reasoning accounts qualitatively for the observed order of increasing lability toward exchange with radiocyanide: $Co(CN)_6^{-3} \sim Fe(CN)_6^{-3} < Cr(CN)_6^{-3} \ll Mn(CN)_6^{-3}$.

One additional point should be considered, namely, why the exchange should proceed through a hepta-coördinated complex with water rather than with cyanide as the seventh group. The answer may lie in the known reluctance of similarly charged ions to react and in the high concentration of water as compared to cyanide ion. As a means of extending this and other aspects of the picture, it will be of interest to examine the kinetics of the exchange of radiocyanide with $Cr(CN)_6^{-3}$; the exchange rates for the iron and cobalt complexes appear to be too slow to permit quantitative study.

LOS ANGELES, CALIFORNIA RECEIVED MARCH 5, 1951

[CONTRIBUTION FROM THE UNIVERSITY OF NOTRE DAME]

Reactions of Furan Compounds. XI. Side Chain Reactions of Furfural and Furfuryl Alcohol over Nickel–Copper and Iron–Copper Catalysts[1]

BY ROBERT M. LUKES AND CHRISTOPHER L. WILSON

The reactions of furfural and furfuryl alcohol in the presence of hydrogen have been studied over catalysts containing nickel–copper and iron–copper mixtures at atmospheric pressure and elevated temperatures. Furfural is reduced to furfuryl alcohol most effectively using nickel–copper catalysts although the 10 iron–90 copper was also fairly good. The best yield (97%) was obtained at 110° with 80 nickel–20 copper. Pure copper was useless. Over 200° the chief reaction was the formation of furan and again the nickel–copper catalysts were best, the highest yield (46%) being afforded by 50 nickel–50 copper. In the iron series that containing 10 iron–90 copper was best but the product also contained much methylfuran. Pure copper again had no activity.

Furfuryl alcohol reacted best over the iron–copper catalysts to give methylfuran. With 10 iron–90 copper the yield was 80%. The nickel materials were very poor and copper again inactive. On the basis of the results the best catalyst for the direct conversion of furfural into methylfuran should be that containing 10 iron–90 copper. Experiments at 250° gave 25% yield. The reactions are discussed in relation to the view that catalysis in hydrogenation, hydrogenolysis and decarbonylation is facilitated by the presence of unfilled 3*d*-electron levels in the catalytic metals.

Earlier in this series[2] the formation of furan and methylfuran from furfural using nickel- or cobalt-containing catalysts was described. Under optimum conditions with a 44 nickel–56 copper catalyst at 280–290°, the yield of furan was over 60%. These preliminary results have now been extended using sintered metal powder catalysts[3] consisting of 100 nickel, nickel–copper mixtures with 80 and 50 nickel, and iron–copper mixtures with 96, 50 and 10 iron. Since all reduction experiments with furfural indicate that the first product is always furfuryl alcohol, this substance has also been studied in order to unravel the reaction steps. The temperature range 100–400° has been covered. Below 200°, not investigated earlier,[2] reactants and products were essentially liquid since all experiments were carried out at atmospheric pressure; above this point they were mainly vapors. The change of state did not result in any pronounced discontinuity of catalytic result as can be seen from Figs. 2, 3 and 4, but large changes of temperature did do so. Hydrogen was added to the input in all experiments since experience has shown that even in reactions such as side chain elimination, in which hydrogen is not used up, its presence is essential to prevent rapid deterioration of the catalyst. With each catalyst, the effect of changing temperature on the products was determined by carrying out a series of consecutive experiments without reactivating the catalyst. The last experiments in each series were made at the temperatures of the first ones in order to determine the extent of catalyst deterioration. Only when this was slight or negligible were the data acceptable. One such suitable set of experiments is given at the end of the experimental section.

The main reaction paths are indicated in Fig. 1. Reduction (a) has been fairly extensively studied before but little has been done systematically to determine the relationship between nature of the catalyst and progress of reaction. This is now remedied in part. The double arrow (a and c) between the aldehyde and the alcohol does not necessarily imply equilibrium, but merely that the reaction may proceed in either direction depending on conditions. In the present experiments, a flow technique was employed and equilibrium was not attained.

