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# Hydrogenolysis

## I. Nickel-Kieselguhr as Catalyst for the Conversion of Alcohols to Ethers and Hydrocarbons

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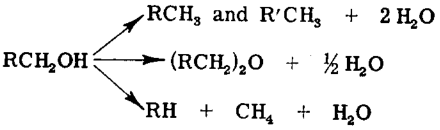
The hydrogenolysis of alcohols in the presence of nickel-kieselguhr catalysts has been investigated in a micropulse reactor at 150–190° and at atmospheric pressure. Three main reactions occurred with primary aliphatic alcohols: reductive dehydroxymethylation, dehydroxylation, and the formation of ethers. The nickel-catalyzed conversion of alcohols to ethers is a novel reaction and can be applied even for the synthesis of neopentyl ether.

The methods of preparation of nickel-kieselguhr affects the composition of the products. For the preferential formation of ethers the catalyst was prepared by precipitating the nickel from an aqueous nickel nitrate solution with ammonium carbonate. When potassium carbonate was used as the precipitating agent the yield of ether was lower. The intrinsic acidic sites of the catalyst appear to be responsible for the reductive dehydroxylation and for the formation of the ethers. Kieselguhr as such was not a catalyst for these reactions, while a nonsupported nickel under certain conditions could influence the ether formation.

Hydrogenolytic dehydroxymethylation (1a–e) and dehydroxylation (2) of primary alcohols over nickel catalysts had been a subject of study in our laboratory. We wish now to report a novel reaction occurring over a nickel catalyst, namely the conversion of primary and secondary alcohols to the corresponding ethers. This reaction seems to be of a general applicability and also can be used for the preparation of neopentyl ether, which until now has not been reported in the literature.

The method used for the preparation of ethers consisted of passing the alcohols and hydrogen at substantially atmospheric pressure, at temperatures of 150–190°, over a nickel catalyst as such, or preferentially over nickel-kieselguhr catalyst. The extent of conversion of the alcohols and the composition of the products depend to a great extent on the preparation of the catalyst. The products may result from the following competitive reactions:



$$\mathrm{RCH_2OH}\begin{cases}\to \mathrm{RCH_3}\ \text{and}\ \mathrm{R'CH_3} + 2\,\mathrm{H_2O}\\ \to (\mathrm{RCH_2})_2\mathrm{O} + \tfrac{1}{2}\mathrm{H_2O}\\ \to \mathrm{RH} + \mathrm{CH_4} + \mathrm{H_2O}\end{cases}$$

$R'CH_3$ is the product of skeletal isomerization accompanying the reductive dehydroxylation of the alcohols.

For a preferential formation of ethers the catalysts were prepared by precipitating the nickel from an aqueous nickel nitrate solution with ammonium carbonate, in the presence of dispersed kieselguhr. When potassium carbonate was used as a precipitating agent the yield of ethers formed was low. It seems that alkali metal ions adsorbed on the catalyst, not withstanding repeated washings, neutralized the intrinsic

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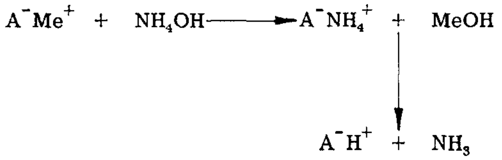
sites of the nickel essential for ether formation. Similarly the commercial Harshaw nickel-kieselguhr catalyst must have contained sufficient sodium ions to catalyze preferentially the dehydroxymethylation reaction. The treatment, however, of this catalyst with aqueous ammonium hydroxide improves considerably its selectivity towards ether formation. It appears that a part of the alkali metal ions are displaced from the acidic sites of the catalyst by the ammonia ions according to the following equation:



$$\begin{array}{llll} A^-Me^+ + NH_4OH \longrightarrow & A^-NH_4^+ & + & MeOH \\ & & \downarrow & \\ & A^-H^+ & + & NH_3 \end{array}$$

The presence of intrinsic acidic sites in a nickel catalyst has been reported previously (e). Recently Peri (*3*), using infrared spectroscopic methods, had noticed that nickel-silica aerogels contain acidic sites that adsorb ammonia strongly.

