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Reactions of Alcohols

VIII. Dehydration of Binary Mixtures of Primary Alkanols Over Nickel–Cab-O-Sil Catalysts. Synthesis of Mixed Ethers*

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Equimolar binary mixture of primary alkanols was dehydrated over 5% nickel–Cab-O-Sil catalyst in the presence of hydrogen at 160 and 190° to a mixture of two symmetrical and one mixed ether. The following mixtures of alcohols were used: *n*-butyl alcohol with ethyl-, propyl-, 3-methylbutyl-, isobutyl-, and neopentyl alcohol; isobutyl alcohol with ethyl-, *n*-propyl-, and neopentyl alcohol, and ethyl alcohol with neopentyl alcohol.

The total yield of ethers was 94 to 97% at 160° and 72 to 85% at 190°, the remaining were products of dehydrogenation. The composition of the ethers depended greatly on the structure of the alcohols used. Steric factors play an important role in the rate of formation of the ethers.

In the previous papers of this series (*1–6*), it was shown that primary alkanols undergo dehydration to ethers over a nickel catalyst at 130–200°, in the presence of hydrogen. It was also demonstrated that mixed ethers can be produced when a binary mixture of alcohols is pulse-injected over a nickel–kieselguhr catalyst (*2*). The purpose of the present study was to investigate systematically in a continuous flow system the effect of the structure of alcohols on the yield and selectivity of the ethers produced. The microflow apparatus and experimental conditions used were similar to the ones described previously (*6*). The catalyst consisted of 5% nickel on Cab-O-Sil.

Nine combinations of equimolar mixtures of alcohols were used, Table 1. Three combination of alcohols were studied: (1) *n*-butyl alcohol with ethyl-, *n*-propyl-, 3-methylbutyl-, isobutyl, and neopentyl alcohol; (2) isobutyl alcohol with ethyl-, *n*-propyl, and neopentyl alcohol; (3) neopentyl alcohol with ethyl-, *n*-butyl-, and isobutyl alcohol.

The experiments were made at 160, 190, and 200°. The results obtained at 220° are not included because, at this temperature, part of the ethers underwent hydrogenolysis and thus it became difficult to interpret the data. At the lower temperatures the ethers were resistant to hydrogenolysis.

From a mixture of binary alcohols three ethers were produced: two symmetrical and one mixed ether, Table 1. The relative rate of symmetrical ethers produced from the passage of *n*-butyl alcohol with other alcohols over nickel catalyst is as follows: diethyl > dipropyl > di-3-methylbutyl > diisobutyl > dineopentyl. A similar order of reactivities was obtained when isobutyl alcohol mixed with the various alcohols was passed over the catalyst, Table 1, group 2. The yield of mixed ethers produced from neopentyl alcohol with ethyl-, butyl-, and

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TABLE 1
COMPOSITION OF ETHERS FROM BINARY MIXTURES OF ALCOHOLS OVER 5% NICKEL-CAB-O-SIL[a]

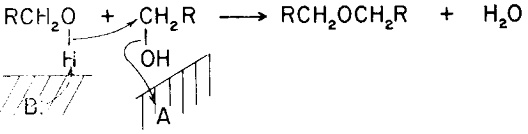
Temp (°C):	160					190				
Group alcohols A/B	Conversion (mole %)	Yield of ethers (mole %)	Composition of ethers			Conversion (mole %)	Yield of ethers (mole %)	Composition of ethers		
			AOA	AOB	BOB			AOA	AOB	BOB
1 n-C_4H_9OH/C_2H_5OH	41.0	96.6	3.3	46.4	50.5	80.2	84.0	5.1	46.6	48.2
n-C_4H_9OH/n-C_3H_7OH	33.0	96.7	6.1	50.6	43.3	64.6	83.4	8.9	55.9	35.1
n-$C_4H_9OH/(CH_3)_2CHCH_2CH_2OH$	30.8	96.4	17.8	49.8	32.3	63.0	81.0	25.1	50.8	24.1
n-$C_4H_9OH/(CH_3)_2CHCH_2OH$	25.3	96.8	44.5	47.9	7.5	52.9	81.1	38.1	51.6	10.1
n-$C_4H_9OH/(CH_3)_3CCH_2OH$	22.8	99.1	61.9	37.2	0.9	49.5	83.6	64.7	34.5	0.7
2 $(CH_3)_2CHCH_2OH/C_2H_5OH$	39.5	97.5	2.8	41.8	55.3	78.7	83.0	4.4	43.9	51.6
$(CH_3)_2CHCH_2OH/n$-C_3H_7OH	33.7	97.3	4.0	46.3	49.6	62.5	84.8	5.8	47.9	46.2
$(CH_3)_2CHCH_2OH/n$-C_4H_9OH	25.3	96.8	7.5	47.9	44.5	52.9	81.1	10.1	51.8	38.1
$(CH_3)_2CHCH_2OH/(CH_3)_3CCH_2OH$	15.3	94.1	72.9	26.4	0.7	41.2	72.3	71.8	27.5	0.7
3 $(CH_3)_3CCH_2OH/C_2H_5OH$	34.9	96.8	1.6	50.7	47.7	76.1	88.0	1.4	48.8	49.7
$(CH_3)_3CCH_2OH/n$-C_4H_9OH	22.8	99.1	0.9	37.2	61.9	44.5	83.6	0.7	34.5	64.7
$(CH_3)_3CCH_2OH/(CH_3)_2CHCH_2OH$	15.3	94.1	0.7	26.4	72.9	41.2	72.3	0.7	27.5	71.8

[a] Catalyst: 300 mg; flow of alcohols, 7.1 ml/hr/ml of catalyst (equimolar mixture of alcohols was passed); molar ratio of total alcohol to hydrogen = 1/2.6.