Reduction of Furfural to Furfuryl Alcohol (reaction (a), Fig. 1).—Almost any hydrogenation catalyst will reduce furfural to the alcohol although industrially a copper catalyst is preferred since it does not favor nuclear reduction even at high pressure. The temperature is preferably below 200° since above this point hydrogenolysis to methylfuran supervenes. Unsupported copper is inactive but becomes effective when carried on a material such as asbestos,[4] kieselguhr,[5] active carbon[5] or zinc oxide containing sodium carbonate.[6] Raney copper[7] or cuprous oxide supported

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[1] A summary was read before the Organic Division of the American Chemical Society in Philadelphia, April, 1950; Previous paper in this series, THIS JOURNAL, **70**, 1313 (1948).

[2] Wilson, *J. Chem. Soc.*, 61 (1945); Boles, Hungarian Patent 132,763 (1944); *C. A.*, **43**, 4301 (1949).

[3] Wilson, THIS JOURNAL, **70**, 1312 (1948).

[4] Brown, Gilman and Van Peursem, *Iowa State Coll. J. Sci.*, **6**, 133 (1932).

[5] Burnette, *ibid.*, **19**, 9 (1944); Katsuno, *J. Soc. Chem. Ind. Japan*, **46**, 859 (1943); *C. A.*, **43**, 1719 (1949).

[6] Graves (to du Pont), U. S. Patent 2,077,409 (1937); *C. A.*, **31**, 3964 (1951).

[7] Mizuguchi and Iwase, *J. Soc. Chem. Ind. Japan*, **46**, 1037 (1943); *C. A.*, **42**, 6353 (1948).

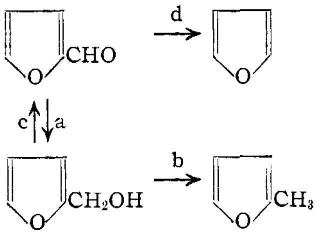

Fig. 1.—Reactions of furfural and hydrogen over catalysts.

on vanadium, aluminum or chromium oxides are also satisfactory especially if promoted with alkaline earth oxides[8] but the best catalyst by far appears to be copper chromite which under the conditions employed is reduced to an intimate mixture of metallic copper and chromium oxide. The alcohol has been obtained in yields up to 99% using temperatures and pressures up to 175° and 100 atm., respectively.[9] Atmospheric pressure and 98° suffice[10] if the copper chromite is promoted by alkaline earth oxides.

In the present work reduction of the aldehyde to alcohol proceeded, as Fig. 2 shows, readily over the three nickel catalysts. Of those with iron in them, only that containing 10% was any good. The others, like unsupported copper, were almost inactive. This is an interesting situation, with implications which are discussed later, in which two metals, iron and copper, are both catalytically inactive, but a little iron added to much copper produces a very effective catalyst. All the same, the 80 nickel–20 copper was somewhat better and gave the best (97%) yield at 110°. Under these conditions with a fresh catalyst consumption was complete. These results compare favorably with the best recorded in the literature making use of copper chromite.

During the experiments, reduction of the furan to the tetrahydrofuran ring was never observed. This step seems to require high pressure. Sometimes, however, partial reduction of the ring may occur. Thus, the formation of butaldehyde and methyl propyl ketone along with furan and methylfuran is best explained by easy ring fission of intermediate 4,5-dihydro-compounds (see later).

As the temperature was raised, unchanged furfural began to appear in the reaction product. The amount rose to a maximum usually between 150 and 200°. This effect was probably due to a rapidly decreasing contact time which resulted as the boiling point of the reactants and products was passed and which more than offset the increase in reaction rate due to a higher temperature, rather than to a temperature dependence of a hydrogenation–dehydrogenation quasi-equilibrium. This conclusion was supported by later experiments with furfuryl alcohol as input which seldom gave any furfural.