It was observed in this laboratory that contact hydrogenation sites of a nickel catalyst can be deactivated by the introduction of organosulfur compounds such as mercaptans and thiophene; the latter can thus amplify and/or increase the function of the acidic sites of the nickel (*2*). In the presence of organic sulfur compounds only reductive dehydration occurs at the expense of reductive dehydroxymethylation of the primary alcohols. Such a modified nickel catalyst is acidic enough even to catalyze the alkylation of toluene with isobutylene to form *tert*-butyltoluenes (*4*). Previously reported reactions of alcohols were made under pressure, conditions not favorable for the conversion of alcohols to ethers.

## EXPERIMENTAL PROCEDURE

The experiments were made in a pulse-pressure microreactor developed in this laboratory and described previously (*5*). A 3/8-inch ID stainless steel reaction tube was used. It was filled with 200 mg of catalyst supported by a layer of 640-$\mu$ size glass beads. When using catalyst of a very fine grain size, a layer of glass wool was also used as a support to prevent the entrainment of the catalyst by the hydrogen passing through the reaction tube, which was an integral part of a gas chromatograph. The apparatus was checked for leaks under hydrogen pressure, and heated. The flow rate of hydrogen was adjusted. The hydrogen was purified over a high-pressure Deoxo catalyst (Engelhart Industries, Inc., Newark, New York) and over a dryer containing Molecular Sieve 4A (Union Carbide Corporation, Linde Division, New York, New York).

The reduction of the catalyst was made *in situ* in steps at 125°, 250°, 225°, 300°, 350°, and 400°C to avoid local overheating. The course of this pretreatment was followed by observing the total signal obtained on the recorder of the chromatograph caused by volatile products, mostly water, formed during reduction and emerging from the reactor. The temperature at each level was held until the reduction ceased.

The temperature of the pretreated catalyst in the reactor was lowered to the desired level, the hydrogen flow rate and the pressure were adjusted, and the alcohol was injected, about 10 $\mu$l, by means of a Teflon-tipped microsyringe. The temperature of the reaction was measured by means of an internal thermocouple. The effluents from the reactor were trapped at a liquid nitrogen temperature in a coil which was an integral part of the chromatographic column (*5*). After all the effluent was collected, which required a few minutes, the small Dewar flask containing the liquid nitrogen was removed, and 6 min were allowed for this section of the column to warm up, through heat exchange with the surrounding air; the rest of the column was maintained at room temperature during this step. After this period, the temperature programming was applied for the whole column and the compounds having higher boiling points were driven off in the known manner. This technique permitted in one step the analysis of gaseous compounds boiling within the range of $C_2$ hydrocarbons and high molecular weight compounds.

The quantitative evaluation of the

product obtained was determined by measuring the peak area using an electronic integrator with an attached printer, and making allowances for the peak area retentions.

## CATALYSTS

**Ni-1.** It was a commercial nickel-kieselguhr hydrogenation catalyst obtained from Harshaw Chemical Company, Cleveland, Ohio, and designated as Ni-0101-T. The catalyst in the form of 1/8-inch cylinders, was ground to 20/40 sieve size. It contained 44% nickel, 0.10% potassium, and 0.53% sodium,[*] its surface area was 172 $m^2/g$.

**Ni-2.** The kieselguhr was provided by Harshaw Chemical Company, Cleveland, Ohio, and it was the same as used in their commercial Ni-0101-T catalyst. This kieselguhr according to an analysis by emission spectroscopy[†] contained Fe, ~4.5%; Mg, ~0.2%; Al, ~4.5%; Ca, ~0.1%; and trace amounts ~10 to 100 ppm of Mn, Cr, Ni, Cu, and V. Independent analysis for alkali metals showed the presence of 0.37% of sodium. The kieselguhr, 25 g, was ground to a paste with 30 g of nickel nitrate hexahydrate (Malinckrodt, analytical reagent) dissolved in 40 ml of water. Enough water was added to the paste to render it a free-flowing slurry. The slurry was added under constant stirring to a solution of 20 g of ammonium carbonate monohydrate in 100 ml of distilled water. The mixture was allowed to stand with occasional stirring for 48 hr; it was then filtered, washed with 50 ml of water, dried at 110°, and ground to a powder. The dried catalyst contained 14.7% nickel and 0.25% sodium.

