[Contribution from the General Electric Research Laboratory]

# The Concurrent Hydrogenation and Hydrolysis of Furfuryl Alcohol

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The combined hydrogenation and hydrolysis of furfuryl alcohol over chromium-modified Raney nickel at low pressure has been studied. The addition of an acid hydrolysis catalyst was found to be unnecessary; it is proposed that a hydrated form of the hydrogenation catalyst effects the hydrolysis. Competitive reactions in the process are discussed.

A combined hydrogenation and hydrolysis reaction of furfuryl alcohol in dilute acetic acid over Raney nickel at 160° and 65 atmospheres pressure to give 1,2,5-pentanetriol has been disclosed by Leuck, Pokorny, and Peters.[1] It was felt that this reaction could be carried out under less heroic conditions if, instead of a soluble acid, a strong-acid ion exchange resin were used. Acid in such a form should reduce the acid attack on Raney nickel, and, at worst, would resinify the furfuryl alcohol[2] no more than do soluble acids. Furthermore, it was thought that it might be advantageous to employ a new commericially-available chromium-modified Raney nickel.[3]

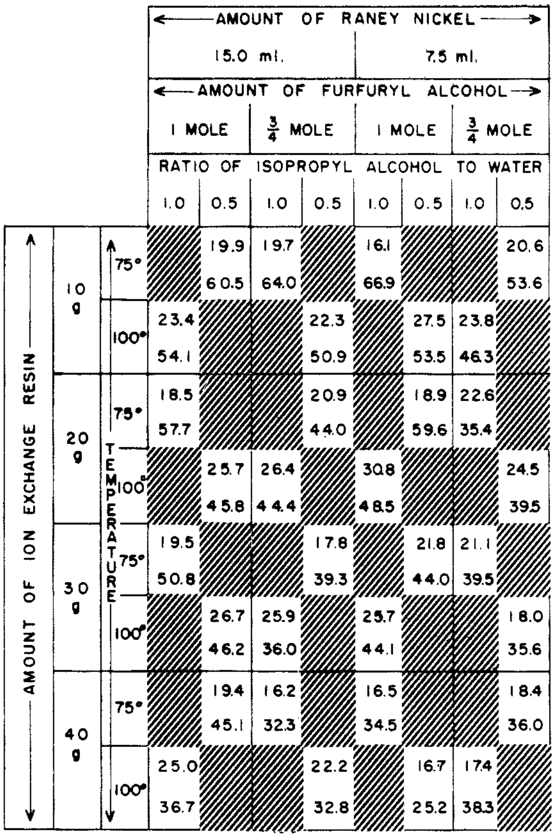
In preliminary experiments a solution of furfuryl alcohol in aqueous isopropyl alcohol was hydrogenated and hydrolyzed smoothly in one step, over chromium-modified Raney nickel and Amberlite IR-120 ($H^+$) ion-exchange resin at 100°C. and 4–5 atmospheres pressure, to yield 20–25% of 1,2,5-pentanetriol and 50–60% of tetrahydrofurfuryl alcohol. In order to determine the factors affecting the yield of 1,2,5-pentanetriol, and to point the way towards increasing that yield, a statistically designed experiment was carried out. The variables investigated and their levels are listed in Table I. The experimental design consisted of a particular half of all possible combinations of these factors.[4]

TABLE I

List of Variables Studied and Their Levels

| Variables | Levels |
|---|---|
| Amount of ion exchange resin | 10 g., 20 g., 30 g., 40 g. |
| Reaction temperature | 75°, 100° |
| Ratio of isopropyl alcohol/water | 0.5, 1.0 |
| Amount of furfuryl alcohol | 0.75 mole, 1.00 mole |
| Amount of Raney nickel[a] | 7.5 ml., 15.0 ml.[b] |

[a] "Raney nickel" refers to the chromium modified variety.[3] [b] Apparent volume after settling and decantation of water.



