dropping funnel. Each experiment involved one mole of input. Hydrogen flow was continued at the full rate for half an hour after all the liquid had been dropped into the catalyst chamber. Thereafter it was reduced to 2.5 liters per hour for a further three hours before disconnecting the collecting vessels. With reaction temperatures below 200° this three hours was extended to 12 hours to ensure complete drainage.

Products were caught in three traps. The first connected to the furnace tube by a ground joint collected high boiling material at atmospheric temperature. The succeeding two traps were cooled to −78°.

Separation, Identification and Analysis of Products.—Material in the first trap was separated from any water and then stripped of all substances, b.p. below 150°, using a five-plate column. The distillate was added to the contents of the second and third traps, the combined material dried over calcium chloride and carefully fractionated using a ten-plate Dufton-type column embodying a nichrome spiral. Furan was collected from 30 to 35°, methylfuran from 60 to 66°, butyraldehyde in the fraction 70–80° and methyl propyl ketone between 90 and 110°. Cyclopentanone distilled along with other substances at 120 to 140°.

Furan was identified as its maleic anhydride adduct, m.p. 115–116° dec., obtained in fine needles by adding to a saturated solution of maleic anhydride in ether and allowing to stand at room temperature for 12 hours. Methylfuran was converted into levulinic aldehyde bis-dinitrophenylhydrazone, m.p. 230–231° after crystallization from ethyl acetate, by adding to a saturated solution of dinitrophenylhydrazine dissolved in hydrochloric acid (3 *N*). Neither of these reactions was quantitative but by applying a rough correction factor determined with pure materials, it was shown that both distilled materials were at least 95% pure.

The aldehyde and the ketones were each identified as dinitrophenylhydrazones. Cyclopentanone was also identified as the semicarbazone, m.p. 198–201°, prepared from a methanol solution of semicarbazide acetate. Each carbonyl compound was estimated in its respective fraction either by precipitation with dinitrophenylhydrazine or by the reduction in weight of the fraction on shaking with excess sodium bisulfite solution (40%). The latter method was preferred with butyraldehyde since its fraction sometimes contained a little methylfuran.

The high boiling fraction was distilled using a five-plate column and a cut taken at 150–170°. It contained all the furfural, identified as the dinitrophenylhydrazone, m.p. 215–219°, without recrystallizing, and estimated by bisulfite extraction, and the furfuryl alcohol, identified as 3,5-dinitrobenzoate, m.p. 79–80°, prepared in pyridine and crystallized from ligroin. More accurate figures for furfural were obtained following the analytical procedure of Dunlop and Trimble.[18]

The results of a typical set of experiments are given in Table I and used to draw the appropriate parts of Figs. 2, 3 and 4. The other catalyst gave similar sets of data.

TABLE I

REACTIONS OF FURFURAL OVER A PURE NICKEL CATALYST

(Input for each experiment: furfural 1.0 mole, hydrogen 40 liters in two hours)

	Product, g.		
Temp., °C.	Furfural recovered	Furan	Furfuryl alcohol
100	2	1	80
166	10	8	60
204	20	25	17
254	0	25	2
304	0	25	0
350	0	11	0
350	0	12	0
300	0	24	0
263	0	27	2
202	23	23	25
165	15	1	60
100	1.5	1	80

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[18] Dunlop and Trimble, *Ind. Eng. Chem., Anal. Ed.*, **11**, 602 (1939).

NOTRE DAME, INDIANA RECEIVED FEBRUARY 16, 1951

[CONTRIBUTION FROM THE UNIVERSITY OF NOTRE DAME AND THE OHIO STATE UNIVERSITY]

Reactions of Furan Compounds. XII. Elimination of the Side Chain of Tetrahydrofurfuryl Alcohol Using Nickel–Copper Catalysts[1]

BY WILLIAM H. BAGNALL, ERIC P. GOODINGS AND CHRISTOPHER L. WILSON

The elimination of the side chain of tetrahydrofurfuryl alcohol has been further studied using catalysts containing 20, 44, 80 and 100% nickel. Tetrahydrofuran is the chief product and the yield is greatest (85%) with 44 nickel. Pure nickel is much less effective and pure copper completely inactive. The results are discussed in relation to modern views on catalytic activity and the high yield of tetrahydrofuran is thought to be connected with not an optimum lattice dimension, but the almost complete filling of the *d*-levels of nickel which occurs at about 44 nickel–copper. This is believed to result in a stronger suppression of the destructive hydrogenative side reactions leading to ring fission than of the dehydrogenation-decarbonylation side chain elimination. Many by-products have been isolated, identified and estimated and their origin discussed. Two hitherto undetected substances, 5-hydroxypentanoic acid lactone and pentanoic acid, have been found in the products. The pentanoic acid has been shown to arise by further hydrogenation of the lactone.