**Ni-3.** The same procedure was used as for Ni-2, with the exception that 20 g of potassium carbonate instead of ammonium carbonate was used as the precipitating agent. The catalyst was washed repeatedly with water until neutral to litmus paper. The dried catalyst contained 16.4% nickel, 0.40% potassium, and 0.44% sodium, and its surface area was 69 $m^2/g$.

**Ni-4.** To 5 g of ammonium carbonate monohydrate, ground to a paste with 12 ml of distilled water, was added 6 g Harshaw Ni-0101-T hydrogenation catalyst. The slurry was left to stand for 48 hr with occasional stirring, then filtered and the filter cake dried at 110°. The catalyst contained by weight 42.6% nickel, 0.12% potassium, and 0.38% sodium. Its surface area was 172 $m^2/g$.

## RESULTS

### *Primary Alcohols*

The experimental results obtained from the reaction of *n*-butyl-, isobutyl-, and neophentyl alcohol over nickel-kieselguhr Ni-1, Ni-2, Ni-3 and Ni-4 catalysts are given in Tables 1, 2, and 3, respectively. With 2-methyl-1-butyl- and 3-methyl-1-butyl alcohol only Ni-2 and Ni-4 catalysts

TABLE 1

HYDROGENOLYSIS OF *n*-BUTYL ALCOHOL[a]

| | Selectivity (mole %)[b] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Catalyst: | Ni-2 | | | Ni-3 | | | Ni-4 | | |
| Experiment: | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| Temperature (°C): | 129° | 150° | 174° | 152° | 169° | 194° | 130° | 150° | 174° |
| Conversion (mole %): | 14.6 | 28.9 | 48.9 | 19.0 | 38.8 | 47.2 | 35.2 | 58.2 | 85.5 |
| Propane | 11 | 14 | 28 | 61 | 52 | 61 | 26 | 45 | 49 |
| *n*-Butane | 1 | 1 | 3 | 1 | 3 | 5 | | 1 | 6 |
| Butyl ether | 88 | 84 | 69 | 38 | 45 | 34 | 73 | 54 | 45 |

[a] Catalyst, 200 mg; pressure, 4 atm; hydrogen flow, 120 ml/min; injection, 10 μl.

[b] The selectivity is based on 100 moles of the title compound reacted.

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[*] The analysis for sodium and potassium and the surface areas of the catalysts were determined by Mobil Company through the courtesy of Dr. P. B. Venuto.

[†] The analysis of the kieselguhr was made by Monsanto Company through the courtesy of Dr. J. F. Roth.

### TABLE 2

### Hydrogenolysis of Isobutyl Alcohol[a]

| | Selectivity (mole %)[a] | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Catalyst: | Ni-2 | | | Ni-3 | | | | Ni-4 | | | Ni-1 | | |
| Experiment: | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 |
| Temperature (°C): | 130° | 152° | 170° | 139° | 155° | 176° | 188° | 130° | 150° | 178° | 132° | 151° | 168° |
| Conversion (mole %): | 13.7 | 33.0 | 44.7 | 7.3 | 19.5 | 29.1 | 45.3 | 29.5 | 47.4 | 87.0 | 12.9 | 41.8 | 77.4 |
| Propane | 13 | 17 | 22 | 42 | 41 | 42 | 56 | 32 | 42 | 48 | 79 | 87 | 91 |
| Isobutane | 3 | 4 | 4 | 2 | 2 | 3 | 4 | 1 | 3 | 4 | 2 | 2 | 2 |
| *n*-Butane | 1 | 1 | 1 | 1 | 1 | 1 | 1 | trace | 1 | 1 | 0 | 0 | 0 |
| Isobutyl ether | 83 | 78 | 73 | 55 | 55 | 54 | 38 | 67 | 54 | 47 | 19 | 11 | 7 |

[a] See footnotes, Table 1.

