half the fraction leaving the ether insoluble. This was dried over solid potassium hydroxide and distilled, b.p. 220–230°. It was completely miscible with water, and with dinitro-phenylhydrazine gave the expected derivative of 4-hydroxy-butanal. Quantitative estimation in this way showed the ether sample was about 80–90% pure. The impurities were probably esters since refluxing with 20% alkali gave a product, b.p. 229.5–230.5°, which was 96% pure. *Anal.* Calcd. for $C_9H_{16}O_3$: C, 62.9; H, 9.35. Found: C, 63.0; H, 7.5; purity by dinitrophenylhydrazine, 94.4%.

Later experiments showed that the ether was best isolated by refluxing the crude fraction with alkali and then steam distilling off the ether.

Isolation of 5-Hydroxypentanoic Acid Lactone.—The combined alkaline extracts referred to above were strongly acidified and the upper layer collected and dried over magnesium sulfate. About half of it had b.p. 218–228° and distilled as a colorless mobile liquid which on standing was converted into a wax-like solid, m.p. 45–90°. This solid, unlike the original liquid, was insoluble in water. Alkali titration of the wax in aqueous acetone gave equivalents ranging between 1130 and 1140. Refluxing with excess alkali and back titration gave a figure of 163. On heating, the polymer cracked back to monomer, b.p. 223.5–227°. Traces of mineral acid catalyzed the polymerization process and if these were rigorously excluded, the monomer could be preserved for many weeks. Material b.p. 229–229.5° was identified by analysis and the reactions described below. *Anal.* Calcd. for $C_5H_8O_2$: C, 60.0; H, 8.10. Found: C, 61.00; H, 8.2. *Oxidation of Lactone to Glutaric Acid:* The distilled monomeric material, 15 g., in water, 200 cc., was made alkaline and treated with potassium permanganate, 31.5 g., at 50°. After one hour, the mixture was filtered, concentrated to one third of its bulk and acidified. After evaporation to dryness, the residue was extracted with alcohol giving glutaric acid, 3.5 g., which after crystallization from benzene had m.p. 93–95.5° not depressed by admixture with an authentic specimen. *Conversion of Lactone to 5-Bromo-pentanoic Acid:* The material was refluxed with hydrobromic acid (48%) containing 5% sulfuric acid. The bromo-acid was crystallized from ligroin and had m.p. 40–40.5° (literature, 39–40°). *Conversion to 5-Hydroxypentanamide:* This reaction has already been referred to. The monomeric lactone was dissolved in an equal volume of dry benzene and saturated with ammonia gas. The amide which separated crystallized from ethyl acetate in fine needles, m.p. 107–107.5°, mixed m.p. with an authentic specimen (see below) was 107.5–108°. *Anal.* Calcd. for

$C_5H_{11}O_2N$: C, 51.3; H, 9.5; N, 12.0. Found: C, 51.7; H, 9.3; N, 11.4.

IV. Preparation of Authentic Lactone.[20]—5-Hydroxypentanal, 98 g., containing cobalt acetate, 0.4 g., was treated with a stream of air at 81–90° for 48 hours. The total volume of air passed was 2400 liters. Distillation gave 5-hydroxypentanoic acid lactone, 5 g., b.p. 228–230°. It was converted into the amide m.p. 108–109° for mixed melting point as described above.

The lactone polymer frequently separated from the high boiling fraction from 20 and 44 nickel catalysts on standing particularly when the conversion was high and little tetrahydrofurfuryl alcohol remained.

V. Behavior of Dihydrofuran Over 44 Nickel Catalyst (a) With Hydrogen.—Dihydrofuran, 35 g., was passed over the catalyst at 230° during one hour together with 22.5 liters of hydrogen. The product consisted of propane, 6 g., dihydrofuran, 0.7 g., tetrahydrofuran, 9.8 g.; there was no detectable furan or propylene.

(b) With Nitrogen.—Reaction (a) was repeated but using nitrogen instead of hydrogen and the products were propylene, 3 g., furan, 3.5 g. (identified as maleic anhydride adduct), tetrahydrofuran, 4.8 g., and a little high boiling material.