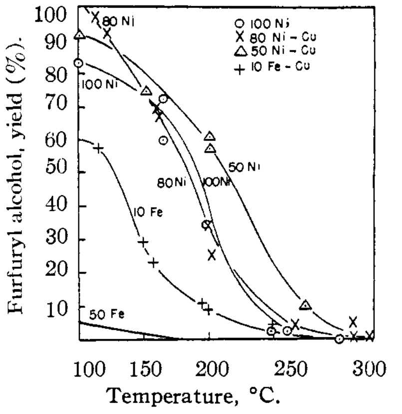

Fig. 2.—Reduction of furfural to furfuryl alcohol over various catalysts. (Input for each expt.: furfural, 1.0 mole, hydrogen, 40 liters during two hours.)

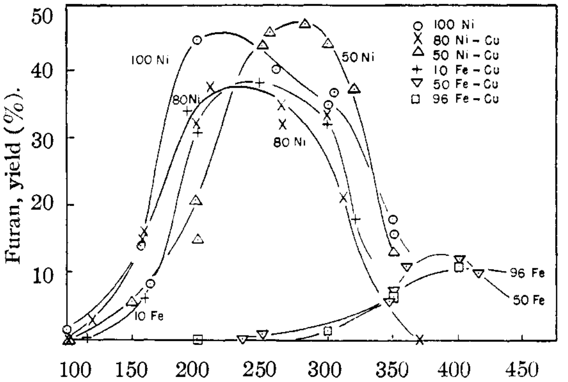

Fig. 3.—Furan from furfural using various catalysts. (Input for each expt.: furfural, 1.0 mole, hydrogen, 40 liters during two hours.)

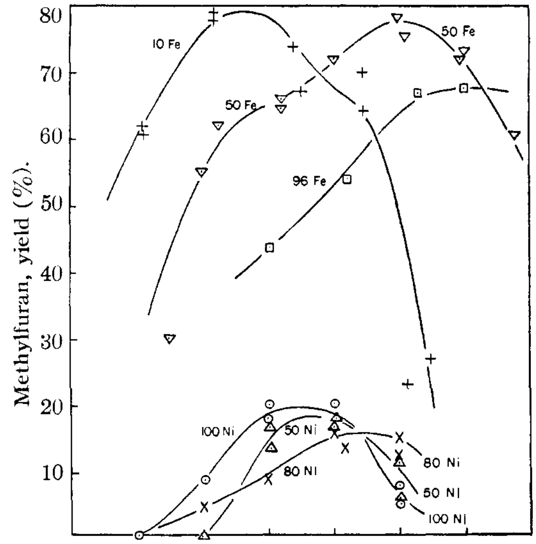

Fig. 4.—Methylfuran from furfuryl alcohol using various catalysts. (Input for each expt.: furfuryl alcohol, 1.0 mole, hydrogen, 40 liters during two hours.)

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(8) Le Francois, *Iowa State Coll. J. Sci.*, **19**, 41 (1944); Stewart (to Iowa State Coll. Research Foundation), U. S. Patent 2,400,959 (1946); *C. A.*, **40**, 4860 (1946); Bremner and Keeys, *J. Chem. Soc.*, 1068 (1947); 1663 (1949); Jones, Bremner and Keeys (to Imperial Chemical Industries), British Patent 621,743 (1949); *C. A.*, **43**, 7049 (1949).

(9) Wojcik, *Ind. Eng. Chem.*, **40**, 210 (1948); Salzberg (to du Pont) U. S. Patent 2,129,507 (1938); *C. A.*, **32**, 8716 (1938); Calingaert and Edgar, *Ind. Eng. Chem.*, **21**, 878 (1934).

(10) Brown and Hixon, *ibid.*, **41**, 1382 (1949); Roberti, *Ann. chim. applicata*, **26**, 530 (1933); *C. A.*, **30**, 4165 (1936); Menzel, *Iowa State Coll. J. Sci.*, **12**, 142 (1937).