### TABLE 3

### Hydrogenolysis of Neopentyl Alcohol[a]

| | Selectivity (mole %)[a] | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Catalyst: | Ni-2 | | | Ni-3 | | | | Ni-4 | | | | Ni-1 | | |
| Experiment: | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 |
| Temperature (°C): | 150° | 170° | 190° | 145° | 170° | 190° | 210° | 152° | 160° | 180° | 200° | 148° | 174° | 204° |
| Conversion (mole %): | 12.0 | 21.6 | 27.7 | 2.9 | 8.3 | 15.0 | 26.9 | 11.8 | 19.8 | 40.2 | 65.6 | 2.8 | 23.8 | 64.6 |
| Propane | 0 | trace | 1 | 7 | 2 | 2 | 2 | 10 | 5 | 4 | 4 | trace | 5 | 4 |
| Isobutane | 6 | 5 | 8 | 28 | 33 | 43 | 49 | 20 | 29 | 49 | 61 | 38 | 54 | 68 |
| Neopentane | 1 | 2 | 4 | 5 | 11 | 10 | 17 | 14 | 18 | 20 | 17 | 32 | 28 | 21 |
| Isopentane | 21 | 26 | 29 | 11 | 13 | 12 | 11 | 17 | 19 | 13 | 11 | 8 | 5 | 3 |
| Neopentyl ether | 72 | 67 | 59 | 49 | 37 | 28 | 22 | 39 | 29 | 14 | 7 | 22 | 8 | 3 |
| Unknowns | 0 | 0 | 0 | 0 | 4 | 5 | 8 | 0 | 0 | 0 | 0 | trace | trace | 1 |

[a] See footnotes, Table 1.

### TABLE 4

### Hydrogenolysis of 2-Methylbutyl and 3-Methylbutyl Alcohol[a]

| | Selectivity (mole %)[a] | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Alcohol: | 2-Methylbutyl alcohol | | | | | | 3-Methylbutyl alcohol | | | | | |
| Catalyst: | Ni-2 | | | Ni-4 | | | Ni-2 | | | Ni-4 | | |
| Experiment: | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 |
| Temperature (°C): | 130° | 148° | 184° | 140° | 160° | 190° | 126° | 150° | 198° | 130° | 152° | 183° |
| Conversion (mole %): | 17.3 | 28.3 | 51.3 | 39.9 | 70.0 | 88.1 | 16.6 | 34.1 | 65.2 | 33.9 | 68.0 | 90.1 |
| *n*-Butane | 11 | 15 | 28 | 42 | 56 | 73 | — | — | — | — | — | — |
| Isobutane | — | — | — | — | — | — | 11 | 14 | 24 | 41 | 49 | 63 |
| Isopentane | 9 | 12 | 9 | 3 | 8 | 14 | 1 | 4 | 6 | 1 | 2 | 11 |
| *n*-Pentane | 2 | 4 | 3 | 1 | 2 | 4 | — | — | — | — | — | — |
| 2-Methylbutyl ether | 78 | 69 | 60 | 54 | 34 | 9 | — | — | — | — | — | — |
| Isopentyl ether | — | — | — | — | — | — | 88 | 82 | 70 | 58 | 49 | 26 |

[a] See footnotes, Table 1.

were used and the results are summarized in Tables 4 and 5, respectively.

It was observed that when the starting alcohols had two hydrogens on the $\beta$-carbon atom, e.g., *n*-butyl- and 3-methylbutyl alcohol, the reaction products over all the four catalysts consisted of compounds of the reductive dehydroxymethylations and dehydroxylation and of ethers. The reductive dehydroxylation product contained the same skeleton as the starting alcohol. However, when the $\beta$-carbon of the alcohols contained less than two hydrogen atoms, as in the case of isobutyl-, 2-methylbutyl-,

TABLE 5
HYDROGENOLYSIS OF *n*-OCTYL ALCOHOL[a]

| | Selectivity (mole %)[b] | | |
|---|---|---|---|
| Experiment: | 49 | 50 | 51 |
| Temperature (°C): | 153° | 166° | 180° |
| Conversion (mole %): | 10.3 | 23.2 | 57.4 |
| *n*-Heptane | 71 | 68 | 74 |
| *n*-Octane | trace | 6 | trace |
| Octyl ether | 29 | 26 | 26 |

[a] Experimental conditions: Catalyst Ni-1, 20 ml, of 16–20 mesh size. The catalyst was diluted with an equal amount of 8–12 mesh size glass beads and reduced at 350° in a flowing hydrogen overnight. Pressure, 16 atm; hydrogen/alcohol = 25/1 moles; hourly liquid space velocity, 0.3.

[b] See footnote *b*, Table 1.

