18. *Reactions of Furan Compounds. Part V. Formation of Furan from Furfuraldehyde by the Action of Nickel or Cobalt Catalysts: Importance of Added Hydrogen.*

By Christopher L. Wilson.

Above 200° furfuraldehyde vapour was decomposed into furan and carbon monoxide on contact with a catalyst containing nickel or cobalt. Under favourable conditions the yield of furan attained 65%. Sufficient hydrogen had to be added along with the furfuraldehyde to obtain high conversion and prevent rapid deterioration of the catalysts.

Small amounts of methylfuran and *n*-butaldehyde accompany the furan.

The same kind of catalysts which were effective in eliminating the side chain of tetrahydrofurfuryl alcohol (Part III, this vol., p. 52) have now been shown to decompose furfuraldehyde into furan and carbon monoxide. Perhaps the most interesting feature of the reaction was that hydrogen had to be added along with the furfuraldehyde, otherwise the conversion was very small and the catalyst deteriorated extremely rapidly.

Loss of the side chain of the aldehyde was not entirely unexpected, since catalysts such as nickel, cobalt, and platinum are known (cf. Hurd, " Pyrolysis of Carbon Compounds," p. 240) to bring about elimination of carbon monoxide from aldehydes, and furfuraldehyde itself, when reduced as a vapour over a Sabatier–Senderens nickel catalyst at 270°, afforded a small amount of what was assumed to be furan (Padoa and Ponti, *Gazzetta*, 1907, **37**, 105). These experiments were repeated by Pringsheim and Noth * (*Ber.*, 1920, **53**, 114), who identified furan; although they did not record the yield, it is evident that this could not possibly have been greater than 50% and was probably very much less.

The beneficial effect of hydrogen in decarbonylation was unexpected. The only other observation of a like nature is that of Wojcik and Adkins (*J. Amer. Chem. Soc.*, 1933, **55**, 1293), who found that the presence of hydrogen enhanced the elimination by nickel of the primary aliphatic alcohol group in the liquid phase. In this reaction the aldehyde is almost certainly an intermediate. With furfuraldehyde the effect of hydrogen was most pronounced; *e.g.*, with nickel at 280° the consumption of aldehyde fell from 86 to 9% when hydrogen was replaced by carbon dioxide or nitrogen. Restoration of the hydrogen supply raised consumption again but only to 43%, indicating that irreparable deterioration had occurred.

Catalytic Effect of Different Metals.—Catalysts containing nickel or cobalt gave rise to furan accompanied by a minor proportion of methylfuran. Iron and copper chromite catalysts gave only methylfuran, and metallic copper deposited on pumice was inactive. Results for different catalysts are collected in Table I. The figures for consumption have but little absolute meaning since they depend on many factors, including

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* These authors' use of an iron reaction tube to hold the catalyst has been misunderstood (cf. Kaufmann and Adams, *J. Amer. Chem. Soc.*, 1923, **45**, 3029) to imply the use of an *iron* catalyst.

the amount of active catalyst present. The preparation and activation of each of the catalysts was described in Part III.

Table I.

Conversion of Furfuraldehyde into Furan and Methylfuran by Means of Various Catalysts.

(Temp. 280—290°. Input: aldehyde, 1·0 g.-mol./hr.; each expt., 0·5 g.-mol.; hydrogen, 15 l./hr.).

Catalyst.	Consumption of aldehyde, %.[1]	Yield of furan, %.[1]	Yield of methylfuran, %.[1]
Ni gauze	66	53	8
Ni on pumice	75	42	14
Ni chromite	30	33	10
Raney alloy (Ni,Al)	77	33	8·5
Monel metal (Ni,Cu)	69	65	2
Ferry alloy (Ni,Cu)	66	63	6
Cupronickel (80 : 20)	40	48	2
Permalloy: (*a*) Ni–Fe oxide [3]	55	46	11
(*b*) Ni–Fe [4]	37	45	12
Co on pumice	42	21	18
Fe on pumice	21	0	18
Cu chromite [2]	65	0	80

[1] "Consumption" and "yield" have the significance assigned to them in Part III.
[2] In this experiment hydrogen input was increased to 45 l./hr.
[3] Catalyst produced by reduction of the oxidised alloy below 400°.
[4] Catalyst produced by reduction of the oxidised alloy at 550°.

