JOURNAL OF CATALYSIS 34, 338-344 (1974)

Reactions of Binary Mixtures of Primary and Secondary Alcohols Over Reduced Nickel Oxide–Cab-O-Sil Catalysts in the Presence of Hydrogen

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Received November 6, 1973; revised April 15, 1974

Gas phase dehydration of binary mixtures of two secondary or a primary and a secondary alcohol over reduced nickel oxide on Cab-O-Sil was studied in the temperature range of 160–190°C in a current of hydrogen. The relative yields of ethers differed from what would be expected from the reactivities of each compound taken by itself. Ether yields were reduced, and in particular for the more reactive secondary alcohols in the presence of a less reactive secondary alcohol, and even more so when the second alcohol is primary. These results can at least partly be explained as a consequence of competition of the two alcohols for active sites on the catalyst, and by the effect of water. They also lend further support to the assumption that the higher basicity of secondary alcohols is responsible for the difference of behavior compared with primary alcohols.

INTRODUCTION

In previous work in this series, it was shown that correlations between reactivities and Taft's steric factors E_s (*1*) exist both for primary (*2*) and secondary alcohols (*3*), whereas no such correlations can be set up for polar factors. On comparing ether formation in secondary and primary alcohols, it was found *inter alia* that for the former, the reactivity towards ether is much lower, and that retardation by water vapors is much more pronounced. Among the possible explanations for these facts the polar factor was adduced, in that secondary alcohols are stronger bases. Accordingly, it may be postulated that the energy level of adsorption on acidic sites lies lower, and that, if the level of the transition state remains the same for primary and secondary alcohols, the difference in energy levels is larger for the latter and the reaction rate is thus decreased.

It seemed that by working with pairs, in which at least one component was a secondary alcohol, further insight into the mechanism of ether formation could be obtained. Pairs of primary alcohols have been previously investigated (*4*) and their behavior could be predicted quite well from the reactivities of the single components.

EXPERIMENTAL PART

The experiments were conducted in a micropulse reactor described previously (*5*) and modified for continuous flow operation (*6*). Samples of the gas leaving the reactor passed into a gas-chromatograph. The columns have been described previously (*3*). The catalyst was 7% nickel on Cab-O-Sil reduced at 450°C. Conditions studied were: temperature, ratio between the two alcohols, ratio between alcohols and hydrogen, and flow rate of alcohols.

RESULTS

Binary mixtures of secondary alcohols. The experimental results which are given in Table 1 (for comparison see Table 2) were calculated on ketone-free basis. The dehydrogenation to ketone (*5*), which under

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TABLE 1
REACTIONS OF BINARY MIXTURES OF SECONDARY ALCOHOLS[a]

Alcohols		Percentage of alcohol appearing as[b]				
A	B	Temp (°C)	Alcohol	Symmetric ether	Mixed ether	Hydrocarbon
2-Butanol	2-Pentanol	160	A	2.0	1.9	8.2
			B	2.2	1.9	8.6
		190	A	2.4	2.3	10.6
			B	2.8	2.3	11.2
2-Propanol	3,3-Dimethyl-2-butanol	190	A	4.8	0	4.8
			B	0	0	7.4
2-Propanol	2-Butanol	160	A	1.2	0.8	2.2
			B	2.0	0.8	8.8
		190	A	2.6	1.6	4.4
			B	3.2	1.6	13.6
2-Propanol	2-Pentanol	160	A	0.6	0.4	2.4
			B	2.4	0.4	9.4
		190	A	1.2	0.6	4.8
			B	3.6	0.6	14.4

[a] Rate of flow: 11.8 ml H_2/min. Molar ratio of H_2 and each alcohol 3.1:1.

[b] On acetone-free basis.

the conditions of the reaction reaches equilibrium (*3*), takes place at different sites of the catalyst and can therefore be considered a side-reaction which is not relevant to the present study.

TABLE 2
REACTIONS OF SECONDARY ALCOHOLS[a]

Alcohol	Temp (°C)	Percentage of alcohol appearing as[b]	
		Ether	Hydrocarbon[c]
2-Propanol	160	5.5	3.2
	190	11.7	6.3
2-Butanol	160	4.3	9.2
	190	5.6	11.8
2-Pentanol	160	3.9	9.6
	190	4.5	11.6
3,3-Dimethyl-2-butanol	160	0	6.7
	190	0	9.9

[a] Taken from Ref. (*3*). Experimental conditions as in Table 1.