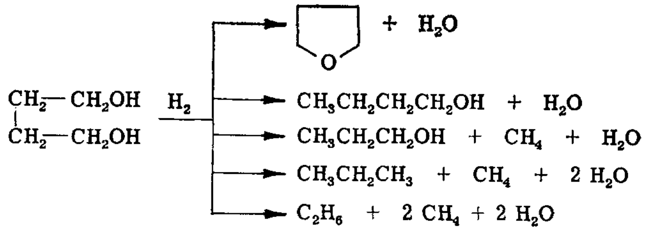
and neopentyl alcohol, the reaction products contained hydrocarbons having a rearranged skeleton. Isobutyl alcohol produced some *n*-butene while neopentyl alcohol afforded a substantial amount of isopentane and 2-methylbutanol produced *n*-pentane.

The extent to which the various reactions occurred depended mainly on the catalyst used. Catalyst Ni-2, which had a comparable nickel content as Ni-3, but which differed from the latter only by its method of preparation, showed a higher overall activity and higher selectivity in promoting ether formation and skeletal rearrangement than catalyst Ni-3. Catalyst Ni-4 and Harshaw hydrogenation catalyst, Ni-1, both having a much higher nickel content than the catalysts mentioned above, differed in their reactivity and selectivity towards ether formation. Ni-4 was more active and selective than Ni-1. Both catalysts Ni-2 and Ni-4 had one common feature, namely, both were contacted with a solution of ammonium carbonate before reduction; the former was precipitated from aqueous nickel nitrate by means of ammonium carbonate solution, the latter, a commercially available catalyst, was treated with aqueous ammonium carbonate.

The ether formation was not limited to reactions made in a pulse-pressure microreactor. *n*-Octyl alcohol yielded *n*-heptane and *n*-octyl ether when passed in a flow-type reactor over Ni-1 catalyst at 153° and 180°, respectively, and 16-atm pressure (Table 5).

### *1,4-Butanediol and 1,5-Pentanediol*

The reductive hydrogenolysis of 1,4-butanediol over a commercial Harshaw catalyst (Ni-1) afforded tetrahydrofuran as the main product (Table 6). The other compounds formed in the reaction were products of reductive dehydroxylation and/or reductive dehydroxymethylation. Ethane was produced by a total reductive dehydroxymethylation, while propyl alcohol by a partial dehydroxymethylation. *n*-Butyl alcohol was formed by a reductive dehydroxylation of the 1,4-butanediol, and propane by a combination of a reductive dehydroxymethylation and a dehydroxylation reaction.



Tetrahydrofuran underwent only slight hydrogenolysis, as indicated by Experiment 53, Table 6. 1,5-Pentanediol underwent mainly dehydration to tetrahydropyran in the presence of Ni-1 catalyst (Table 7). All the other compounds formed were products of a reductive dehydroxylation and dehydroxymethylation of the diol.

### *Alcohol Mixtures*

In order to prove the possible formation of mixed ether, semiquantitative experi-

TABLE 6

HYDROGENOLYSIS OF 1,4-BUTANEDIOL AND TETRAHYDROFURAN[a]

| | Selectivity (mole %)[b] | |
|---|---|---|
| Compound: | 1,4-Butanediol | Tetrahydrofuran |
| Experiment: | 52 | 53 |
| Temperature (°C): | 125° | 127° |
| Conversion (mole %): | — | 4.5 |
| Ethane | 3.5 | 26.3 |
| Propane | 2.8 | 48.9 |
| Butane | 0.1 | 2.6 |
| Tetrahydrofuran | 56.3 | — |
| Propyl alcohol | 33.9 | 0.0 |
| Butyl alcohol | 3.4 | 22.2 |

[a] Catalyst Ni-1, 200 mg; for experimental conditions see footnote *a*, Table 1.

[b] See footnote *b*, Table 1.

ments were made by injecting a mixture of primary alcohols ROH and R′OH. All three possible ethers were produced, ROR, ROR′, and R′OR′. When an equimolar ratio of *n*-butyl- and *n*-pentyl alcohol was used, the ratio of the ethers formed was 1:2:1.

### *sec-Butyl Alcohol*

At 175°C and 4 atm pressure in the presence of Ni-1 catalyst, about 40% of the sec-butyl alcohol underwent reaction. About 10% of the alcohol was converted to *n*-butane and 30% to *sec*-butyl ether. Smaller amounts of unidentified compounds also were formed.

