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Reactions of Secondary Saturated Alcohols Over Reduced Nickel Oxide–Cab-O-Sil Catalysts in the Presence of Hydrogen Variables Affecting Ether Formation

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Dehydration of secondary alcohols in the gas phase over nickel catalysts was investigated by passing the gaseous mixture of the alcohol and hydrogen over a catalyst of reduced NiO on Cab-O-Sil in the temperature range 160–190°C. The reactivity of secondary alcohols towards ether formation is appreciably less than that of primary alcohols at similar conditions. The activity of the catalyst which depends on the percentage of nickel and on its reduction temperature is appreciably reduced by small additions of sodium ion to the catalyst and by small amounts of water in the gas stream. The structure of the alcohol influences the extent of ether formation. It decreases as the alcohol becomes more bulky. It seems that the polarity of the alcohol, as indicated by Taft's correlation, also participates in determining the extent of ether formation. These results are consistent with the interpretation that the activity of reduced nickel oxide as a catalyst for dehydration of alcohols is due to its intrinsic acidity and probably also to its intrinsic basicity.

INTRODUCTION

In previous papers (1–8) a detailed investigation of dehydration of primary alcohols in the presence of hydrogen over reduced nickel oxide was presented. In most of these dehydration reactions ether is the main product, the other dehydration products being the paraffin formed by hydrogenation of the olefin produced by elimination of water from the alcohol molecule. Paraffins with one carbon less than the original alcohols are also formed by dehydroxymethylation reaction which competes with the dehydration reaction. It was also reported (*1*) that secondary alcohols undergo dehydration to ethers and olefins over the same catalyst, but these reactions were not investigated in detail.

The present paper deals with the reactions of secondary alcohols over reduced nickel oxide catalyst in the presence of a stream of hydrogen. The following effects have been investigated: nickel content of the catalyst and its reduction temperature, the structure of alcohol and its polarity, the presence of water in the gas phase, and of sodium ion in the catalyst. These effects are compared with those in primary alcohols as reported in the previous papers (*2, 3, 6, 7*).

EXPERIMENTAL PART

1. *Apparatus and Procedure*

The experiments were conducted in a micropulse reactor described previously (*9*) and modified for a continuous flow system operation (*6*). Samples of the products leaving the reactor passed directly into a gas chromatograph. Two separate columns were used: (a) 30 ft, 20% Ucon 75 H supported on 60/80 Chromosorb W; (b) 30 ft, 15% Carbowax 20 M on the same support.

The molar ratio of alcohol to hydrogen in the gas stream entering the reactor was 1:3.1 in all cases.

2. Catalysts

The catalysts were prepared from nickel nitrate hexahydrate, ammonium carbonate and Cab-O-Sil M-5 as described previously (*7*). The nickel oxide was reduced *in situ* in a flow of 20 ml/hr hydrogen overnight. In most of the experiments the nickel content of the dried catalyst was 7% and the temperature of reduction was 450°C. The exceptions are the experiments which were made to study the effect of temperature of reduction and the effect of nickel concentration. The amount of the dried catalyst introduced into the reactor tube was in all the experiments such that the absolute amount of nickel was 28 mg (400 mg for 7% catalyst, 280 mg for 10%, etc.). Catalyst containing sodium was prepared as described before (*3*).

Results and Discussion

Stability of catalyst. The stability of the 7% Ni catalyst was investigated by measuring the conversion and composition of products in a standard reaction after every series of experiments. The catalyst did not change its activity towards this reaction during several weeks of use. The standard procedure employed was to pass 2-propanol at 160°C at a flow of 11.8 ml H_2/min (molar ratio alcohol:H_2 was 1:3.1, see Table 2). The stability of other catalysts was checked by the standard reaction after 2 or 3 days of use. The stability of the 15% catalyst was checked in this way at every temperature of reduction.