The most satisfactory catalyst, combining fair yield of furan with long active life, was nickel gauze. All the others deteriorated much more rapidly. However, the small proportion of methylfuran in the product from Monel metal and cupronickel is noteworthy.

Two other substances were identified in the reaction product, *viz.*, propylene in the exit gases and *n*-butaldehyde in the methylfuran fraction. The amount of aldehyde produced varied with the catalyst: the yield from nickel gauze was 1·4%, from Raney, Ferry, and Monel alloys 2·8, 2·3, and 2·6%, respectively, and from the two Permalloy catalysts about 6%. These two substances probably arise by ring fission of furan, but confirmation is lacking.

Effect of Temperature and Pressure.—As the temperature of the catalyst was raised from 200° to 300°, consumption of aldehyde increased from about 10 to almost 100%, whereas yield of furan usually fell by 10—14 units % over this range. The majority of the catalysts operated satisfactorily between 270° and 290°; a temperature in this range usually combined good yield with high consumption. Data illustrating the effect of variation of temperature with a nickel catalyst are given in Table II. The slight deterioration of this catalyst is evident by comparison of expts. 1 and 8. Other catalysts behaved much the same except that deterioration was more pronounced.

Table II.

Furan from Furfuraldehyde at Various Temperatures with a Nickel Gauze Catalyst.

(Input: Aldehyde, 1·0 g.-mol./hr.; each expt., 0·5 g.-mol. Hydrogen, 15 l./hr.
Consecutive experiments without reactivation.)

Temp.	300°	250°	230°	200°	280°	280°	280°	300°	320°	350°	400°
Consumption of $C_4H_3O{\cdot}CHO$, %	99	52	38	14	65	66	61	73	69	57	99
Yield of furan, %	42	57	61	56	51	53	55	47	42	38	2

Reduction of pressure from atmospheric to about 200 mm. caused a diminution of consumption at 280° from 65 to 26%. The yield of furan (70%) seemed appreciably higher, however, and no methylfuran could be isolated. The alloy catalysts were almost completely inactive at low pressures.

Variation of Input Rates.—With constant aldehyde input, increase in added hydrogen improved consumption but did not appreciably affect yield. At high rates of flow, yield fell slightly owing to incomplete trapping of the products. Data illustrating this are contained in Table III.

Table III.

Furan from Furfuraldehyde with a Nickel Gauze Catalyst: Effect of Variation of Hydrogen Input.

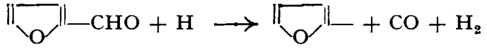
(Temp. 280°. Aldehyde input, 1·0 g.-mol./hr.; each expt., 0·5 g.-mol.)

Hydrogen input, l./hr.	3	15	40	75
Consumption of aldehyde, %	23	47	62	69
Yield of furan, %	53	57	53	48

The desirability of a high ratio of hydrogen to aldehyde for good consumption was confirmed by experiments with different aldehyde input rates, the hydrogen flow being kept constant at 15 l./hr. Increase of aldehyde input from 0·5 to 1·0 and then 3·0 g.-mols./hr. lowered consumption from 87 to 66 and then to 38%. The yield of furan remained effectively constant at 51—53%.

Mechanism.—Since the added hydrogen, apart from the small amount used in the formation of methylfuran, issued from the catalyst tube unchanged, its effect was purely catalytic. Two explanations of this appear possible. Hydrogen either functions by keeping the active centres on the catalyst clean by washing away poisons, or it takes a direct part in the elimination. The first view is supported by the fact that elimination occurred, although only to a very limited extent, even in the absence of added hydrogen (cf. also Hurd, Goldsby, and Osborne, *J. Amer. Chem. Soc.*, 1932, **54**, 2553). Moreover, the catalyst failed to regain completely its original activity when the hydrogen was restored.