[b] On ketone-free basis.

[c] Alkanes formed by the hydrogenation of olefins produced from the dehydration of alcohols.

Using 2-butanol and 2-pentanol as the pair of alcohols, the quantities of the two symmetric ethers produced are about equal, although somewhat higher for the dipentyl ether, and the amount of mixed ether is about twice as much as that of the symmetric ethers. The latter is to be expected from consideration of statistical probability for a pair of alcohols of equal reactivity (*3*). In the mixture of 2-propanol with 3,3-dimethyl-2-butanol the latter does not form ether. Again, this is to be expected from its behavior when reacted by itself. The results obtained with mixtures of 2-propanol with 2-butanol or 2-pentanol, on the other hand, show an entirely unexpected picture. While 2-propanol, when taken singly, is more reactive than the other two alcohols in a mixture of alcohols, less di-2-propyl ether is formed than the symmetric ethers from the higher alcohols. Another remarkable result is that the absolute values of conversion are in all cases considerably lower than expected.

Mixtures of primary alcohols and 2-propanol. The results which are summarized in Table 3 were calculated on acetone free

TABLE 3

Reactions of Binary Mixtures of 2-Propanol and Primary Alcohols[h]

				Percentage of alcohol appearing as[a]			
				Ethers		Hydrocarbon formed through	
No.	Primary	Temp (°C)	Alcohol	Symmetric	Mixed	Dehydration[b]	Dehydroxymethylation
1	1-Butanol	160	Prim.	10.6	1.2	0	0[g]
			Sec.	0.1	1.4	1.1[g]	—
2		190	Prim.	40.4	4.4	0	2.6[g]
			Sec.	0.2	5.2	3.8[g]	—
3[c]		190	Prim.	48.3	6.0	0	4.1[g]
			Sec.	1.5	7.1	2.2[g]	—
4[d]		190	Prim.	52.2	1.5	0	3.4[g]
			Sec.	0	5.2	8.4[g]	—
5[e]		190	Prim.	6.4	5.5	0	8.7[g]
			Sec.	2.9	2.2	4.9[g]	—
6[f]		190	Prim.	13.5	12.3	0	9.7[g]
			Sec.	6.9	4.8	13.1[g]	—
7	2-Methyl-1-propanol	160	Prim.	2.6	0.9	0.9	0.9[g]
			Sec.	0.6	1.0	0.9[g]	—
8		190	Prim.	10.2	2.7	2.1	1.5[g]
			Sec.	1.7	2.9	3.6[g]	—
9	2-Methyl-1-butanol	160	Prim.	2.5	0.8	0.9	1.0
			Sec.	1.0	0.8	1.0	—
10		190	Prim.	9.6	2.6	2.0	2.8
			Sec.	3.3	3.1	1.8	—
11	3-Methyl-1-butanol	160	Prim.	9.6	1.2	0	0.2
			Sec.	0.2	1.2	1.0	—
12		190	Prim.	38.6	4.4	0.6	3.5
			Sec.	0.2	5.3	1.8	—
13	2,2-Dimethylpropanol	160	Prim.	1.3	1.3	1.2	0.2
			Sec.	1.7	1.5	1.2	—
14		190	Prim.	3.7	2.9	2.4	0.9
			Sec.	4.4	3.4	2.2	—

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[a] On acetone-free basis.

[b] The olefins formed from the dehydration were reduced to alkanes by hydrogen present.

[c] Molar ratio of hydrogen and each alcohol = 9.3:1:1.

[d] Molar ratio hydrogen:2-propanol:1-butanol = 9.3:1:3.

[e] Molar ratio hydrogen:2-propanol:1-butanol = 9.3:3:1.

[f] Molar ratio as in footnote *e*, rate of flow of hydrogen 3.9 ml/min.

[g] The dehydroxymethylation product of the primary alcohol, propane, is identical with dehydration product of 2-propanol. The contribution of each alcohol to the propane production was calculated from the mass balance. This introduces a considerable error.