Products of reactions. Secondary alcohols undergo three types of reactions over reduced nickel oxide catalysts: (a) ether formation, (b) paraffin formation, probably through dehydration to olefins followed by hydrogenation, (c) ketone formation. When diisopropyl ether saturated with water was fed to the reactor at the conditions at which ether formation takes place, the product contained only the original materials. This shows that the diisopropyl ether is stable under the conditions of reaction and its formation is not reversible. This is probably true for other secondary ethers too. On the other hand, the ketone formation is reversible and reaches equilibrium under the conditions used in this study. This was shown by introducing into the reactor acetone and methyl ethyl ketone. The compositions of products were the same as that obtained by starting with 2-propanol and 2-butanol, respectively. Furthermore, the alcohol: ketone ratio was independent of the rate of flow of secondary alcohols studied. These ratios are presented in Table 1. It can be assumed, therefore, that ketone–alcohol equilibrium is independent of the dehydration reactions. The results of formation of ethers and paraffins summarized in Table 2 are therefore calculated on a ketone-free basis.

Comparisons between dehydration reactions in secondary and in primary alcohols. Comparison of the results presented in Table 2 with the previous results (*6, 7*) or with those presented in Table 3 shows that there are two differences between primary and secondary alcohols: (a) The yields of dehydration products, namely ethers and paraffins with the same number of carbon atoms, are usual lower in pri-

TABLE 1
Reactions of Secondary Alcohols Over Reduced Nickel Oxide Catalyst,[a] Ketone:Alcohol Molar Ratio

	Ketone: alcohol molar ratio		
Alcohol Temp (°C):	160	175	190
2-Propanol	0.084	0.118	0.193
2-Butanol	0.117	0.146	0.186
2-Pentanol	0.118	—	0.190
3-Pentanol	0.124	0.152	0.190
3-Methyl-2-butanol	0.126	—	0.188
3,3-Dimethyl-2-butanol	0.127	—	0.188
Cyclopentanol	0.166	—	0.200
Cyclohexanol	0.166	—	0.200

[a] Catalyst = 7% Ni on Cab-O-Sil.

TABLE 2
Reactions of Secondary Alcohols Over Reduced Nickel Oxide Catalyst[a]
Composition of Dehydration Products[b]

	(°C):	160		175		190	
Alcohol	Rate of flow[c]	Conversion[a]	Selectivity[e]	Conversion[d]	Selectivity[e]	Conversion[d]	Selectivity[e]
2-Propanol	3.9	18.7	65	—	—	—	—
	7.8	10.2	61	16.0	64	22.8	65
	11.8	8.7	63	—	—	18.0	65
	17.3	7.4	65	—	—	—	—
	23.6	6.5	68	—	—	—	—
	36.9	4.4	69	7.1	70	10.0	63
	73.8	2.5	70	4.8	68	7.2	67
2-Butanol	3.9	16.5	32	—	—	—	—
	7.8	15.2	32	17.0	31	20.6	31
	11.8	13.5	32	—	—	17.4	32
	17.3	12.7	32	—	—	—	—
	23.6	11.6	32	—	—	—	—
	36.9	9.2	32	12.0	32	13.0	33
	73.8	7.8	34	9.3	34	11.0	35
2-Pentanol	11.8	13.5	29	—	—	16.0	28
	36.9	8.0	29	—	—	11.0	29
3-Pentanol	3.9	15.2	17	—	—	—	—
	7.8	13.8	18	16.3	17	20.2	16
	11.8	12.4	18	—	—	17.4	17
	17.3	11.5	18	—	—	—	—
	23.6	10.9	19	—	—	—	—
	36.9	9.5	18	11.0	17	13.0	17
	73.8	6.8	19	9.7	17	11.1	17
3-Methyl-2-butanol	7.8	18.2	4	—	—	21.6	4
	11.8	16.6	4	—	—	18.7	4
	36.9	11.7	4	—	—	15.6	4
	73.8	10.1	4	—	—	13.4	4
3,3,-Dimethyl-2-butanol	7.8	6.7	0	—	—	9.9	0
Cyclopentanol	11.8	13.0	52	—	—	17.0	51
	36.9	9.0	52	—	—	12.0	51
Cyclohexanol	11.8	11.0	57	—	—	16.0	56
	36.9	7.0	56	—	—	10.0	57

