to cause a reduction of carbon dioxide to oil is evident from the different behaviors of the essentially neutral potassium sulfate and the alkaline sodium sulfide as additives. The present work appears to show that the courses of the complex series of reactions occurring on a cobalt catalyst surface during the interaction of hydrogen and the oxides of carbon are strongly influenced by the presence of catalyst additives through a mechanism considered to involve activation and/or selective, beneficial poisoning. In the presence of the additives, the surface of the catalyst was undoubtedly

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(5) H. Pichler, *Brennstoff Chemie*, **24**, 39 (1943).

altered, and probably in such a way as to influence particularly the poisoning that normally occurs during synthesis. By the proper choice of such additives, it appears possible to obtain further information about the nature of the catalysts involved and the mechanisms of the surface reactions occurring, and to modify catalysts so as to improve oil yields, increase catalyst stability, and to extend the range of synthesis temperatures.

PROVIDENCE, RHODE ISLAND RECEIVED AUGUST 20, 1951

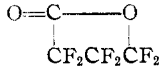
[CONTRIBUTION FROM THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY]

The Properties and Reactions of Perfluorobutyrolactone

BY MURRAY HAUPTSCHEIN, CHARLES S. STOKES AND ARISTID V. GROSSE

Various physical and chemical properties of perfluorobutyrolactone are described. This novel type lactone reacts with water, ethanol, ammonia, hydrogen iodide and ethyl mercaptan to form the perfluorosuccinic acid, ethyl ester, amide, mixed acyl fluoride–acyl iodide and dibasic thiol ester, respectively. The latter derivative is the first member of a new class of compounds to be reported. A general mechanism for these reactions has been elucidated. The method of formation of perfluorobutyrolactone was shown not to be general. Perfluorovalerolactone was not detected in the corresponding reaction of silver perfluoroadipate with iodine, 1,4-diiodoöctafluorobutane being the only organic product isolated. Several infrared spectra are given and discussed.

In a previous communication[1] we had presented evidence which proved that perfluorobutyrolactone was the main product formed by the thermal degradation of silver hexafluoroglutarate with an excess of iodine. We have now actually isolated this perfluorolactone, b.p. 18°, m.p. $-59°$, $d^{-32.4}_{4}$ 1.6646, $d^{-42.2}_{4}$ 1.6889, in a very pure state under rigorously anhydrous conditions. The infrared absorption spectrum (Fig. 1) is relatively simple and demonstrates the absence of any hydrogen in the molecule. The sharp and intense band at 5.34 microns is indubitably due to the lactone carbonyl group. The normal hydrocarbon lactones have a band at 5.5–5.7 microns and there is therefore a shift to shorter wave lengths in the case of the fluorocarbon analogs.