### *tert-Butyl Alcohol*

This alcohol was decomposed at much lower temperatures than all other alcohols investigated. At 115°, 70% of the *tert*-butyl alcohol reacted to form a mixture of isobutane and isobutylene. At 175° the conversion was practically 100%.

## DISCUSSION

The present study has shown that in the presence of a nickel-kieselguhr catalyst and hydrogen, primary alcohols undergo ether formation, in addition to the previously reported dehydroxymethylation reaction. The dehydration of the alcohols to ethers occurred at 130–180°, a much lower temperature than used when alumina is employed as the catalyst. The formation of ether is usually accompanied by reductive dehydroxylation producing an alkane with the same number of carbon atoms as the reacting alcohol, but accompanied in some instances by skeletal rearrangement.

The extent of the various reactions depended on the structure of the alcohols, the preparation of the catalysts, and the experimental conditions.

### *Reductive Dehydroxylation*

This reaction can proceed either through dehydration followed by hydrogenation of the olefins or/and by a direct hydrogenolysis of the hydroxyl group. The formation of neopentane from neopentyl alcohol may be interpreted as a direct splitting of the hydroxyl group by hydrogen (Table 3). However, neopentane could have been produced from the hydrogenolysis of 1,1-dimethylcyclopropane produced by a dehydration of neopentyl alcohol, similar to the reaction observed when alumina was used as a catalyst (*6*). The yield of neo-

TABLE 7

HYDROGENOLYSIS OF 1,5-PENTANEDIOL[a]

| - | Selectivity (mole %)[b] | | | | |
|---|---|---|---|---|---|
| Experiment: | 54 | 55 | 56 | 57 | 58 |
| Temperature (°C): | 107° | 127° | 147° | 179° | 191° |
| Conversion (mole %): | 13.8 | 24.6 | 43.5 | 52.1 | 55.4 |
| Propane | 1.4 | 1.2 | 5.4 | 5.5 | 32.0 |
| Butane | 0.0 | 0.4 | 0.6 | 0.9 | 3.6 |
| Tetrahydropyran | 78.2 | 77.7 | 75.5 | 69.8 | 37.1 |
| Butyl alcohol | 18.1 | 19.1 | 17.2 | 22.5 | 26.3 |
| Pentyl alcohol | 2.3 | 1.6 | 1.3 | 1.3 | 1.0 |

[a] Catalyst Ni-1, 200 mg; for experimental conditions see Footnote *a*, Table 1.

[b] See footnote *b*, Table 1.

pentane depends to a great extent on the catalyst used. Ni-1 catalyst, Harshaw commercial nickel-kieselguhr catalyst containing 44% nickel, yielded 21–32% neopentane. The same catalyst treated with ammonium carbonate, Ni-4, yielded less neopentane but a greater amount of isopentane. A similar correlation exists between Ni-2 and Ni-3, Table 3, Expts. 23–28. The formation of isopentane is probably the result of a dehydration reaction followed by hydrogenation. Skeletal isomerization accompanying reductive dehydroxylation was also observed in the case of primary alcohols, containing a methyl group on β-carbon atom, as in isobutyl alcohol (Table 2) and 2-methylbutanol (Table 4); some *n*-butane and *n*-pentane were produced, respectively. Under similar experimental conditions 3-methylbutanol yielded only isopentane (Table 4, Expts. 43–48). The extent of reductive dehydroxylation increases with the number of methyl substituents on the β-carbon atom.

### *Reductive Dehydroxymethylation*

The hydrogenolysis of primary alcohols to paraffins, having one carbon atom less than the parent alcohol, in the presence of nickel-kieselguhr and other catalysts, was reported previously (*1*). The reaction seems to proceed through the intermediate formation of an aldehyde, following the decarbonylation of the latter to the corresponding saturated hydrocarbon, with a subsequent reduction of carbon monoxide to methane.

The reductive dehydroxymethylation depends on the nature of the catalyst. The dehydroxymethylation proceeds more readily over nickel-kieselguhr (Ni-3) obtained by the precipitation of nickel nitrate with potassium carbonate, than over the same catalyst, but precipitated with ammonium carbonate (Ni-2), Tables 1–4. Unlike the dehydroxylation, the dehydroxymethylation reaction is not accompanied by skeletal isomerization. From 2-methylbutanol only *n*-butane and from 3-methylbutanol only isobutane were obtained (Table 4). The extent of reductive dehydroxymethylation increases with the temperature of the reaction. This is not surprising since at higher temperatures the formation of aldehydes, the assumed intermediates in the reaction, is favored.