The experiments described in this paper are a continuation of those given in Part III[2] and relate in particular to the effect of nickel–copper mixtures on the formation of tetrahydrofuran (I) by elimination of the side chain of tetrahydrofurfuryl alcohol (II) as carbon monoxide and hydrogen. In agreement with earlier findings[2] pure copper has again been shown to be completely inactive even when supported on kieselguhr. This is quite a common experience for hydrogenation–dehydrogenation reactions at ordinary pressures.[3] Addition of some zinc oxide to the copper-on-kieselguhr did produce a limited activity in conformity with its promoting effect on dehydrogenation,[4] but the product contained mainly di- and tetrahydrofuran and high boiling materials and no detectable tetrahydrofurfural. Small yields of the aldehyde have been reported previously using copper[5] or a copper–

II I

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[1] Summary given at the A. C. S. Meeting in April, 1948.

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

[3] V. N. Ipatieff, B. B. Corson and I. D. Kurbatov, *J. Phys. Chem.* **43**, 589 (1939); H. Morris and P. W. Selwood, THIS JOURNAL, **65**, 2245 (1943).

[4] H. S. Taylor and G. I. Lavin, *ibid.*, **52**, 1917 (1930).

[5] A. Hinz, G. Meyer and G. Schücking, *Ber.*, **76B**, 688 (1943).

chromium oxide–silica gel[2] catalyst. Like copper, brass failed to induce appreciable reaction but a mixture of 90 copper–tin (bronze) whilst giving no tetrahydrofuran gave as the principal product dihydropyran at 240 to 270° probably because of the dehydrating influence of tin oxide.

The addition of metals like nickel or cobalt to copper is known to result[3] in high activity and this was confirmed in the present work. The catalysts were employed in the form of granular sintered pure metal powders and were activated before use and reactivated, after becoming deteriorated, by oxidation and reduction. This type of catalyst has shown marked reproducibility in behavior. The four catalysts with which most experiments were made contained 100, 80, 44 and 20% nickel.

Effect of Temperature and Catalyst Composition.—Catalyst activity rose with temperature and with each metal mixture a maximum yield of tetrahydrofuran, the chief product in each case, was obtained at a certain temperature. This is illustrated for the 44 nickel catalyst by the following figures (temperature and yield of tetrahydrofuran in parentheses) obtained under standard conditions of input (0.5 mole of alcohol and 22.5 liters of hydrogen per hour): 200° (34%), 220 (67), 240 (87), 260 (84), 280 (78) and 300 (48). If these results are plotted, it is apparent that the maximum yield is attained at 242°. In this as in all other papers in this series, yield is calculated on alcohol consumed in a run and not on input; consumption of course, rose steadily with temperature and at the point of optimum yield was usually over 80%. The lowered yield of tetrahydrofuran at high temperature was due mainly to further decomposition to give propane, propene and carbon monoxide. At the lower end of the temperature scale, the yield of tetrahydrofuran was reduced by the formation of ethers by addition of water and alcohols to 2,3-dihydrofuran.[2]

The optimum temperature rose with nickel content of the catalyst. The data are summarized in Table I.

TABLE I

YIELD OF TETRAHYDROFURAN WITH NICKEL–COPPER CATALYSTS AT OPTIMUM TEMPERATURE

Ni, %	0	20	44	80	100
Temp., °C.		233	242	255	260
Yield, %	13	69	85	62	45

A plot of % nickel against yield of tetrahydrofuran shows the best catalyst has a composition very near 44 nickel giving 85% yield of tetrahydrofuran. According to Armstrong and Hilditch[6] the only advantage of adding copper to nickel is that it lowers the temperature of reduction for nickel oxide. On the other hand, the work of Rienäcker and his collaborators indicates that for nickel–copper mixtures, activity varies in a complex manner with composition. Thus in the hydrogenation of ethylene[7] activity of nickel remained fairly constant as copper was added until 20 nickel remained at which point activity fell sharply. Hydrogenation of benzene vapor or styrene in methanol was similar[8] although using reduced oxide catalysts, the sharp drop occurred at about 40 nickel. With cinnamic acid in alcoholic solution[9] activity dropped almost to zero at about 20 nickel after, however, having passed a maximum at about 50 nickel. The occurrence of a maximum at this position provides an interesting analogy for the present work.