[a] Catalyst: 7% Ni on Cab-O-Sil.
[b] On ketone-free basis.
[c] (ml H_2/min) at 1 atm, see Experimental Part.
[d] Percentage of conversion on ketone-free basis.
[e] Molar percentage of ether in products (ketone-free basis).

mary alcohols; (b) in secondary alcohols the dehydration is much more in the direction of hydrocarbon formation. The second point is to be expected, since removal of hydroxyl group is easier in secondary alcohols as they are more basic. The order of activity of the noncyclic secondary alcohols with respect to hydrocarbon formation is also as expected; it follows the order of stabilities of double bonds found in the work of Kistiakowsky *et al.* (*10*). The yields of hydrocarbons from cyclic alcohols are somewhat lower than those expected from the relative stability of double bonds, but it may be explained by the assumption that the olefin is formed by *trans* elimina-

TABLE 3
REACTIONS OF PRIMARY ALCOHOLS OVER REDUCED NICKEL OXIDE CATALYST[a]

Alcohol	Conversion	Selectivity[b]
1-Propanol	10.6	99
1-Butanol	11.2	>99
2-Methyl-1-propanol	8.0	98
2-Methyl-1-butanol	7.5	98
3-Methyl-1-butanol	10.9	99
Neopentanol	5.8	72[c]

[a] Catalyst: 7% Ni on Cab-O-Sil. Rate of flow: 11.8 ml H_2/min at 1 atm. Temp = 160°C.

[b] Toward ether formation (molar percent).

[c] Other products: 7% isobutane, 7% isopentane, and 14% neopentane.

tion which requires a special arrangement of the alcohol and the acidic and basic sites of the catalyst, and this is more difficult to obtain with a cyclic molecule of alcohol.

Low reactivity of secondary relative to primary alcohols toward ether formation may be due to steric or to polar effect. The question of which effect is dominant can be decided by correlating the results with Taft's σ^* and E_s values. For a rigorous correlation, the initial rates at various partial pressures of alcohols should be determined, but the accuracy of such determination cannot be high in the series of secondary alcohols, because, as shown in Fig. 1, plots of ether yield against reciprocal space velocity do not approach linearity even at conversions as low as 4–5%.* A possible reason for this is given later in the discussion of the retarding effect of water. In order to overcome this difficulty the yield obtained at 160°C and 11.8 ml hydrogen/min was defined arbitrarily as the measure of the reaction rate, and this value divided by the yield of ether from n-butanol was plotted against σ^* and E_s values (Figs. 2 and 3, respectively). Experiments with some primary alcohols were made at the same conditions in order to compare the reactions of secondary alcohols with primary alcohols.

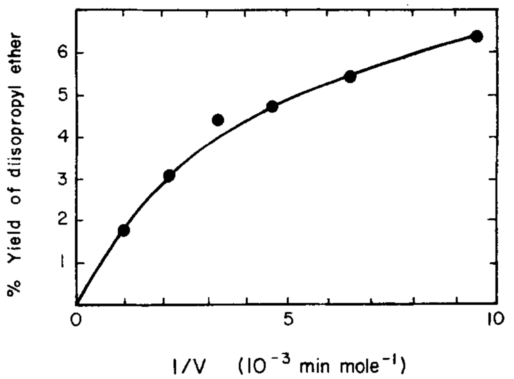

FIG. 1. Yield of diisopropyl ether at 160°C vs $1/v$. v = rate of flow of 2-propanol.