Unlike hydrogen, nitrogen or carbon dioxide did not promote the elimination. Hydrogen may, therefore, be an essential reaction partner but it is not easy to suggest how this happens. It may be that collision between a hydrogen atom and the aldehyde affords a hydrogen molecule, carbon monoxide, and a furyl radical in a



manner somewhat analogous to the recombination of two hydrogen atoms in the presence of a third body to dissipate the excess energy. The furyl radical subsequently acquires a further hydrogen atom. Although the concentration of hydrogen atoms in the free space under the conditions of the present experiments would appear to be vanishingly small, it may be that reactions of this type do occur on the surface of the catalyst.

Finally, it should be noted that the catalytic reaction described supersedes older methods for preparing furan (cf. *Org. Synth.*, Coll. Vol. I, p. 269; Wagner and Simons, *J. Chem. Educ.*, 1936, **13**, 265; Hurd, Goldsby, and Osborne, *loc. cit.*).

EXPERIMENTAL.

The technique was as described in previous parts of this series.

Catalysts.—The preparation, activation, and reactivation of the catalysts were described in Part III (*loc. cit.*), but an additional one, pure cobalt on pumice, was prepared as follows. Cobalt nitrate ("AnalaR," hexahydrate, 150 g.) containing less than 0·002% of nickel was heated to 100°, and granulated pumice (8—16 mesh, 100 g.) added. Heating was continued until the mass was dry and granular, and it was then reduced in the catalyst tube at 350—380°. This catalyst behaved exactly like that (*loc. cit.*) containing 0·11% of nickel.

Analysis of Products.—Propylene was shown to be present in the gaseous products by formation of the dibromide. The liquid product caught in the traps was distilled from a Claisen flask embodying a 10″ column. Furan (70—80%), methylfuran, and *n*-butaldehyde were contained in the fraction, b. p. < 150°. Unreacted aldehyde distilled between 150° and 170°, and a small residue remained in which furfuraldehyde was estimated by the contraction on shaking with aqueous bisulphite.

The fraction, b. p. <150°, was dried over calcium chloride and distilled through a short column to separate furan, b. p. 30—33·5°, identified if necessary by preparation of the maleic anhydride adduct, m. p. 104—105° (decomp.) (Diels and Alder, *Ber.*, 1929, **62**, 554). The last traces of aldehyde and water were best removed by standing over potassium or sodium hydroxide and distillation. Methylfuran and *n*-butaldehyde distilled together between 60° and 75°. They were separated by aqueous bisulphite. The aldehyde was identified as the 2 : 4-dinitrophenylhydrazone, orange needles from ethyl alcohol, m. p. 121—123°, not depressed by admixture with an authentic specimen; the absence of other carbonyl compounds in this fraction was indicated by the homogeneity of the dinitrophenylhydrazone. Methylfuran after drying over sodium hydroxide had b. p. 63—65° (Found : C, 73·0; H, 7·05. Calc. for C_5H_6O : C, 73·2; H, 7·3%) and was readily distinguished from tetrahydrofuran, b. p. 64—66°, by either the rapid darkening and resinification on addition of a drop of concentrated hydrochloric acid or by the m. p. (83—84°) of its maleic anhydride adduct (Alder and Backendorf, *Annalen*, 1938, **535**, 101). The only other substances present in the fraction of b. p. <150° were water (1—1·5%) and furfuraldehyde (2—6%).

The liquid of b. p. 150—170° was mainly (at least 95%) furfuraldehyde, and the small residue contained some of this aldehyde and a substance insoluble in bisulphite. Distillation showed that the latter contained at least 40% of a liquid, b. p. 76—78°/14 mm., 174—176°/770 mm. (Found : C, 65·15; H, 5·5. Calc. for $C_6H_6O_2$: C, 65·4; H, 5·5%). It gave a scarlet 2 : 4-dinitrophenylhydrazone which, after recrystallisation from ethyl acetate, had m. p. 168—172° (Found : C, 50·8; H, 4·5; N, 18·4. Calc. for $C_{12}H_{10}O_5N_4$: C, 49·8; H, 3·5; N, 19·3%). 2-Acetylfuran, b. p. 173°, gives a dinitrophenylhydrazone, m. p. 222° (*A.*, 1941, ii, 112), and moreover would be expected to be soluble in aqueous bisulphite, so identification is not complete.

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