### *Ethers*

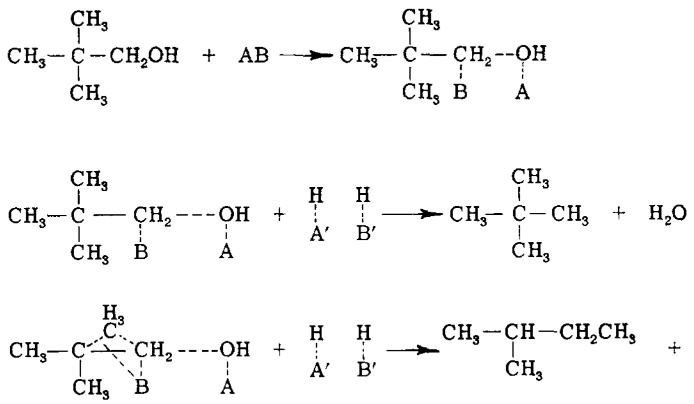
The formation of ethers from alcohols in the presence of nickel catalysts is a novel reaction. It was, however, reported that small amounts of ethers were produced when alcohols or aldehydes are passed in the presence of hydrogen over reduced cobalt catalyst (*7*), evaporated platinum film (*8*), or over a palladium film (*9*).

Neopentyl alcohol, in which all the three β-hydrogens are substituted by methyl groups, produces good yields of neopentyl ethers in the presence of nickel-kieselguhr catalysts. The structure of the alcohols seems to have little effect on the yield of the ethers. Terminal diols, such as butanediol and pentanediol, gave high yields of ethers. Secondary alcohols also gave ethers in good yields; however, this class of compounds was not investigated in detail.

The yield of the ethers depended on the preparation of the nickel catalyst. Ni-2 catalyst prepared from nickel nitrate and ammonium carbonate in the pressure of kieselguhr produced higher yields of ethers than Ni-3, in which potassium carbonate was used as the precipitating agent. Similarly, commercial catalyst treated with ammonia was a more effective catalyst for ether formation than the original catalyst, Ni-4 vs. Ni-1.

Ni-3 catalyst, which was prepared from nickel nitrate and potassium carbonate, can be activated through washings with aqueous ammonium carbonate to produce a catalyst, which after reduction at 300° was more effective for ether formation, and incidently, for skeletal isomerization accompanying reductive dehydroxylation. Ammonia seems to displace potassium ions bound to the acidic sites of the catalyst, thus creating catalytic sites for the dehydration of the alcohols.

Ether formation was observed to occur in the temperature range of 130–180°; the



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2OH + AB \rightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{B}{CH_2}\cdots\underset{A}{OH}$$ (Step 1)

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{B}{CH_2}\cdots\underset{A}{OH} + \underset{A'}{H}\ \underset{B'}{H} \rightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 + H_2O$$ (Step 2)

$$CH_3-\overset{H_3C}{\underset{CH_3}{C}}\cdots\underset{B}{CH_2}\cdots\underset{A}{OH} + \underset{A'}{H}\ \underset{B'}{H} \rightarrow CH_3-\underset{CH_3}{CH}-CH_2CH_3 + H_2O$$ (Step 2a)

yield of the ethers went through a maximum, as a consequence of the generally decreasing ether selectivity with increasing overall conversion.

### *Mechanism*

The sites responsible for the dehydroxylation and ether formation were shown to possess acidic properties, since ammonia gas when passed over this catalyst, immediately before carrying out the experiment, caused a loss of its activity towards these reactions. The ammonia adsorption was reversible and the activity of the catalyst could be restored by treating it with hydrogen at 350–400°.