The results of experiments with primary alcohols are presented in Table 3. In Table 4 log y/y_0 and Taft's values of the various alcohols are presented, y being the yield of ether at the above conditions and y_0 the yield of di-n-butyl ether, which was chosen as a standard. Figures 2 and 3 are based on the data of Table 4. Although these plots are not based on true rate constants, they are probably a good reflection of the actual rate constants. It is therefore sig-

TABLE 4
VALUES FOR TAFT'S CORRELATION

Serial no.	Alcohol	$-\log (y/y_0)$	$-\sigma^*$ [b]	$-E_s$[b]
1	2-Propanol	0.311	0.190	0.47
2	2-Butanol	0.505	0.210	1.13
3	2-Pentanol	0.540	0.220[c]	1.20[c]
4	3-Pentanol	0.800	0.225	1.98
5	3-Methyl-2-butanol	1.318	0.215[c]	—
6	Cyclopentanol	0.270	0.200	0.51
7	Cyclohexanol	0.301	0.150	0.79
8	1-Butanol	0.000	0.130	0.39
9	1-Propanol	0.024	0.115	0.36
10	2-Methyl-1-propanol	0.153	0.125	0.93
11	2-Methyl-1-butanol	0.178	—	0.96[c]
12	3-Methyl-1-butanol	0.012	—	0.35
13	2,2-Dimethylpropanol	0.421	0.140	1.74

[a] Based on the data of Tables 2 and 3 for reactions at 160°C and 11.8 ml H_2/min.

[b] From Ref. (*12*).

[c] By interpolation.

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*Figure 1 shows the reaction with 2-propanol. Similar curves can be drawn with other secondary alcohols (Table 2).

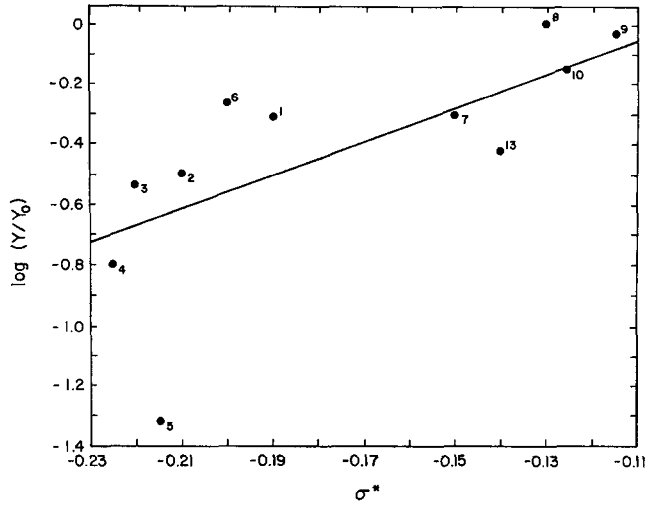

FIG. 2. Logarithms of rate constant ratios vs polar effect of alcohols. The numbers of points are the serial numbers of Table 4.

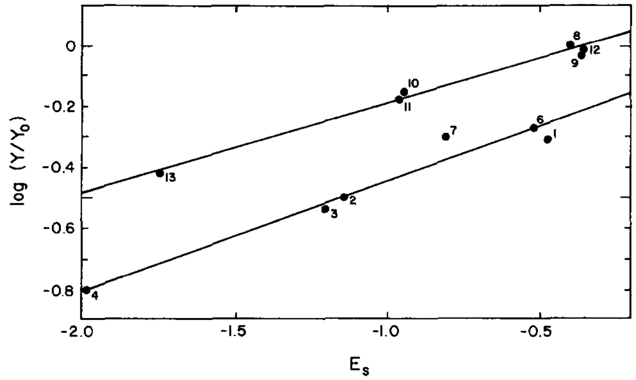

FIG. 3. Logarithms of rate constant ratios vs steric effect of alcohols. The numbers of points are the serial numbers of Table 4.

nificant that practically no correlation can be found between the value log y/y_0 and the polar factor. The line in Fig. 2 was drawn according to the least squares method; whereas in the plot of the same parameter vs the steric factor, Fig. 3, straight lines are obtained on which the experimental results can be accommodated without difficulty. Figure 3 shows that for both primary and secondary alcohols there is a good correlation with E_s, and even the sensitivity to steric factor is very similar in both series,† but there is an almost constant difference between the two series which is not due to a steric effect represented by E_s. This difference is probably caused by the greater basicity of the secondary alcohols which have σ^* values about 0.08 less than primary alcohols (Table 4).