Nickel and copper form a complete series of substitutional alloys each having the same face-centered cubic structure with a lattice spacing varying almost exactly linearly from that of nickel (3.517 Å.) to that of copper (3.607 Å.).[10] The difference (0.09 Å.) between the extremes is quite small and changes of this magnitude are not considered to result in greatly differing catalytic behavior.[11] Thus, lattice dimensions do not alone adequately explain the catalytic influences. It is now believed that for reactions such as hydrogenation, dehydrogenation and hydrogenolysis which require electron transfer to the catalyst in the rate-controlling stage, vacant *d*-orbitals are necessary in the surface atoms.[12] Nickel possesses such vacancies but copper does not and when the two are mixed *s*-electrons from the latter fill up the holes in the former. Magnetic measurements have shown that this process is about complete at 40 nickel and this is just where the best catalytic behavior is found in the present work[13] and about where activity falls off rapidly in the hydrogenation of benzene and styrene.[8] Supposing, as seems probable, that side chain elimination in tetrahydrofurfuryl alcohol proceeds through the aldehyde requiring both dehydrogenation and decarbonylation, then both steps would be suppressed by adding copper to a nickel catalyst. The yield of tetrahydrofuran, however, is determined by a competition between rate of formation, further decomposition and side reactions and it is becoming evident that one serious side reaction is the hydrogenative ring fission of intermediate 2,3-dihydrofuran[2] or some entity, maybe an adsorbed radical, which precedes it. The conclusion to be drawn, therefore, is that when copper is added to nickel, the hydrogenative ring fission is suppressed more effectively than dehydrogenation of the alcohol or decarbonylation of the aldehyde. The ring oxygen atom with its unshared electrons may play a prominent part in an adsorption stage leading to ring fission.

By-products.—Table II gives the amounts of various low-boiling substances formed along with tetrahydrofuran. It should be stressed that the figures vary somewhat with conditions and should not be considered too rigidly representative of a given catalyst.

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(6) E. F. Armstrong and T. P. Hilditch, *Proc. Roy. Soc.* (*London*), **A102**, 27 (1922).

(7) G. Rienäcker and E. A. Bommer, *Z. anorg. allgem. Chem.*, **242**, 302 (1939).

(8) P. W. Reynolds, *J. Chem. Soc.*, 265 (1950).

(9) G. Rienäcker and R. Burmann, *J. prakt. Chem.*, **158**, 95 (1941).

(10) E. A. Owen and L. Pickup, *Z. Krist.*, **88**, 116 (1934).

(11) G. Wagner, G. M. Schwab and R. Staeger *Z. physik. Chem.*, **B27**, 439 (1934).

(12) D. D. Eley, *Quarterly Reviews*, **3**, 209 (1949); D. A. Dowden, *J. Chem. Soc.*, 242 (1950).

(13) The choice of 44 nickel was not accidental. A catalyst of this composition was employed in Part III in the form of wire clippings. This wire ("ferry") is used by the electrical industry just because it is non-ferromagnetic.

TABLE II

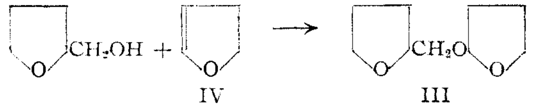
COMPOSITION (WT. %) OF MATERIAL B.P. BELOW 160°

Ni in catalyst, %	20	44	80	100
Furan	0.1	0.1	1.1	3.0
Butanal	0.8	1.8	1.1	9.0
2-Pentanone	2.9	0.5	0.6	0.6
Cyclopentanone	1.2	0.1	0.5	0.4
Butanol	4.3	4.4	4.1	1.5