| AMOUNT OF ION EXCHANGE RESIN | TEMPERATURE | AMOUNT OF RANEY NICKEL | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 15.0 ml. | | | | 7.5 ml. | | | |
| | | AMOUNT OF FURFURYL ALCOHOL | | | | | | | |
| | | 1 MOLE | | $\frac{3}{4}$ MOLE | | 1 MOLE | | $\frac{3}{4}$ MOLE | |
| | | RATIO OF ISOPROPYL ALCOHOL TO WATER | | | | | | | |
| | | 1.0 | 0.5 | 1.0 | 0.5 | 1.0 | 0.5 | 1.0 | 0.5 |
| 10 g | 75° | ▨ | 19.9<br>60.5 | 19.7<br>64.0 | ▨ | 16.1<br>66.9 | ▨ | ▨ | 20.6<br>53.6 |
| | 100° | 23.4<br>54.1 | ▨ | ▨ | 22.3<br>50.9 | ▨ | 27.5<br>53.5 | 23.8<br>46.3 | ▨ |
| 20 g | 75° | 18.5<br>57.7 | ▨ | ▨ | 20.9<br>44.0 | ▨ | 18.9<br>59.6 | 22.6<br>35.4 | ▨ |
| | 100° | ▨ | 25.7<br>45.8 | 26.4<br>44.4 | ▨ | 30.8<br>48.5 | ▨ | ▨ | 24.5<br>39.5 |
| 30 g | 75° | 19.5<br>50.8 | ▨ | ▨ | 17.8<br>39.3 | ▨ | 21.8<br>44.0 | 21.1<br>39.5 | ▨ |
| | 100° | ▨ | 26.7<br>46.2 | 25.9<br>36.0 | ▨ | 25.7<br>44.1 | ▨ | ▨ | 18.0<br>35.6 |
| 40 g | 75° | ▨ | 19.4<br>45.1 | 16.2<br>32.3 | ▨ | 16.5<br>34.5 | ▨ | ▨ | 18.4<br>36.0 |
| | 100° | 25.0<br>36.7 | ▨ | ▨ | 22.2<br>32.8 | ▨ | 16.7<br>25.2 | 17.4<br>38.3 | ▨ |

Fig. 1.—Experimental Layout and Results. In each cell the top figure is the per cent yield of 1, 2, 5-pentanetriol; the bottom figure is the per cent yield of tetrahydrofurfuryl alcohol. The Raney nickel is chromium-modified.

*Results and discussion.* Figure 1 gives both the layout of the experiment and the yields of 1,2,5-pentanetriol (top figures) and tetrahydrofurfuryl alcohol (bottom figures) based on furfuryl alcohol. Statistical analysis showed that variations in the amount of ion exchange resin and the reaction temperature had significant effects on the yields of both these compounds. Also, changing the amount of furfuryl alcohol in the reaction significantly af-

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[1] G. J. Leuck, J. Pokorny, and F. N. Peters, U. S. Patent 2,097,493, Nov. 2, 1937.

[2] *Cf.* A. P. Dunlop and F. N. Peters, *The Furans, A.C.S. Monograph No. 119*, Reinhold Publishing Corp., New York, N. Y., 1953, p. 220 ff. for an extensive discussion of the behavior of furfuryl alcohol under acid attack.

[3] It is claimed that small amounts of chromium improve the performance of Raney nickel. See I. Scriabine, J. F. Billan, A. F. S. Bellone, and M. Gaillard, U. S. Patent, 2,502,348, March 28, 1950.

[4] This design was a one-half replicate of a 4 × 2 × 2 × 2 × 2 factorial experiment. For a discussion of such designs see, for example, K. A. Brownlee, *Industrial Experimentation*, 4th American Ed., Chemical Publishing Co., New York, 1953, Chap. XVI.

fected the yield of tetrahydrofurfuryl alcohol.[5] No other main effects or interactions significantly affected the yield of either compound. Table II summarizes the effects of these significant factors.