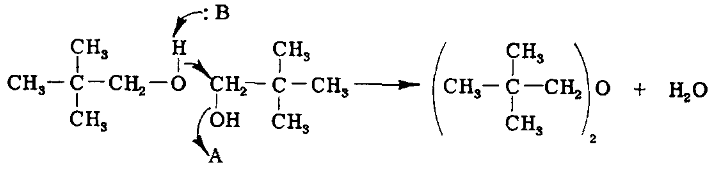
The acidic sites may attract an alcohol molecule on the oxygen atom inducing the polarization of the carbon–oxygen bond (Step 1). This bond may then be attacked by a hydride and a proton from the dissociation of hydrogen on the nickel catalyst (Step 2). When β-hydrogen in the alkanols is substituted by a methyl group the latter may assist in the removal of the hydroxyl group (Step 2a). This can be illustrated using neopentyl alcohol as an example.

A, A′ and B, B′ indicate the acidic and basic sites of the nickel catalyst. These sites may be attributed to nickel oxide which is present in the catalyst. The rupture of a nickel–oxygen bond within the nickel oxide crystal on heating would produce a positively charged nickel (acid sites) and a negatively charged oxygen (basic sites). The situation is probably similar to the formation of acidic and basic sites on calcining alumina (*10*).

The increase in the strength and/or the number of acidic sites when nickel-kieselguhr is used as a catalyst could be explained through the interaction of silica with nickel as discussed by Peri (*3*). The proposed heterolytic dissociation of hydrogen (Step 2) is similar to that suggested for the hydrogen–deuterium exchange on aluminas (*11*).

The anchimeric assistance in removal of the hydroxyl group may account for the greater yield of the reductive dehydroxylation of alcohols, having methyl substituents on the β-carbon atom.

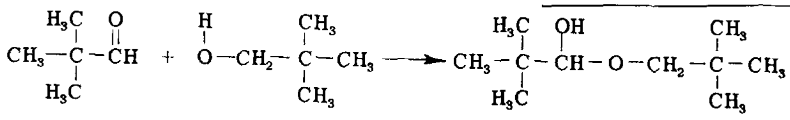
The formation of ethers from alcohols is known to occur with acidic catalysts. It is therefore plausible to assume that acidic and basic sites of the nickel catalyst participate in the reaction in a concerted manner, similar to the explanation given for the formation of 1,4-epoxycyclohexane from *trans*-1,4-cyclohexanediol over alumina (*12*) (A, acid sites; B, basic sites).



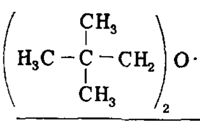
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{H}{O}\ \overset{:B}{}\ \underset{OH\ \cdots A}{CH_2}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \rightarrow \left(CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2\right)_2O + H_2O$$

Independent studies have shown that the

hydrogen prolongs the life of the catalyst. The main function of the hydrogen seems to be to keep the surface of the catalyst clean. It is, however, not excluded that the ether could have been formed through the condensation of an aldehyde with an alcohol to form hemiacetal, followed by the hydrogenolysis of the hydroxyl group.

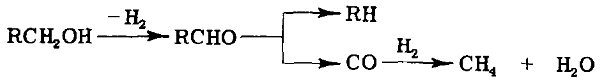


$$(CH_3)_3C{-}CHO + HO{-}CH_2{-}C(CH_3)_3 \longrightarrow (CH_3)_3C{-}CH(OH){-}O{-}CH_2{-}C(CH_3)_3$$



$$[(CH_3)_3C{-}CH_2]_2O$$

The reductive dehydroxymethylation most likely proceeded through decarbonylation of aldehydes produced from the dehydrogenation of alcohols, with a subsequent reduction of carbon monoxide to methane.



$$RCH_2OH \xrightarrow{-H_2} RCHO \begin{cases} \longrightarrow RH \\ \longrightarrow CO \xrightarrow{H_2} CH_4 + H_2O \end{cases}$$

The mechanism of decarbonylation in homogeneous systems has been recently proposed (*13*, *14*).

Kieselguhr by itself does not have catalytic properties under the experimental conditions used. Nickel catalyst prepared according to the method used for the preparation of Ni-2, from nickel nitrate and ammonium carbonate, in the absence of kieselguhr, had a lower catalytic activity and selectivity for dineopentyl ether than Ni-2. However, a mixture composed of the nickel catalyst and kieselguhr, ground in a mortar and calcined at 400° in the presence of hydrogen, showed an improved catalytic activity and selectivity over nickel toward ether formation.

The method of preparation of a nonsupported nickel catalyst has an effect on the yield and the conversion of alcohols to ethers and a detailed study of this interdependence is being pursued.

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