Furan from Furfural (reaction (d), Fig. 1.)—As shown in Fig. 3, elimination of carbon monoxide was the chief reaction of furfural above 200°. Again, as in reduction of furfural, all the catalysts except the two with largest iron content were effective. The best yield (46%) of furan was obtained using 50 nickel–50 copper, pure nickel ran a good second. The product from the 10 iron catalyst contained much (yield 25%) methylfuran along with the furan. Methylfuran was absent in the product from the nickel catalysts. (In this as in earlier papers in this series, yield is calculated on consumed, not on total input.)

Comparison of Fig. 3 with Fig. 2 shows how increase in temperature swings the main reaction from hydrogenation to elimination just as if the latter possessed a much higher energy of activation. It is also possible that change from an essentially liquid to a vapor organic phase which characterizes these two reactions is an important controlling factor changing not only the energetics but also the molecularity of the slow step. A study of the effect of pressure might clarify this. One other interesting feature of the nickel catalysts is evident from Fig. 3. The yield of furan at optimum temperature was highest with that catalyst containing most copper (50%) and lowest with that with least (20%). There is thus a complete absence of any linear relationship between catalytic behavior and composition, a point which is taken up again later.

Methylfuran from Furfuryl Alcohol (reaction (b), Fig. 1.).—When furfuryl alcohol instead of furfural was passed over the catalysts the chief reaction was to give methylfuran. Unlike the reactions of furfural, this hydrogenolysis is seen by Fig. 4 to proceed best (to give 80% methylfuran) over the iron catalysts. Of these, that containing most copper was most effective whilst pure copper failed completely. The nickel catalysts were poor. The only reference in the literature to the hydrogenolysis of furfuryl alcohol described the use of copper chromite which at 200–225° gave a 70% yield.[11] Since the first reduction product of furfural is the alcohol, it should be possible to reduce all the way to methylfuran if a catalyst effective both for reduction and hydrogenolysis were employed. Nickel-containing materials promote reduction (Fig. 2) but fail hopelessly for hydrogenolysis (Fig. 4). The iron catalysts are excellent in hydrogenolysis but only that with highest (90%) copper content is any use in reduction. Of all the catalysts described in the present paper, the 10 iron–90 copper mixture should, therefore, be the best for reducing furfural directly to methylfuran. This was shown to be so although at the optimum temperature (250°) the yield was only 25%. Surprisingly enough, the yield even at 100° was 20% falling slightly as 170° was reached thereafter rising steadily to the maximum. The other major product (33%) was furan (Fig. 3). The only effective catalyst described in the literature for the reduction of furfural to methylfuran seems to be copper chromite. At atmospheric pressure and temperatures between 200 and 250°, the optimum yield is 90%.[12]

Several carbonyl substances were found in the reaction product. The most frequently encountered were butyraldehyde formed from furan and 2-pentanone from methylfuran by reductive ring fission.[13] The two catalysts with largest iron (50 and 96) content gave small amounts of cyclopentanone. Furfural at 400° gave 4.5 g. per mole input; this was about three times that from furfuryl alcohol. Cyclopentanone has been observed before in catalytic reactions of furan compounds but in each case seems to result by rearrangement of dihydropyran.[14] This can hardly explain the present observation.

Mechanism of the Catalysis.—Hydrogenolysis of furfuryl alcohol to methylfuran formally resembles, in part at any rate, the dehydration of an alcohol and it is not suprising, therefore, that a typically dehydrating substrate like chromium oxide is a component of a most effective catalyst. Using this type of argument, it was thought at first that the effectiveness of the iron-containing catalysts was due to the presence of iron oxides, formed in the first (oxidation) stage of catalyst activation and not reduced completely in the second stage. Iron oxides are known to be difficult to reduce even at a high temperature. This view, however, was discounted because the most effective hydrogenolysis catalyst was that containing *least* iron. Iron oxide should be a minimum in this material since iron content is lowest. Also, the presence of copper, in this case in highest amount, is known to facilitate reduction of iron oxide. The reason for the activity must, therefore, be sought elsewhere.