[h] Conditions as in Table 1, unless otherwise stated.

basis. It is of interest to note the drastic reduction in conversion of 2-propanol to ether, when paired together with the primary alcohols over nickel-Cab-O-Sil. In the experiments when equimolar ratio of alcohols is used and the primary alcohols are not sterically hindered, as in 1-butanol or 3-methyl-1-butanol, the formation of the symmetric di-2-propyl ether from 2-propanol is virtually suppressed. When the ratio of 2-propanol is increased, the conversion to ether increases, as expected. On increasing the ratio of hydrogen to alcohol, the conversion to ether also increases in spite of the reduced partial pressure of the alcohols. The conversion of the primary alcohols to the symmetric ethers is almost in each case somewhat lower than that obtained for the reaction of the primary alcohol in the absence of 2-propanol. This can be seen by comparing the data in Table 3 with those of Table 5, without addition of water.

In contrast to the reduced conversion to ethers, the yields of hydrocarbons are in most cases similar to those which are obtained when the alcohols react singly. These results are summarized in Table 4. A notable exception to this rule is the strongly reduced yield of propane in the presence of primary alcohols.

DISCUSSION

General. It has been proposed previously (*2–4*, *6–8*) that ether formation takes place through a concerted reaction between two

TABLE 4

REACTIONS OF MIXTURES OF ALCOHOLS[a]: YIELDS OF HYDROCARBONS FORMED BY DEHYDRATION AT 190°C AND 11.8 ml/min

Alcohols		Yield of hydrocarbon formed by dehydration of alcohol A[b]
A	B	
2-Propanol	—	6.3
	2-Butanol	4.4
	2-Pentanol	4.8
	3,3,Dimethyl-2-butanol	4.8
	2-Methyl-1-butanol	1.8
	3-Methyl-1-butanol	1.8
	2,2-Dimethylpropanol	2.2
2-Butanol	—	11.8
	2-Propanol	13.6
	2-Pentanol	10.6
2-Pentanol	—	11.5
	2-Propanol	14.4
	2-Butanol	11.2
3,3,Dimethyl-2-butanol	—	9.9
	2-Propanol	7.4
2-Methyl-1-propanol	—	2.0
	2-Propanol	1.9
2-Methyl-1-butanol	—	2.1
	2-Propanol	2.0
2,2-Dimethylpropanol	—	2.7
	2-Propanol	2.4

[a] On ketone-free basis. The olefins produced by dehydration undergo rapid hydrogenation to alkanes.

[b] The results with 1-butanol and 2-methyl-1-propanol are not recorded because of the uncertainty in the numerical values (see Table 2, footnote *g*).

TABLE 5

REACTIONS OF PRIMARY ALCOHOLS AND OF 2-PROPANOL WITH AND WITHOUT THE PRESENCE OF WATER[a]