TABLE II

MEAN PER CENT YIELDS[a] OF 1,2,5-PENTANETRIOL AND TETRAHYDROFURFURYL ALCOHOL FOR SIGNIFICANT FACTORS[b]

| | Mean Yield, % | |
|---|---|---|
| Factor | 1,2,5-Pentanetriol | Tetrahydrofurfuryl Alcohol |
| Ion exchange resin | | |
| 10 g. | 21.7 ± 2.0[c] | 56.2 ± 3.7 |
| 20 g. | 23.5 ± 2.0 | 46.9 ± 3.7 |
| 30 g. | 22.0 ± 2.0 | 42.0 ± 3.7 |
| 40 g. | 19.0 ± 2.0 | 35.1 ± 3.7 |
| Reaction temperature, °C. | | |
| 75 | 19.2 ± 1.4 | 47.7 ± 2.6 |
| 100 | 23.9 ± 1.4 | 42.4 ± 2.6 |
| Furfuryl alcohol | | |
| 0.75 mole | [d] | 41.8 ± 2.6 |
| 1.00 mole | | 48.3 ± 2.6 |

[a] Based on furfuryl alcohol. [b] Averaged over all factors except the one in question. [c] The 95% confidence limits. [d] Changing the amount of furfuryl alcohol did not significantly affect the yield of 1,2,5-pentanetriol.

An increase in the amount of ion exchange resin progressively decreased the yield of tetrahydrofurfuryl alcohol but did not, contrary to expectation, simultaneously increase the yield of 1,2,5-pentanetriol. Indeed, at the highest level of ion exchange resin (40 g.) the yield of the triol was significantly lowered. The lower average yield of tetrahydrofurfuryl alcohol occurring with the smaller amount of furfuryl alcohol was taken as an added indication of the harmful effect of a large amount of ion exchange resin. Consistent with the fact that the lowest yields of both 1,2,5-pentanetriol and tetrahydrofurfuryl alcohol were obtained with the combination of a large amount of resin and a small amount of furfuryl alcohol, it was observed that these final reaction mixtures were dark yellow. Under the opposite condition of a low ratio of resin to starting material, the reaction mixtures were water-white and gave the highest yields of both 1,2,5-pentanetriol and tetrahydrofurfuryl alcohol. The higher temperature gave an increased yield of 1,2,5-pentanetriol and a correspondingly lower yield of tetrahydrofurfuryl alcohol.

The standard errors of single yields of 1,2,5-pentanetriol and tetrahydrofurfuryl alcohol were 2.7% and 5.0% respectively.

In order to extend this inquiry, a number of supplemental reductions of furfuryl alcohol were performed (Table III). Since the only factors affecting the yield of 1,2,5-pentanetriol were temperature and amount of ion exchange resin, some reactions were carried out at lower resin concentrations and higher temperatures in an attempt to increase the yield (Nos. 1–3). Surprisingly, the yield of 1,2,5-pentanetriol was effectively unchanged when *no resin at all* was used. Obviously then, the catalyst which effects the hydrolysis is *not* the resin, but is either the solvent or the hydrogenation catalyst. Addition of acid to the reaction (Nos. 11, 14) gave no increase, but the addition of a base (No. 5) caused a decrease in the yield of 1,2,5-pentanetriol. Changing the organic solvent (Nos. 4, 7, 9) gave no