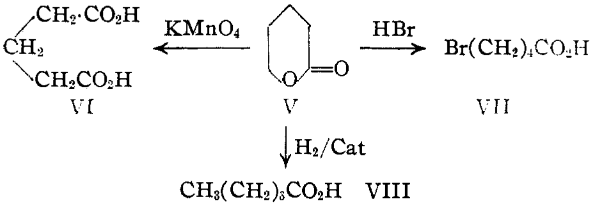
In Part III,[2] it was suggested that furan originated by side chain elimination in furfuryl alcohol present as impurity. Since it has now been shown that tetrahydrofurfuryl alcohol freed from furfuryl alcohol either by refluxing with a little concentrated hydrochloric acid or by partial conversion to tetrahydrofuran over a nickel catalyst still gives furan in an amount comparable with that before such treatments, this view of its origin must, therefore, be abandoned. A more acceptable idea was arrived at after some experiments with 2,3-dihydrofuran. This product, which is a recognized by-product, gives appreciable furan together with tetrahydrofuran and propylene when passed over a 44 nickel–copper catalyst in a stream of nitrogen. It may be the precursor of some, if not all, of the tetrahydrofuran and its further decomposition would adequately account for the furan. 2-Pentanone was believed in this earlier paper[2] to arise from methylfuran formed by side chain hydrogenolysis of furfuryl alcohol. As with furan, however, tetrahydrofurfuryl alcohol free from furfuryl alcohol still gives some of the ketone. An alternative explanation of its formation is ring fission of the normal dehydration product, methylenetetrahydrofuran, or its isomer methyldihydrofuran into which it rearranges on heating.[14]

There is nothing to add to the earlier ideas on the formation of cyclopentanone by catalyzed rearrangement of dihydropyran.[15] Dihydropyran seems to be absent from the product when nickel–copper catalysts are used but it has been isolated from the material given by cobalt–copper catalysts.[16]

Some of the high-boiling by-products presented intriguing problems. Tetrahydrofuryl tetrahydrofurfuryl ether (III) was present and has been isolated before.[2] It probably arises by addition of tetrahydrofurfuryl alcohol to 2,3-dihydrofuran (IV) a reaction which has now been carried out



in the liquid phase using a trace of mineral acid as catalyst. A small amount of the corresponding butyl ether, b.p. 170–172°, is also present and is responsible for the very characteristic odor of the furnace product. Both ethers together correspond with only about 1.3% of the input alcohol but they are present even though 2,3-dihydrofuran may be absent which suggests again that the furan is present at some intermediate stage. The most interesting high boiling by-product was 5-hydroxypentanoic acid lactone (V). Its presence was first suspected because of rapid fading of the end-point during back-titration of a sample being analyzed for tetrahydrofurfuryl alcohol by acetylation. The lactone distilled along with the ether (III). It was separated by alkali treatment and identified by oxidation to glutaric acid (VI) conversion to 5-bromopentanoic acid (VII) m.p. 40–40.5°, and formation of a characteristic crystalline addition compound with ammonia. More lactone was formed with high copper content of the catalyst and particularly if the hydrogen carrier gas was replaced with nitrogen.



With a fresh nickel catalyst, the reaction product contained a very small amount of pentanoic acid (VIII). Separate experiments showed that it was formed by hydrogenative ring fission of the lactone (V).

Effect of Carrier Gas.—The addition of hydrogen to the input had the very desirable effect of keeping the activity of the catalyst high. Even when not in use a stream of hydrogen served to increase the activity of a partially deteriorated catalyst. Nitrogen had no such revivifying effect and carbon monoxide or dioxide caused rapid catalyst failure. The effect of hydrogen would seem to be connected with the removal of involatile material which gradually collects on the catalyst and poisons it. A similar effect in the Fischer–Tropsch reaction using a cobalt–thoria–kieselguhr catalyst has been attributed[17] to the removal of hydrocarbon waxes. Hydrogen also rejuvenates a nickel catalyst deteriorated in the decomposition of ethanol.[18] It is also possible that reactivation by hydrogen is due to removal of carbon monoxide since this is a powerful catalyst poison for nickel.[19] Such a reactivation process, however, would lead to methane which seems always to be absent in the present type of side chain elimination reactions.

With each of the catalysts studied, replacement of hydrogen by nitrogen caused a small but appreciable rise in consumption of tetrahydrofurfuryl alcohol. At 250°, with 80 and with 20 nickel, consumption increased from about 74 to 85% whilst with 44 nickel, it rose from 96 to 98%. Change of carrier gas also affected the yield of tetrahydrofuran using the 20 and 44 nickel catalysts. Table III shows that replacing hydrogen by nitrogen lowered the yield 5% in the first and 8% in the second case, approximately. The use of hydrogen, therefore, not only prolongs the active life of the catalyst but also increases the yield of tetrahydrofuran.

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[14] Part XV. THIS JOURNAL, **73**, 4803 (1951).

[15] C. L. Wilson, *ibid.*, **70**, 1313 (1948).