No.	Alcohol	Temp (°C)	Added water[b]	Total water, partial pressure (atm)	Percentage of alcohol appearing as							
					Alcohols	Ethers	Propane	*n*-Butane	Isobutane	*n*-Pentane	Isopentane	Neopentane
1	1-Butanol	160	0	0.018	88.7	11.1	0.1	0	—	—	—	—
2		190	0	0.107	38.0	57.6	4.4	0	—	—	—	—
3		190	0.080	0.120	45.8	49.8	4.4	0	—	—	—	—
4		190	0.160	0.136	52.4	43.2	4.4	0	—	—	—	—
5		190	0.250	0.152	60.0	35.6	4.4	0	—	—	—	—
6[c]		190	0	0.134	23.5	70.0	6.5	0	—	—	—	—
7[c]		190	0.250	0.174	48.5	45.0	6.5	0	—	—	—	—
8[d]		190	0	0.048	17.5	75.0	7.5	0	—	—	—	—
9[d]		190	0.250	0.070	26.5	66.0	7.5	0	—	—	—	—
10[e]		190	0	0.054	9.0	82.5	8.5	0	—	—	—	—
11[e]		190	0.250	0.076	17.0	74.0	9.0	0	—	—	—	—
12	2-Methyl-1-propanol	160	0	0.013	92.0	7.8	0.1	0	0.1	—	—	—
13		190	0	0.079	55.7	38.8	3.3	0.2	2.0	—	—	—
14	2-Methyl-1-butanol	160	0	0.012	92.5	7.3	—	0.1	—	0	0.1	—
15		190	0	0.076	57.9	37.0	—	3.0	—	0.2	1.9	—
16		190	0.250	0.120	80.6	14.1	—	3.1	—	0.2	2.0	—
17	3-Methyl-1-butanol	160	0	0.018	89.1	10.8	—	—	0.1	—	0	—
18		190	0	0.103	40.6	55.2	—	—	3.7	—	0.5	—
19	2,2-Dimethyl-1-propanol	160	0	0.012	94.2	4.2	—	—	0.4	—	0.4	0.8
20		190	0	0.033	83.5	12.6	—	—	1.1	—	0.9	1.9
21		190	0.250	0.097	93.4	2.8	—	—	1.2	—	0.8	1.8
22	2-Propanol[f]	160	0	0.019	91.3	5.5	3.2	—	—	—	—	—
23		190	0	0.039	82.0	11.7	6.3	—	—	—	—	—
24		190	0.04	0.042	87.8	6.1	6.1	—	—	—	—	—
25		190	0.09	0.050	92.8	0.5	5.7	—	—	—	—	—
26		190	0.14	0.063	94.4	0.2	5.4	—	—	—	—	—
27[c]		190	0	0.079	64.9	21.1	14.0	—	—	—	—	—
28[c]		190	0.04	0.081	71.0	16.0	13.0	—	—	—	—	—
29[d]		190	0	0.014	81.4	11.8	6.8	—	—	—	—	—
30[d]		190	0.14	0.023	92.5	1.0	6.5	—	—	—	—	—

[a] Conditions as in Table 1.

[b] Expressed as moles water: moles alcohol entering.

[c] Rate of flow 3.9 ml hydrogen/min.

[d] Molar ratio hydrogen: alcohol = 9.3:1.

[e] Combination of footnotes *c* and *d*.

[f] Molar percents on acetone-free basis, using for calculation data in Table 1, Ref. (*3*).

alcohol molecules one of which is adsorbed on an acid site, the other on a basic site. High yield of ether will be obtained when the sites are in proper geometric arrangement and if the alcohol is not hindered sterically. Thus, a good correlation between reactivity and the steric factor was established within each of the series of primary and secondary alcohols. The fact that secondary alcohols are much less reactive towards ether formation requires an additional explanation. It seems reasonable to connect the low reactivity of the secondary alcohols with their basicity. One can postulate that for the concerted reaction to take place and for the products to be desorbed it is necessary that adsorption on the acid and basic sites be rather weak and of comparable strength. If the alcohol is strongly basic, the delicate balance which is required for good conversion into ether will be upset. This reasoning leads to the conclusion that while within each series the decisive factor is steric, the difference between the series is due to the polar factor.

The different behavior of 2-propanol by itself and in mixture with 2-pentanol (Tables 1 and 2) is probably due to a competition for the acid sites of the catalyst, where 2-pentanol has the upper hand due to its higher basicity. This interpretation is supported also by the fact that over silica–alumina a mixture of 2-propanol and 2-pentanol yields the symmetric ethers in a ratio similar to that obtained from these alcohols when reacted singly (unpublished data).

The above model is also in agreement with the high activity of secondary alcohols in reactions where only one molecule and one site participate. Apart from the dehydrogenation reaction which most probably takes place on nickel sites, the conversion of secondary alcohols to olefins with subsequent hydrogenation to paraffins, is very pronounced. Whereas for 1-butanol, selectivity towards ether formation is almost quantitative, it is as low as 32% for 2-butanol, on ketone-free basis. It is also significant that the selectivity for ether as compared with paraffin fomation decreases with increase in basicity of the alcohols. At 160°C and at the conditions used in most experiments in the present work it is for the single alcohols as follows: 63% for 2-propanol, 32% for 2-butanol, 29% for 2-pentanol, 18% for 3-pentanol, etc. (see Table 2). The fact that the dehydration to olefin is generally little influenced by the presence of a second alcohol (Table 4) also shows that the adsorption and reaction of single relatively strongly basic molecules on sites of relatively strong acidity is easy and is not hindered by the ether reaction which takes place on less acid sites in concert with neighboring basic sites. The rather strong decrease in olefin formation in the presence of certain primary alcohols, generally bulky molecules, can at this stage not be satisfactorily explained.