The lower rate of ether formation with greater basicity of secondary alcohols can be rationalized by assuming that the sec-

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† It should be noted that this sensitivity is smaller than that found previously (7). This difference can be ascribed to the different supports, Cab-O-Sil vs kieselguhr. Few results with Cab-O-Sil presented in the previous paper also indicate that sensitivity to steric factor is smaller in Cab-O-Sil.

ondary alcohols reach lower energy level when adsorbed on acidic sites while the energy of the transition state for ether formation is about the same as in primary alcohols. If this is the case, the ΔF^* of the formation of etheric bond is greater, and if this step is rate determining, the whole reaction rate should be smaller. Another factor which may cause relatively low ether formation from secondary alcohols is retardation by the water formed in the dehydration reaction. Retardation by water which is much greater in secondary alcohols is discussed below.

Activation parameters. Activation parameters were calculated from the data given in Table 2. The yields of ethers at a flow of 11.8 ml hydrogen/min were taken as being proportional to the rate constants, as explained above. From the available data only the difference between ΔS^* for a given substance and that of 2-propanol could be calculated. The results are presented in Table 5 together with values for primary alcohols calculated previously (*7*). These results show that although secondary alcohols react slower, their ΔH^* is even lower than that of primary alcohols. Their low reactivity must therefore be due to the entropy factor. Possibly, these low values of ΔH^* and ΔS^* are a result of greater charge separation in the transition state due to greater basicity causing a greater negative charge on the attacking oxygen and greater positive charge on the attacked carbon. This causes a definite orientation of the charged species of the catalyst, and this orientation is also lowering the ΔH^* by stabilizing the charged organic species. This hypothesis is analogous with the known fact that ionizing an organic molecule in solution is accompanied with a very low ΔS^* which is attributed to the orientation of solvent molecules (*11*).

TABLE 5
ACTIVATION PARAMETERS FOR ETHER FORMATION[a]

Alcohol	ΔH^* (kcal/mole)	$\Delta S^* - \Delta S_0^*$ (e.u./mole)[c]
2-Propanol	8.3	0
2-Butanol	2.2	−14
2-Pentanol	2.0	−15
3-Pentanol	2.4	−16
3-Methyl-2-butanol	0.2	−23
Cyclopentanol	2.2	−14
Cyclohexanol	3.9	−10
1-Butanol[b]	16.2	−7[d]
2-Methyl-1-propanol[b]	17.2	−6[d]

[a] Based on reactions at 11.8 ml H_2/min, for secondary alcohols.

[b] From Ref. (*7*).

[c] ΔS_0^* is ΔS^* for di-2-propyl ether formation.

[d] Absolute value.

Within the series of secondary alcohols, ΔS^* is lower as the reaction is slower. This is to be expected since the main factor affecting the reaction rate within the series is the steric effect as appears from Fig. 3.