$$\underset{\text{CF}_2\text{CF}_2\text{CF}_2}{\text{O=C——O}}$$

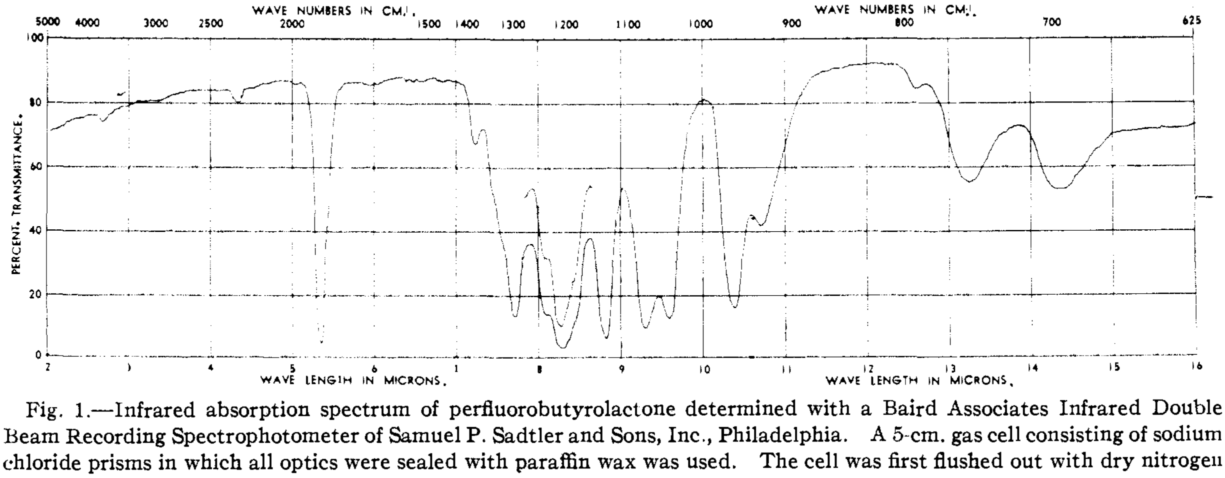
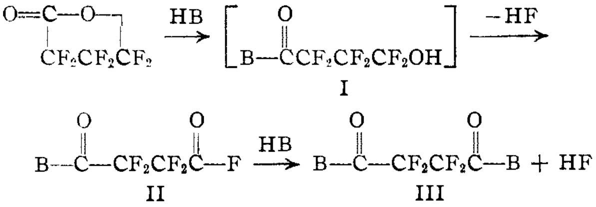


Fig. 1.—Infrared absorption spectrum of perfluorobutyrolactone determined with a Baird Associates Infrared Double Beam Recording Spectrophotometer of Samuel P. Sadtler and Sons, Inc., Philadelphia. A 5-cm. gas cell consisting of sodium chloride prisms in which all optics were sealed with paraffin wax was used. The cell was first flushed out with dry nitrogen gas to exclude moisture, and the anhydrous lactone was distilled into the cell at atmospheric pressure.

It is of interest to mention at this point that the thermal degradation of silver perfluoroadipate with iodine did not yield any perfluorovalerolactone, but proceeded in the "normal" manner to form the corresponding diiodide, $ICF_2CF_2CF_2CF_2I$,[2] b.p. 150°, m.p. $-9°$, d^{27}_{4} 2.4739, d^{0}_{4} 2.5466, $n^{26.2}_{D}$ 1.4273, n^{0}_{D} 1.4401, MR_D found 46.98, AR_F 1.19.

The infrared spectrum of this perfluoro diiodide (Fig. 2) is quite similar to that of 1,3-diiodohexafluoropropane.[1]

The highly reactive perfluorobutyrolactone has been allowed to react with water, ethanol, ammonia, hydrogen iodide and ethyl mercaptan to form products that are accounted for by the following general mechanism.



$$\underset{\text{CF}_2\text{CF}_2\text{CF}_2}{\text{O=C—O—}} \xrightarrow{HB} \underset{\text{I}}{\left[B{-}\overset{O}{\overset{\|}{C}}CF_2CF_2CF_2OH\right]} \xrightarrow{-HF} \underset{\text{II}}{B{-}\overset{O}{\overset{\|}{C}}{-}CF_2CF_2\overset{O}{\overset{\|}{C}}{-}F} \xrightarrow{HB} \underset{\text{III}}{B{-}\overset{O}{\overset{\|}{C}}{-}CF_2CF_2\overset{O}{\overset{\|}{C}}{-}B} + HF$$

When B corresponded to OH, OC_2H_5, NH_2 and SC_2H_5, $HOOC–CF_2CF_2–COOH$, $C_2H_5O–OC–CF_2$-$CF_2COOC_2H_5$, $H_2NOCCF_2CF_2CONH_2$ and C_2H_5S–

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(1) M. Hauptschein and A. V. Grosse, THIS JOURNAL, **73**, 2461 (1951). See also M. Hauptschein, C. S. Stokes and A. V. Grosse, *ibid.*, **74**, 848 (1952).

(2) R. N. Haszeldine, *Nature*, **167**, 139 (1951), found that 1,4-diiodoöctafluorobutane was one of the products formed in the addition polymerization of tetrafluoroethylene and tetrafluorodiiodoethane, but no physical constants were reported.