VI. Preparation of Authentic Tetrahydrofuryl Tetrahydrofurfuryl Ether.—Dihydrofuran, 75 g., was added slowly to tetrahydrofurfuryl alcohol, 87 g., containing one drop of concentrated hydrochloric acid. Heat was evolved. After one hour the mixture was shaken with sodium hydroxide solution, dried over solid potassium hydroxide and distilled. The ether had b.p. 230–232°, 129 g., 88.5% yield. *Anal.* Calcd. for $C_9H_{16}O_3$: C, 62.85; H, 9.35. Found: C, 62.9; H, 7.5. There was 6 g. of high boiling acetal product not identified. The purity by dinitrophenylhydrazine was 100.0%. The ether was completely miscible with water but readily salted out.

VII. Conversion of Lactone to Valeric Acid Over 44 Nickel Catalyst.—The pure lactone, 50 g., was passed over the catalyst at 230° with 22.5 liters of hydrogen during one hour. The product, 44.9 g., consisted of n-valeric acid, 13.1 g., identified as anilide, m.p. 61–61.5°, mixed m.p. 62–63°, together with unchanged lactone, 21.9 g., identified as amide, m.p. 107–108.5°.

(20) J. G. M. Bremner, D. G. Jones and A. W. C. Taylor (to Imperial Chemical Inds.), U. S. Patent 2,429,799 (1947) [C. A., 42, 923 (1948)].

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Reactions of Furan Compounds. XIII. Behavior of Tetrahydrofurfuryl Alcohol Vapor Over Cobalt–Copper Catalysts

BY ERIC P. GOODINGS AND CHRISTOPHER L. WILSON

Tetrahydrofurfuryl alcohol has been passed over granulated sintered metal powder catalysts containing 20, 50 and 80 cobalt–copper and pure cobalt at temperatures between 190 and 340°. The main product is a mixture of 2,3-di- and tetrahydrofuran in 27, 34, 37 and 36% yield, respectively. There was much decomposition into water and gaseous products particularly with high cobalt content. In addition to the hydrogenated furans, the following substances have been shown to be present in the products and in many cases they have been estimated: propane, propene, butene (probably 2-), furan, dihydropyran, tetrahydropyran, butanal, 1-butanol, 2-pentanone, cyclopentanone, butyric acid, pentanoic acid, 5-hydroxypentanoic acid lactone, tetrahydrofurfuryl pentanoate and tetrahydrofurfuryl tetrahydrofuryl ether. The pyran derivatives and the derived compounds, cyclopentanone and butene, were favored by high temperature and high copper content. Hydroxypentanoic acid lactone and the derived pentanoic acid and ester seemed to be favored by high copper content of catalyst. The origin of the various by-products has been discussed. The behavior of cobalt–copper catalysts has been compared and contrasted with that of nickel–copper mixtures and an explanation attempted making use of existing knowledge of the electronic structure of the mixed metal systems.

The main interest in cobalt–copper catalysts lies in their value in the Fischer–Tropsch synthesis of hydrocarbons from carbon monoxide and hydrogen at moderate pressures. Pure cobalt is poor in this reaction but the addition of 2% copper greatly increases activity.[1] This is considered due, in

(1) F. Fischer and H. Tropsch, *Brennstoff-Chem.*, 7, 97 (1926); *Ber.*, 59B, 830, 832 (1926); F. Fischer, *Brennstoff-Chem.*, 16, 1 (1935).

part, to the lower temperature sufficing for reduction of the mixed oxides. Since the elimination of the side chain of tetrahydrofurfuryl alcohol as carbon monoxide and hydrogen is, in some ways, the reverse of the Fischer–Tropsch synthesis, it appeared of interest to try cobalt–copper catalysts and to compare their behavior with analogous nickel mixtures. Earlier experiments showed that pure

cobalt supported on pumice was ineffective for the side chain elimination[2] but a mixture of 44 cobalt–copper deposited on kieselguhr has now been shown to possess high activity although reaction was unfortunately accompanied by extensive decomposition and the formation of hydrocarbon fragments and water even at 240°. The product contained only 18% tetrahydrofuran and 6% 2,3-dihydrofuran. The catalyst deteriorated very rapidly.