Retardation by water. The results of reactions of mixtures of water with some secondary and primary alcohols demonstrate that water retards the ether formation, and this retardation is much greater with secondary alcohols (Table 6). Dehydration efficiency to olefins, on the other hand, is reduced to a small extent only. The strong retardation by water may explain the form of the plot in Fig. 1. At very low conversions the amount of water is small

TABLE 6
EFFECT OF ADDED WATER[a]

Alcohol	Water (mole %)	Temp (°C)	Conversion[b]		Selectivity[b]
			Total	Olefins	
2-Propanol	0	160	8.7	3.2	63
	4	160	2.9	2.4	18
	0	190	18	6.3	65
	4	190	6.5	5.4	17
2-Butanol	0	190	17.4	11.8	32
	4	190	9.0	8.1	10
2-Pentanol	0	190	16.0	11.5	28
	4	190	11.0	9.9	10
1-Butanol	0	160	11.2	0.0	>99
	20	160	7.0	<0.1	99
2-Methyl-1-butanol	0	160	7.5	0.1	98
	20	160	2.8	0.1	96

[a] Reactions at a flow of 11.8 ml H_2/min at the conditions of Table 2.

[b] Defined as in Table 2.

and the slope of the line is relatively high —but it decreases as the conversion and the concentration of water becomes higher.

The difference in retardation by water between secondary and primary alcohols may be explained as follows:

a. The activated alcoholic oxygen atom is capable of two competitive reactions: (i) formation of an etheric bond by reaction of this oxygen with the activated carbon atom of a second alcohol molecule, and (ii) reaction between this oxygen and a proton of water, which produces in the overall reaction an exchange of hydrogen between alcohol and water. Possibly, the greater negative charge on the oxygen favors its tendency to react with proton vs the tendency to react with carbon, and therefore the retarding effect of water is more pronounced in secondary alcohols which are more basic.

b. An alternative explanation is that water molecules adsorbed in the neighborhood of alcohol molecules interfere with its proper orientation for ether formation. This effect is greater in secondary alcohols because of their steric structure. This steric factor is not represented by Taft's E_s (the difference between the E_s's of secondary and primary alcohols is not so striking, Table 4), because the latter represents the effect of crowding on the stability of the simple tetrahedral carbon, while the transition state for ether formation on the catalyst may have a more complicated structure.

Both of the above hypotheses can also be adduced to explain the fact that olefin formation is little affected by water. As to the first alternative, olefins would not result from reaction of a molecule containing an activated oxygen, but rather from one where the carbon atom is activated. Therefore, the presence of water should have only a small influence on olefin formation. The second explanation obviously does not apply to the olefins, since the latter do not require a second molecule for their generation.

Effect of sodium ion. Table 7 presents reactions of 2-propanol and 1-butanol at the same conditions as in Table 2 but with a catalyst containing 1% sodium relative to nickel. In both alcohols the yield of dehydration products is decreased by the presence of sodium by about the same factor. In 1-butanol there is also an increase in dehydrogenation products as indicated by *n*-butyraldehyde and propane, the latter being formed by the decomposition of the aldehyde. Acceleration of dehydrogenation reaction cannot be seen in secondary alcohols, because even without the sodium dehydrogenation to ketone reaches equilibrium. The decrease of yield of dehydration products is probably due to the reduction of the acidity of the catalyst by the presence of sodium ions. The experimental data support the hypothesis that ether formation is due to intrinsic acidic sites of the catalyst (*2*). The existence of intrinsic acidity as a source of catalytic activity in reduced nickel oxide catalyst has been shown recently in the study of hydrogenolysis of alkylcyclopropanes (*13*).

TABLE 7
EFFECT OF SODIUM ION[a]

Alcohol	With or without Na^+	% of products[b]		
		Ether	Aldehyde or ketone	Propane
2-Propanol	Without	10.1	13.6	5.5
	With	4.1	15.4	2.3
1-Butanol	Without	58	0	4
	With	25	1	6

[a] Conditions of Table II at 190°C and 11.8 ml H_2/min. Percentage of sodium ion: 1% relative to nickel.

[b] The remainder being the unconverted alcohol.

Effect of temperature of reduction. The effect of temperature of reduction of nickel oxide upon the yield and selectivity of ether formation is summarized in Table 8. Maximum conversion and ether yield is obtained at a reduction temperature of 500°C when the reaction temperature is 160°C and reduction temperature of 450°C when the reaction is carried out at 190°C.