[16] Part XIII, *ibid.*, **73**, 4798 (1951).

[17] E. F. G. Herrington and L. A. Woodward, *Trans. Faraday Soc.*, **35**, 962 (1939); S. R. Craxford, *ibid.*, **35**, 947 (1939).

[18] W. W. Russell and R. F. Marschner, *J. Phys. Chem.*, **34**, 2554 (1930).

[19] O. Beeck, A. E. Smith and A. Wheeler, *Proc. Roy. Soc.* (*London*), **A177**, 80 (1941).

TABLE III

EFFECT OF CARRIER GAS ON YIELD OF TETRAHYDROFURAN

Temperature 250°; each experiment 1 mole of alcohol and 45 liters of carrier

Carrier	20 Ni	44 Ni	80 Ni	100 Ni
N_2	59	80	69	42
H_2	65	88	70	43
N_2	59	80	69	42
H_2	64	87	70	44

Experimental

I. **Apparatus.**—The arrangement of the catalyst chamber has been described before in previous papers of this series. In the present experiments, it was a Pyrex tube 48 × 1.5 in. heated uniformly for about 36 in.

II. **Catalysts.**—These were mostly in the form of granulated (4–16 mesh) sintered metal powders supplied by Powderloys, Ltd., Coventry, England, and by Metals Disintegrating Co., Inc., Elizabeth, New Jersey. They were oxidized at 500°, except with bronze which was treated at 400°, by a stream of air and reduced at the lowest temperature possible with hydrogen. The amount of water produced in the first oxidation–reduction cycle was for each catalyst (weight, composition) as follows: 275 cc. (1400 g. 20 nickel–copper), 157 cc. (1175 g. 44 nickel–copper), 105 cc. (2335 g. 80 nickel–copper), 250 cc. (2450 g. 100 nickel) and 206 cc. (1440 g. 90 copper–10 tin). On a reactivation cycle more water was produced and a correspondingly higher activity produced. Brass was commercial spelter (12 mesh) but was completely inactive probably because it could not adequately be oxidized. *Copper-Zinc Oxide on Kieselguhr:* copper nitrate, 157 g., and zinc oxide, 66 g., were dissolved in water, 1600 cc., and nitric acid, 45 cc. Kieselgnhr, 100 g., was added and the mixture precipitated by adding an equivalent of potassium carbonate. The precipitated material was washed, dried and ignited in air at 530°. Reduction in a slow stream of hydrogen gave 21 cc. of water. Between the temperature limits of 235 and 325° tetrahydrofurfuryl alcohol gave only a small amount of di- and tetrahydrofuran. *Copper:* Copper-on-kieselguhr prepared in the same way as the preceding catalyst but omitting the zinc oxide was much less active and sufficient low boiling product could not be obtained for satisfactory isolation and estimation.

III. **Isolation of Products.**—Liquid product condensable at room temperature was collected in a flask and the remaining material passed through a trap at −78°. Uncondensed gases were allowed to escape. When all the input alcohol had been added, the catalyst chamber was swept by carrier gas for 30 min. Material in the trap was allowed to warm up to room temperature and the volatile gases passed through a second trap at −78°. In this way most of the propane and propylene was separated from any furan and higher boiling substances. Bromine was added to the propane–propylene fraction while keeping the mixture at −78° until saturation was complete. Any volatile substance remaining b.p. below 0°, was propane.

The entire liquid product boiling above room temperature was distilled and separated into two fractions boiling above and below 160°. Separation was fairly clean and was carried out using an eight-plate column with a Whitmore-type still-head. The apparatus was gas tight and was connected with a cooled trap to catch any furan which would tend to escape. *Analysis of Fraction, B.p. Below 160°:* The main constituent was usually tetrahydrofuran together with water, furan, 2,3-dihydrofuran, butanal, butanol, 2-pentanone and cyclopentanone. If allowed to stand, particularly when an acid was present, the fraction underwent change associated with the addition of water and butanol to the double bond of dihydrofuran. Alkali inhibited this change but caused resinification of the carbonyl compounds. Similar changes occurred in the crude reaction product before distillation (see below).