TABLE III

SUPPLEMENTAL REDUCTIONS OF FURFURYL ALCOHOL[a]

| | SOLVENT, ml. | | | CATALYST | | | | YIELDS,[b] % | |
|---|---|---|---|---|---|---|---|---|---|
| No. | $H_2O$ | IPA[c] | Other | Type[d] | ml. | TEMP., °C. | ADDITIVE | Tetrahydrofurfuryl alcohol | 1,2,5-Pentanetriol |
| 1 | 50 | 75 | | A | 20 | 115 | IR-120(H), 5 g. | 63.7 | 22.0 |
| 2 | 50 | 75 | | A | 20 | 130 | IR-120(H), 5 g. | Nil | Nil |
| 3 | 50 | 75 | | A | 20 | 115 | None | 64.3 | 21.5 |
| 4 | 50 | — | 75[e] | A | 20 | 100 | None | 70.5 | 15.6 |
| 5 | 50 | 75 | | A | 15 | 115 | $(C_2H_5)_3N$, 1.0 ml. | 74.5 | 10.2 |
| 6 | 25 | 100 | | A | 20 | 115 | None | 75.5 | 8.8 |
| 7 | 50 | | 75[f] | A | 20 | 115 | None | 71.2 | 17.5 |
| 8 | 50 | 75 | | A[g] | 20 | 115 | None | 66.8 | 8.0 |
| 9 | 50 | | 75[h] | A | 20 | 115 | None | 65.5 | 12.6 |
| 10 | 50 | 75 | | B | 20 | 115 | None | 73.8 | 4.5 |
| 11 | 50 | 75 | | A | 20 | 115 | 1 *M* aq. $H_3PO_4$, 0.8 ml. | 63.5 | 19.3 |
| 12 | 50 | 75 | | C | 20[i] | 115 | None | 73.7 | 5.3 |
| 13 | 50 | 75 | | C | 20[i] | 115 | $H_3PO_4$, 2.5 g. | 48.4 | 25.8 |
| 14 | 50 | 75 | | A | 20 | 115 | $H_3PO_4$, 2.5 g. | Nil | Nil |

[a] All runs were made with 123 g. of furfuryl alcohol. [b] Yields were determined by distillation in the usual manner. [c] IPA = isopropyl alcohol. [d] A = Raney nickel (unless otherwise specified, this means the commercially available, chromium-modified variety, containing 0.7 per cent Cr on an alloy basis); B = commercial Raney nickel containing no added chromium; C = Harshaw Ni-0107 catalyst, ball-milled before use. It contained 65 per cent Ni on kieselguhr; ratio of reduced to unreduced Ni was 0.35. [e] Methanol. [f] *tert*-Butyl alcohol. [g] The catalyst was washed five times with isopropyl alcohol and was boiled in isopropyl alcohol. [h] Methyl Cellosolve (trade name for 2-methoxyethanol). [i] Value is in grams, not ml.

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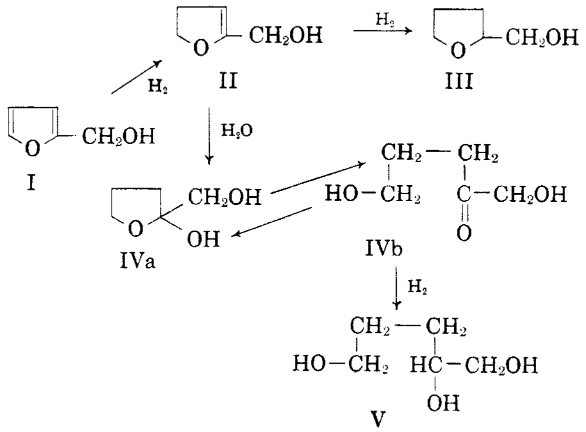
(5) In accord with statistical parlance, all effects referred to as "significant" were statistically significant to at least the 0.05 level.

improvement in the yield, while a substantial reduction in the water concentration (No. 6), greatly decreased the yield of the triol. It was concluded that the hydrogenation catalyst was an acid hydrolysis catalyst.

There is no reason to suppose that the mechanism of this present reaction is different from that described by Dunlop and Peters,[6] a mechanism based upon the formation of a dihydro intermediate II.



This type of mechanism was initially proposed by Topchiev,[7] and supported and confirmed by Schniepp, Geller, and Von Korff[8] and Swadesh, Smith, and Dunlop.[9] However, in direct contrast to the present work, these workers found it imperative to include a separate acid hydrolysis catalyst.