Better results have been obtained using sintered metal powder catalysts containing 100, 80, 50 and 20% cobalt, the balance being copper, although on the whole the behavior of these catalysts was more erratic than with analogous nickel–copper mixtures.[3] Activity was more rapidly lost particularly with high cobalt content even using much hydrogen as carrier gas and the reactions were characterized by the formation of large amounts of low-boiling hydrocarbon fragments by C–C bond fission. This deep-seated decomposition was evidenced by the luminosity of the flame of burning gases issuing from the catalyst chamber after passage through a trap cooled to −78°. The lowest temperature at which luminosity was observed fell as cobalt content of the freshly activated catalyst rose, as follows: 270°, 20%; 240, 50; 230, 80 and 190, 100. Cobalt is known to be less active than nickel in dehydrogenation but more active in C–C bond fission.[4]

With each catalyst, the chief product was tetrahydrofuran containing 2,3-dihydrofuran. As with the nickel catalysts,[3] consumption of alcohol increased with temperature but the trend was confused by rapid catalyst deterioration especially at high temperature. For example with 50 cobalt in consecutive experiments each involving one mole alcohol and 48 liters of hydrogen in two hours (standard conditions in this paper) at different temperatures consumption was: 0%, 200°; 5, 270; 62, 290; 82, 300; 88, 320; 75, 350. A freshly activated catalyst was especially destructive particularly with high cobalt content. For example, with pure cobalt, the first run at 190° gave only 2% hydrogenated furan mixture and much gaseous hydrocarbon product. Activity dropped rapidly and for the third mole, the temperature had to be raised to 250° to maintain practicable consumption. At this temperature, the yield of furans rose to 36% and remained reasonably steady during the passage of 5 mole alcohol, consumption falling the whole while from 80 to 50%. Owing to catalyst deterioration, it was not possible to determine accurately the temperature for optimum yield as was done for nickel–copper[3] but there were indications that the same type of behavior obtained for the cobalt catalysts. The best yields of hydrogenated furans obtained with each catalyst and the temperature of operation were as follows: 20% cobalt, 260°, 27%; 50, 275, 34; 80, 280, 37 and 100, 250, 36. The highest yield (37%) is much lower than that (85%) for the best nickel–copper catalyst. There was no indication of a favored cobalt–copper mixture for tetrahydrofuran formation analogous to 44 nickel–copper.[3]

The effect of changing carrier gas from hydrogen to nitrogen was studied with 80 cobalt at 280°. This switch lowered consumption from 41 to 30% but raised the yield of hydrogenated furans from 37 to 46%. The dihydrofuran content in these two cases was 20 and 27%, respectively. It will be recalled[3] that replacement of hydrogen by nitrogen with 80 nickel–copper caused approximately a 10% rise in consumption with but little effect on yield. Deterioration of the cobalt-containing catalyst was very rapid especially with nitrogen carrier gas and these experiments were not pursued further.

In the products from these cobalt catalysts each and every by-product that has previously been described in this series of papers was identified except 4-pentenal and 4-pentenol obtained using iron–copper catalysts.[5] The following table gives the amounts of some of the components of the low-boiling material from different cobalt catalysts.

MINOR COMPONENTS (WT. %) OF DRY FRACTION B. P. BELOW 160°

Cobalt content	20	50	80	100
Operating temperature	260	275	280	250
Butanal	0.5	3.0	11.0	...
2-Pentanone	1.0	2.3	7.0	...
Cyclopentanone	2.0	4.5	13.0	...
1-Butanol	1.0	4.3	10.0	10.0
Di- and tetrahydropyran	15.0	1.5	0.0	0.0
Furan	...	1.3	1.0	2.5
2,3-Dihydrofuran	7.5	3.8	15.0	7.3