Most of the hypotheses relating to heterogeneous catalysis postulate adsorption on active centers the geometry of which requires minimum movement of nuclei during the transformation, consistent with a maximum free energy of adsorption. Lattice distances at the metal surface would be expected to be the important parameter in such hypotheses. Studies with mixtures such as those of nickel and copper, in which catalytic activity in a given reaction varies greatly with composition and lattice distance changes but little, have shown, however, that the geometrical view alone is insufficient and in recent years it has been supplemented by a consideration of the electronic situation at the surface. In particular, the high activity of the transition metals in reduction is related not only to geometry[15] but also to the presence of unfilled levels in the 3*d*-, 4*d*- and 5*d*-bands of the atoms as shown by magnetic measurements. These "holes" facilitate electron transfer to the substrate. In copper, silver and gold the *d*-levels are filled and the metals

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(11) Holdren (to Iowa State Coll. Research Foundation), U. S. Patent 2,445,714 (1948); *C. A.*, **42**, 8214 (1948); see also Padoa and Ponti, *Gazz. chim. ital.*, **37**, 105 (1907); Peters (to Quaker Oats), U. S. Patent 2,082,025 (1937); *C. A.*, **31**, 4991 (1937).

(12) Mizuguchi, *J. Soc. Chem. Ind. Japan*, **46**, 1640 (1943); *C. A.*, **42**, 6802 (1948); Katsuno, *J. Soc. Chem. Ind. Japan*, **46**, 859 (1943); *C. A.*, **43**, 1719 (1949); Schniepp, Geller and van Korff, THIS JOURNAL, **69**, 673 (1947); Burnette, Johns, Holdren and Hixon, *Ind. Eng. Chem.*, **40**, 502 (1948); Johns and Burnette (to Iowa State Coll. Research Foundation), U. S. Patent 2,458,857 (1949); *C. A.*, **43**, 3465 (1949). Brown and Hixon, *Ind. Eng. Chem.*, **41**, 1382 (1949); Bremner and Keeys, *J. Chem. Soc.*, 1068 (1947).

(13) Wilson, THIS JOURNAL, **70**, 1313 (1948).

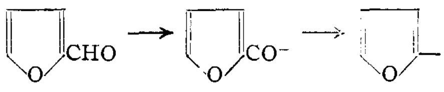
(14) Wilson, *ibid.*, **70**, 1311 (1948).

(15) Beeck, *Review Mod. Physics*, **17**, 61 (1945).

are consequently catalytically inactive although lattice dimension and crystal habit would place them alongside nickel or platinum.[15]

Hydrogenolysis of furfuryl alcohol to methylfuran is considered by Bremner and Keeys[16] to involve the formation of a positive furfuryl cation. This means electron transfer to the metal surface, a process, given a satisfactory ionization potential and electron work function, aided by unfilled *d*-bands. Iron and copper, unlike nickel and copper, do not form a continuous series of substitutional alloys but copper dissolves only about 3% of iron in true solid solution. Addition of more iron produces a second phase consisting of a solution of copper (4%) in iron. If it is supposed, as would be likely, that the lattice dimensions and crystal habit of the copper-rich and the iron-rich phases correspond very nearly with pure copper and iron, respectively, then the high activity of the 10 iron-90 copper mixture in hydrogenolysis (Fig. 4) as well as its fair performance in reduction (Fig. 2) and decarbonylation (Fig. 3) of furfural might be related to its appropriate lattice size were it not for the fact that in each of these reactions pure copper is completely inactive. The addition of iron must, therefore, have some other effect. Electronically, the addition of a metal, such as copper, with filled *d*-bands to one, such as iron, with some empty *d*-bands results in electron transfer from the *s*-bands of copper to the *d*-bands of iron. With excess copper, the vacant *d*-band could become filled completely with consequent disappearance of activity. The present results would indicate, therefore (unfortunately magnetic and crystal data are not available to test the idea) that addition of iron to much copper leads to a partial emptying not of the *s*- but of the *d*-bands of copper just as with copper chromite for which small amounts of chromium have been supposed[17] to cause partial emptying of the copper *d*-bands. Hydrogenation is also considered to involve the formation of positive ions, in this case protons,[17] and any electronic factor facilitating this will enhance reaction if the rate of formation or the concentration of protons can affect the rate-determining step. In the present experiments reduction of furfural proceeded best over nickel catalysts; those containing iron were poor although iron with its empty *d*-bands should, like nickel, facilitate positive ion formation. In reduction, however, another necessity is that the unsaturated centers of the reducible substance should be suitably adsorbed on the surface at an appreciable concentration. This is tantamount to postulating a geometric factor. Reduction differs from hydrogenolysis probably because in the latter, the rate-determining step is that of positive (organic) ion formation whereas in the former, the concentration of hydrogen (protons) and furfural are both directly concerned in the slow step.