It was concluded that chromium-modified Raney nickel, as produced by alkaline digestion, is a hydrate and that this hydrate is the hydrolysis catalyst. This is borne out by the reduced yield of triol when the catalyst was dehydrated before use (Table III, No. 8), and by the fact that when a charge of catalyst was reused, the rate of hydrogenation was undiminished, but tetrahydrofurfuryl alcohol was the sole product. It is conceivable that at the temperatures used by previous workers[7,8] (*ca.* 160°) the hydrate which can catalyze hydrolysis no longer exists. This is consistent with the experience of Burdick and Adkins,[10] who reduced β-furylacrolein over Raney nickel and other catalysts at 160°.

The acid property of chromium-modified Raney nickel is not associated solely with the chromium content, since ordinary commercial Raney nickel behaves similarly (Table III, No. 10).[11]

On the assumption that the mechanism pictured above holds for this present work, it was concluded that the yield of 1,2,5-pentanetriol is limited by the competition between hydrolysis of II while it is still adsorbed on the catalyst surface, and the desorption of II followed by immediate readsorption and hydrogenation to III. The yield of triol is thus determined by the intrinsic ability of Raney nickel to promote the hydrolysis step. Although the yield of triol cannot be increased above a certain maximum, it can be decreased, as for example, by addition of a base, lowering the water concentration, or dehydration of the catalyst (Table III, Nos. 5, 6, and 8, respectively).

## EXPERIMENTAL

The chromium-modified Raney nickel catalyst[12] was washed by continuously fluidizing 0.5-pound batches of it with a stream of distilled water in a 4″ × 40″ vertical glass cylinder at a rate of 0.5 liter per minute for 4 hours. After this treatment the water in contact with the catalyst remained neutral indefinitely.

All reactions were carried out in a Parr low-pressure hydrogenation apparatus (series 3910) using 500-ml. reaction flasks, and a pressure of 3–5 atmospheres gauge. The reaction mixtures consisted of freshly distilled furfuryl alcohol, aqueous isopropyl alcohol, ion exchange resin, and chromium-modified Raney nickel unless otherwise specified in Table III. The same degree of agitation was maintained by having the total volume of the reaction mixture equal to 250 ml. for all runs.

The ion exchange resin used was Amberlite IR-120(H) (Analytical Grade), a product of the Rohm and Haas Co.

A reaction was considered complete when hydrogen absorption ceased, Yields of products, based on furfuryl alcohol, were determined by distillation from a Claisen flask. Tetrahydrofurfuryl alcohol distilled at 25–35° (0.1–0.2 mm.) and 1,2,5-pentanetriol at 110–135° (0.01–0.1 mm.). No unchanged starting material was found. That starting material which was not converted to triol or alcohol formed a resinous distillation residue.

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[6] Reference (3), p. 686.

[7] Topchiev, *Compt. rend. acad. sci. U.R.S.S.*, **19**, 497 (1938); *Chem. Abstr.*, **32**, 8411 (1938).

[8] L. E. Schniepp, H. H. Geller, and R. W. Von Korff, *J. Am. Chem. Soc.*, **69**, 672 (1947).

[9] S. Swadesh, S. Smith, and A. P. Dunlop, *J. Org. Chem.*, **16**, 476 (1951).

[10] H. F. Burdick and H. Adkins, *J. Am. Chem. Soc.*, **56**, 438 (1934).

[11] The acidity of nickel catalysts at high temperatures has been reported. (a) V. N. Ipatieff, F. J. Pavlik, and H. Pines, *J. Am. Chem. Soc.*, **75**, 3179 (1953); (b) H. Pines, A. Rudin, G. M. Bo, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **76**, 2740 (1954); (c) H. Pines, M. Shamaiengar and W. S. Postl, *J. Am. Chem. Soc.*, **77**, 5099 (1955).

[12] Product of Raney Catalyst Co., Chattanooga, Tenn.