Competition for adsorption sites. By an application of the Langmuir–Hinshelwood treatment, Šimonik and Pines (*2*) showed that the experimental results fit satisfactorily a model in which surface reaction is the rate determining step. On this basis, it becomes clear that the presence of a second alcohol should reduce conversion by competing for adsorption sites on the catalyst. The same approach also accounts for the fact that conversion is higher at lower partial pressures of the alcohols. It is evident that at lower pressures a smaller part of the catalytic sites is occupied by the competing alcohol, thus enabling higher conversion.

Effect of water. Secondary alcohols are particularly sensitive to retardation by water (*3*). When they react in mixture with primary alcohols which are more reactive, a relatively large amount of additional water is formed from this source. This should lead to strong reduction of the formation of secondary ethers. In order to determine the importance of this effect a series of experiments were made with 2-propanol mixed with a primary alcohol in which the influence of water formed in the reactions themselves and of varying amounts of added water were studied. The results of these experiments, which were in part reported previously (*3*), are compiled in Table 5. In the column "total water," the amount of water present at the end of the reaction is given. Although this method of presentation is not rigorous, it has however, the advantage of simplicity. In Table 6 predicted amounts of symmetric ethers were calculated for a few representative reactions, using the approach of Ref. (*2*).† The bases for this calculation were on the one hand the data of Table 5 interpolating or extrapolating to the values of total water obtained in the reaction mixture, and, on the other hand, values for equilibrium constants of adsorption adapted from Ref. (*2*). Comparison between the calculated values and those actually observed shows that the

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† The formation of mixed ethers has been disregarded, since their contribution is relatively small.

TABLE 6

MIXTURES OF PRIMARY ALCOHOLS AND 2-PROPANOL AT 190°C: PREDICTED AND OBSERVED PERCENTAGES OF ALCOHOLS CONVERTED TO SYMMETRIC ETHERS

					Percentage of alcohol converted to symmetric ether[a]					
					Predicted					
					Ignoring water effect		Considering water effect		Observed	
No.	Primary alcohol	Molar ratio (H_2: Prim.: Sec.)	H_2 (ml/min)	Actual water content (atm)	Prim.	Sec.	Prim.	Sec.	Prim.	Sec.
1	1-Butanol	3.1:1:1	11.8	0.099	57.6	11.7	>57.6	<0.2	40.4	0.2
2		9.3:1:1	11.8	0.043	75.0	11.8	77.0	<0.2	48.3	1.5
3		9.3:3:1	11.8	0.105	57.6	11.8	54.7	0	52.2	0
4		9.3:1:3	3.9	0.0805	82.5	21.1	72.5	17.4	13.5	6.9
5	2-Methyl-1-butanol	3.1:1:1	11.8	0.049	37.0	11.7	>37.0	1.7	9.6	3.3
6	2,2-Dimethylpropanol	3.1:1:1	11.8	0.036	12.6	11.7	11.9	>11.7	3.7	4.4

[a] On acetone-free basis.

strong decrease of di-2-propyl ether formation is to a large extent due to the water effect. The observed values for primary ethers are considerably lower than the predicted results although of the same order of magnitude.

SUMMARY

The study of binary mixtures containing at least one secondary alcohol demonstrated the following:

a. The amount of ether obtained from 2-propanol was smaller than that from higher secondary alcohols.

b. The amount of di-2-propyl ether obtained in the presence of a primary alcohol was drastically reduced.

c. Yields of ethers in general were lower than those obtained with the single alcohols.

d. Yields of ethers were higher at lower partial pressures of alcohols.

To explain these results in a qualitative way, the following effects were discussed: (a) the upsetting of the balance between adsorption on acid and basic sites of the catalyst, which is essential for the concerted reaction, (b) the competition for adsorption sites, (c) the effect of water.

The results lend support to the assumption that the polar factor plays an important role which becomes apparent by comparison between series of primary and secondary alcohols, whereas within each series the steric factor is decisive.

ACKNOWLEDGMENTS

This work was in part supported by funds from the Jakob S. Schächter endowment chair. Partial financial support of the Mobil Oil Corporation is gratefully acknowledged.

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