Comparing the table with the analogous one for nickel–copper catalysts[3] shows that most of the by-products were formed in greater quantity with cobalt-containing catalysts particularly with high cobalt content. The most interesting feature though is the presence of di- and tetrahydropyran, isolated before only from iron-copper catalyst,[5] and the large amount of cyclopentanone. The cyclic ketone is known to be formed by catalytic rearrangement of dihydropyran.[6] It is surprising that dehydration to dihydropyran is so extensive and since the catalyst contained no dehydrating oxides although cobalt oxide itself is not easily reduced,[4] it must be concluded that dehydration is possible over the metals themselves. More dihydropyran was formed than is apparent from the table since all the catalysts gave much butene, mostly 2-butene, in the volatile products. This is known[6] to be a fission product of dihydropyran but it is absent entirely from the products from nickel–copper catalysts confirming the absence of appreciable dihydropyran in this case. The only evidence for dihydropyran with nickel catalysts was the presence of a small amount of cyclopentanone. Dihydropyran formation over cobalt catalysts was favored by high temperatures.

2,3-Dihydrofuran was present in the product from each catalyst. The amount varied considerably and tended to increase as activity of catalyst fell just as with nickel. It was formed in largest amount with 80 cobalt and rose from 9.0

(2) C. L. Wilson, J. Chem. Soc., 52 (1945).

(3) Part XII, THIS JOURNAL, 73, 4794 (1951).

(4) A. Juliard, Bull. soc. chim. Belg., 46, 549 (1937).

(5) Part XV, THIS JOURNAL, 73, 4803 (1951).

(6) C. L. Wilson, ibid., 70, 1311 (1948).

to 13.7% yield as the catalyst deteriorated. With nitrogen carrier gas dihydrofuran rose to 26.8% yield but the catalyst very rapidly lost its activity. The formation of a large amount of 2-pentanone finally discounts the earlier suggestion[2,3] that it arises from furfuryl alcohol. The only alternative feasible at the present time is ring cleavage of methylenetetrahydrofuran, the normal dehydration product.[5]

The high-boiling part of the product contained 5-hydroxypentanoic acid lactone, pentanoic acid and its tetrahydrofurfuryl ester. These substances have all been isolated before.[3] The quantities were greater than from nickel–copper catalysts and the yield of lactone and ester attained 2 and 5%, respectively, with 50 cobalt catalyst. The pentanoic acid isolated after hydrolysis of the esters contained about 10% butyric acid which could be separated by distillation. This acid has not before been isolated from catalytic experiments with tetrahydrofurfuryl alcohol. The product also contained about 1% tetrahydrofuryl tetrahydrofurfuryl ether. A low cobalt-content catalyst gave more esters but less ether.

As a binary metallic system, cobalt and copper do not form a complete series of substitutional alloys as do nickel and copper but between 10 and 95.5% copper two phases exist. Since both metals crystallize in the face-centered cubic system and have very nearly the same lattice dimensions the differences between the two phases must be related to the only factor which can still change, the distribution of electron levels in the 3d- and 4s-bands. In this they resemble iron and copper. Cobalt contains the equivalent of 1.7 unpaired electrons compared with nickel 0.6[7] and on adding copper the empty 3d-levels of cobalt should be progressively filled. Calculations are unavailable to show where this process would have been complete if cobalt and copper had formed a complete series of substitutional alloys, but it almost certainly would have corresponded with greatly above 60% copper.[7] At such a point a certain catalytic inactivity in ring fission could have been expected[3] but since two phases exist until copper rises to 95.5% the activity below this composition should relate simply to a mixture of two metal substrates with 10 and 95.5% copper, respectively. Any break in activity would occur, therefore, at 95.5% copper since it is at this point that the cobalt-rich phase disappears. These considerations suggest that at the catalyst compositions studied catalytic behavior should undergo a continuous gradation with no specific character at any one composition. The data support this. It would be of interest to study further the range 95.5 to 100% copper since pure copper is already known to be completely inactive.