The best catalysts for hydrogenation (Fig. 2) are also the best for decarbonylation (Fig. 3). This analogy in itself suggests a similarity of mechanism which is further confirmed by the apparent necessity of hydrogen for the elimination. It is likely that at the higher temperature necessary for elimination, the aldehyde is adsorbed, not through its carbonyl double bond as in reduction but by a splitting off of the hydrogen atom to give an adsorbed furoyl radical which then loses carbon monoxide to give a furyl residue. Hydrogen is necessary probably because it helps the first (slow) step.[2] Radicals, rather than ions, seem more appropriate here because they better parallel other aldehyde reactions. It is not known what factors in catalyst make up will enhance radical formation, but such entities will have a strong affinity for a metal surface if only because of the electron image principle. It does not seem very important at the moment to have to decide whether the adsorbed entities are cations or radicals bound by one or two-electron bonds. Unfilled *d*-bands will certainly help the formation of the transition state in each case.



Reference to Fig. 3 shows that the optimum yield of furan using nickel-containing catalysts was highest with maximum copper content although pure nickel runs a very good second. This effect can hardly be due to a geometrical factor dependent on change of lattice dimensions since this varies so little between pure nickel (3.517 Å.) and pure copper (3.608 Å.) and then the variation is linear with composition. It is known from magnetic measurements that all the nickel *d*-bands are about filled when 60% copper is added resulting in a pronounced falling off in hydrogenating power. Experimentally, the yield of furan is lowered mostly by further hydrogenative ring fission so that if this can be suppressed furan yield should be high. This may be what results when 50% copper is added to nickel.

Experimental

Materials.—Commercial furfural (99.5%) was used after one distillation. Furfuryl alcohol was also distilled and had b.p. 169.5–173.0°.

Catalysts.—Copper was used as fine turnings and nickel and the other metal mixtures in the form of granulated (4–16 mesh) sintered metal powders having about 30% porosity and kindly supplied by Metals Disintegrating Co., Elizabeth, N.J.

The sintered metal (2000 g.) was packed into 33 to 40 in. of Pyrex tube (48 mm. external diameter) held vertically inside the iron furnace tube (2 × 48 in.). The furnace was constructed and controlled so that at least 30 in. of the catalyst was held at temperature to within ±2.5°. Temperatures were measured in a thermocouple pocket which ran centrally down the catalyst bed.

Catalyst Activation.—All the metals were completely inactive until they had been oxidized and reduced. Air was drawn over them at 300–350° at such a rate that the hot oxidation zone did not exceed 500° whilst slowly traversing the bed. When this was complete, the temperature was raised to 500–550° for a further 12 hours with the air stream at 60 liters per hour. The temperature was then lowered to the minimum temperature at which reduction by hydrogen (20 liters per hour) was apparent. The temperature was then gradually raised to 300° until no more water formed. An active catalyst was always kept in an atmosphere of hydrogen.

Procedure.—In all experiments, hydrogen flow was set at 20 liters per hour. Liquid input was maintained uniform at 0.5 mole per hour by the use of a constant-head

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(16) Bremner and Keeys, *J. Chem. Soc.*, 1068 (1947); 1663 (1949).

(17) Dowden, *ibid.*, 257 (1950).

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

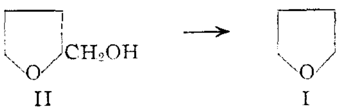
[CONTRIBUTION FROM THE UNIVERSITY OF NOTRE DAME AND THE OHIO STATE UNIVERSITY]

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).