Pines and Kobylinski (*2*) found much lower optimal reduction temperatures for ether formation from 2-methyl-1-butanol

TABLE 8

EFFECT OF REDUCTION TEMPERATURE OF NiO CATALYST[a] ON THE REACTION OF 2-PROPANOL[b]

Temp (°C)			
Reduction	Reaction	Conversion[c]	Selectivity[c]
350	160	3.8	43
350	190	11.7	20
400	160	5.4	60
400	190	18.5	35
450	160	8.7	74
450	190	20.2	57
500	160	13.1	73
500	190	19.0	37
550	160	5.9	72
550	190	10.3	34

[a] 187 mg of 15% Ni/Cab-O-Sil.

[b] At 11.8 ml H_2/min.

[c] Defined as in Table 2.

and neopentanol over unsupported reduced NiO catalyst. Further work should be done to see how the optimal temperature of reduction depends on the support or on the reactants.

Effect of nickel concentration. Experiments were made with catalysts containing various percentages of nickel. The results are summarized in Table 9. The amount of catalyst used was smaller as the nickel content increased so as to keep the absolute amount of nickel the same in each case, 28 mg.

TABLE 9

EFFECT OF NICKEL CONTENT OF THE NiO CATALYST[a] ON THE REACTION OF 2-PROPANOL[b]

Amount of catalyst (mg)	% of Nickel	Temp (°C)	Conversion[c]	Selectivity[c]
400	7	160	8.7	62
400	7	190	18.0	65
280	10	160	8.7	66
280	10	190	19.2	62
187	15	160	8.7	74
187	15	190	20.2	57
93	30	160	8.7	86
93	30	190	22.2	51

[a] 187 mg of 15% Ni/Cab-O-Sil.

[b] At 11.8 ml H_2/min.

[c] Defined as in Table 2.

It is interesting to note that the selectivity at 160°C increases with the nickel concentration, while at 190°C the trend is reversed. Higher selectivity for a more concentrated nickel catalyst can be understood on the basis of increased chance for acidic and basic sites being in the proper configuration for two alcohol molecules to form ether. It is more difficult to understand why this effect should no longer exist at 190°C. It may be that through adsorption of a molecule of alcohol on a basic site, the acidity of the acidic sites neighboring this basic site is enhanced. Thus the average acidity increases with percentage of nickel. Increasing acidity of a site should activate it toward olefin formation more than toward ether formation because the latter depends also on orientation which is not improved by increasing acidity. This leads to the conclusion that increasing nickel content should cause two opposing phenomena: (a) increasing of the ether–olefin ratio by the geometric effect, and (b) decrease of this ratio by enhancing the average acidity of the acidic sites. It may be that the first phenomenon is dominant at lower temperature, but the second increases more rapidly with temperature, and as the temperature becomes higher the second effect becomes dominant. The ratio between the two effects at given conditions should depend on the identity of the alcohol also, and this is probably the reason that Pines, Hensel, and Simonik (*6*) obtained results which are somewhat different from the present. They found that the conversion and selectivity in the dehydration of *n*-butanol, excluding propane formation, which is not a dehydration product, increased slightly from 5 to 10% nickel content and decreased slightly from 10% to 37%.

SUMMARY

There are four principal differences between the reactions of primary and secondary alcohols on reduced nickel oxide catalysts:

a. Primary alcohols are more reactive toward ether formation.

b. Secondary alcohols have greater tendency to dehydrate to olefin.

c. Water retards ether formation from secondary alcohols much more than primary.

d. Dehydrogenation is much faster in secondary alcohols where equilibrium ketone–alcohol is obtained.

The reactivity of both primary and secondary alcohols depends also on the structure of the alcohols.

The results presented are consistent with the hypothesis [Pines and Kobylinski, *J. Cat.* **17,** 375 (1970)] that dehydration of alcohols over reduced nickel oxide catalysts proceeds through intrinsic acidic and basic sites.

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