Experimental

Catalysts. Precipitated 44 Cobalt-Copper.—Cobalt nitrate hexahydrate (227.5 g.) and copper nitrate hexahydrate

(250 g.) were dissolved in water (1500 cc.) and the solution stirred with kieselguhr (previously washed with nitric acid) and precipitated by addition of potassium carbonate (238 g.) in water (120 cc.). The slurry was boiled, filtered and the cake dried at 100° and broken into lumps suitable for the reaction chamber. After oxidizing at 480° in air for 20 hours the material was reduced by hydrogen (5 liters per hour). Reduction began at 130° and was completed at 200° giving 31.5 cc. of water. The amount of water expected by reduction of the metal oxides was 36.4 cc. This catalyst gave high conversion of tetrahydrofurfuryl alcohol but only 20% yield of hydrogenated furans containing 17% dihydrofuran. Much hydrocarbon material was formed. *Sintered Alloys, 20 Cobalt-Copper:* The granular material (1850 g.) was contained in a bed 36 × 1.5 in. diameter. Successive oxidation and reduction cycles gave 77, 144.5, 336.5, 380 and 396 cc. of water. *50 Cobalt-Copper:* Two thousand grams gave on successive reactivations, 100, 230 and 324 cc. of water. *80 Cobalt-Copper* (2270 g.): The catalyst bed was 26 × 1.5 in. and gave on reactivation 53, 41 and 33 cc. of water. *100 Cobalt* (2280 g.): Activation gave 359 cc. water. Much hydrocarbon material resulted at 190° with rapid decrease in activity. Thereafter destructive decomposition was less and good results were obtained at 250°. *Products.*—The following details are additional to what has been described earlier. Material caught at −78° was warmed up to −20° to allow propane and propylene to distil, then to +20°. With 50 and 80 cobalt-copper catalysts in particular this led to the separation of butene which formed a dibromide, b.p. 156–160° from 20 cobalt and 159–168° from 80 cobalt. 1-Butene and 2-butene dibromides have b.p. 165 and 158°, respectively. 2,3-Dihydropyran was separated by fractionation, b.p. 80–86.5°, of the material boiling below 160° after treating with potassium hydroxide. It was identified as 5-hydroxypentanal dinitrophenylhydrazone, m.p. 114–115°. Bisulfite extraction of material, b.p. below 160°, left butyl alcohol, b.p. 114–127°, identified as α-naphthylurethan, m.p. 67–68°, and as 3,5-dinitrobenzoate, m.p. 60–62°. The bisulfite layer on neutralization with alkali and distillation of the dried upper layer gave 2-pentanone, b.p. 102–103°, dinitrophenylhydrazone, m.p. 146–147° and cyclopentanone, b.p. 127–137°, dinitrophenylhydrazone, m.p. 142–143°. Tetrahydrofurfuryl alcohol, pentanoic acid, the lactone and tetrahydrofurfuryl pentanoate were estimated as before.[4] The ester, b.p. 240–244°, was hydrolyzed by refluxing with 30% potassium hydroxide. Pentanoic acid from 20 cobalt was identified as anilide, m.p. 59–60°. Distillation of the material from 80 cobalt gave a fraction, b.p. 220–226°, which contained 45% lactone estimated as ammonia adduct, m.p. 104–106°.

High boiling material was fractionated in a vacuum using a 20-plate column constructed by a stepwise arrangement of circular monel gauze discs 1″ in diameter having a quarter segment bent at right angles to the disc to form the "riser" of the step, the disc forming the "tread." The whole arrangement 36″ long formed a kind of spiral staircase.[8] The steps were 3/8″ apart and the column was particularly free from tendency to flood.

Vacuum distillation showed that the 20 cobalt product contained very little lactone but much pentanoic acid, b.p 182–186°, and its tetrahydrofurfuryl ester, b.p. 240–244°. Butyric acid, b.p. 160–178°, was separated from pentanoic acid, obtained after complete hydrolysis of the ester material. It was identified as anilide, m.p. 91–94°, and constituted about 10% of the total acids isolated. During the distillation, 2,3-dihydrofuran was evolved and caught in the Dry Ice trap. It probably arose from decomposition of tetrahydrofuryl tetrahydrofurfuryl ether. This substance was left after hydrolysis of the esters with 33% sodium hydroxide.

All the derivatives mentioned above showed no m.p. depression when mixed with authentic specimens.

(7) E. P. Wohlfarth, *Proc. Roy. Soc. (London)*, **A195**, 434 (1949).

(8) J. R. Bower and L. M. Cooke, *Ind. Eng. Chem., Anal. Ed.*, **15**, 290 (1943); W. D. Stallcup, R. E. Fuguitt and J. E. Hawkins, *ibid.*, **14**, 503 (1942).