Water was determined by saturation with sodium chloride. Total carbonyl compounds together with dihydrofuran were estimated by precipitation with dinitrophenylhydrazine dissolved in 2 N hydrochloric acid and weighing the precipitate after drying it at 70°. The dry liquid product was divided into two parts. One was treated with solid potassium hydroxide for 24 hr. and the organic portion distilled off below 100°. It consisted only of di- and tetrahydrofurans in which the former was estimated by precipitation with dinitrophenylhydrazine in a weighed sample. In this determination, the solubility of the hydroxybutanal derivative was allowed for (0.043 g. per 100 cc. 2 N hydrochloric acid at 25°). The other portion of the fraction was further dried over magnesium sulfate fractionated through a 12-plate column and the carbonyl compounds determined in the appropriate fractions. Alcohols were identified as their 3,5-dinitrobenzoates and carbonyl compounds as their dinitrophenylhydrazones. In some cases, α-naphthylurethans of alcohols were made. *Changes in Fraction B. p. Below 160° on Standing:* A sample of material from the 20 nickel catalyst at 255–350°, initially boiling below 160°, was dried over magnesium sulfate and allowed to stand at room temperature for one month. The material (543 g.) was then distilled again and gave 22 g., b.p. above 160°. This fraction contained 2-tetrahydrofuryl butyl ether, b.p. 169–178°, a substance with a characteristic and pronounced odor. It was identified by reaction with dinitrophenylhydrazine to give 4-hydroxybutanal dinitrophenylhydrazone and by comparison with an authentic specimen for boiling point and odor.

Analysis of the material b.p. below 40° was only semi-quantitative. The individual constituents never amounted to more than 3% of the total material b.p. below 160°. Furan was isolated from the experiments with the 20 and 80 nickel catalysts and was identified by conversion to its maleic anhydride adduct, m.p. 103.5–105° dec. Of the hydrocarbons, b.p. below 0°, isolated, only those from 80 nickel catalyst were completely saturated. The boiling point indicated this product was essentially propane. Propylene was present in the material from the other catalysts. *Analysis of Fraction B.p. Above 160°:* The main constituent was usually tetrahydrofurfuryl alcohol. Estimation was carried out by allowing a sample (1 g.) to stand with acetic anhydride, 2.00 cc., in the presence of purified pyridine, 0.5 cc., for one hour. Water, 10 cc., was then added and the liberated acetic acid titrated with standard alkali using phenolphthalein as indicator. In some experiments, organic acids were present in the fraction and were determined by titration on a blank sample and the figure allowed for in the acetylation experiment. In addition, particularly with the catalysts of high copper content, the end-point in the titrations faded rather rapidly due to the presence of 5-hydroxypentanoic acid lactone. This was determined by allowing the sample of the fraction to stand with excess alkali and subsequent back titration.

Fractionation at Atmospheric Pressure.—Distillation at atmospheric pressure was soon abandoned in favor of low pressure fractionation since decomposition occurred frequently at temperatures above 200°. The fraction boiling between 220 and 235° contained most of the tetrahydrofuryl tetrahydrofurfuryl ether and 5-hydroxypentanoic acid lactone. The lactone was estimated by treatment with standard alkali as mentioned above or isolated and estimated approximately by saturating with ammonia gas a mixture of the fraction with an equal volume of dry benzene and collecting the precipitated adduct. This was washed with a little dry benzene in which it was only slightly soluble, followed by petroleum ether (b.p. 40–60°).

During distillation of the high boiling material from an 80 nickel catalyst, decomposition occurred with the formation of dihydrofuran, b.p. 53–54°. It is believed that the presence of organic acids caused fission of some addition product of dihydrofuran. Decomposition was also frequently observed during vacuum distillation of similar material.

Tetrahydrofuryl tetrahydrofurfuryl ether was isolated after prolonged refluxing with alkali to remove acids, lactone and possibly esters. It was estimated by precipitation of the hydroxybutanal dinitrophenylhydrazone. Tetrahydrofurfuryl valerate was thought to be present in the material b. p. 232–243° but identification was not certain. *Fractionation in a Vacuum:* The column was constructed of discs of Monel wire cloth of 50 mesh and had about 20 plates at atmospheric pressure. The virtue of this type of packing was that it allowed the distillation of viscous tetrahydrofurfuryl alcohol at 30° without undue flooding. The following typical experiment relates to material obtained from the 44 nickel catalyst. The fraction, b.p. 40–42° (0.1 mm.), containing the ether and the lactone was treated with excess sodium hydroxide solution (30%) in the cold which dissolved about 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 dinitrophenylhydrazine gave the expected derivative of 4-hydroxybutanal. 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% purc. *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-Bromopentanoic 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 $C_{19}H_{16}O_3$: 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°.

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[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

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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 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

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