3-methylbutyl alcohol decreases with the increase of the molecular weight of the alcohols. The selectivity, however, of the formation of the symmetrical ethers, namely diethyl-, dibutyl-, and di-3-methylbutyl ether increases, respectively.

The rate of formation of symmetrical and mixed ethers is influenced by the structure of the alcohols. Substitution of a hydrogen by a methyl group in the β-position of ethyl alcohol reduces the rate of reaction and influences the selectivity of the ethers produced. The order of formation of mixed ethers is the same as that of symmetrical ethers, Table 2. Steric effects play an important role in the rate of reaction as shown by comparison of the reactivity of ethyl- vs propyl-, isobutyl-, and neopentyl alcohol.

There exists strong evidence (*2*, *3*, *7*) that the formation of ethers proceeds by the participation in the reaction of intrinsic acidic and basic sites of the catalyst:



$$RCH_2O + CH_2R \longrightarrow RCH_2OCH_2R + H_2O$$

In the case of mixed ethers it is necessary that both alcohols R^1OH and R^2OH are adsorbed on these sites:

1. A^1–* acid Alcohol R^1OH adsorbed on acidic site,
2. A^2–* acid Alcohol R^2OH adsorbed on acidic site,
3. A^1–* base Alcohol R^1OH adsorbed on basic site,
4. A^2–* base Alcohol R^2OH adsorbed on basic site,

There is only one possibility for the formation of symmetrical ethers, namely the interaction of A^1–* acid with A^1–* base and the interaction of A^2–* acid with A^2–* base.

In the case, however, of mixed ethers A^1–* base can react with A^2–* acid and vice versa. Statistically, therefore, the mixed ethers should be present in twice the concentration of each of the two symmetrical ethers, if steric factors are to be ignored. Experimental results demonstrate, however, that steric effects play a dominant role in the composition of the ethers in the reaction product.

The initial reaction rates for the formation of symmetrical and mixed ethers was determined by plotting the percentage of conversion of alcohols at 160 and 190° vs the reciprocal of space velocity of the individual alcohols and of the mixture of alcohols, Table 2. The plot was linear up to 25% of conversion. Since mixed ethers

TABLE 2

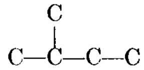
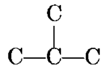
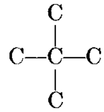
INITIAL RATES OF FORMATION OF ETHERS FROM BINARY MIXTURES OF ALCOHOLS OVER 5% NICKEL ON CAB-O-SIL

Temp (°C):	160 Initial rate of formation [moles/g (catal.) hr × 10^{-3}]; ethers			190 Initial rate of formation [moles/g (catal.) hr × 10^{-3}]; ethers		
Alcohols A/B	AOA	AOB	BOB	AOA	AOB	BOB
Butyl/Ethyl	2.5	73	45	6	125	69
Butyl/Propyl	4.5	58	25	8	100	34.5
Butyl/3-Methylbutyl	10	45	15	18.5	80	20
Butyl/Isobutyl	18	40.5	3.5	26	70.5	8
Butyl/Neopentyl	20.5	26.5	1	39	44.5	2
Isobutyl/Ethyl	2.2	67.0	43	4.5	118	67
Isobutyl/Propyl	3	56.5	29	6	85	45
Isobutyl/Neopentyl	16	11.5	0.5	32	25	0.9
Ethyl/Neopentyl	37.5	54	1.5	60	116	3

are produced from two different alcohols, for the calculation of reciprocal space velocity and for the estimation of initial reaction rates, the total feed of the mixture of alcohols was used. For the determination, however, of the initial rate of formation of symmetrical ethers, only half of the feed of the mixture of alcohols was used.

The initial rate of formation of the various ethers from the binary mixture of alcohols is given in Table 2. The relative rates of formation of symmetrical and nonsymmetrical ethers is given in Table 3.

TABLE 3
RELATIVE RATES OF FORMATION OF SYMMETRICAL AND NONSYMMETRICAL ETHERS

	Rates of formation	
Ethers A =	AOA[a]	AOB[b]
C—C	1.00	1.00
C—C—C	0.68	0.88
 $C-\overset{C}{C}-C-C$	0.75	0.80
 $C-\overset{C}{C}-C$	0.39	0.64
 $C-\overset{C}{\underset{C}{C}}-C$	0.09	0.45

[a] Taken from the calculated rate constants [Ref. (1), Table 2].

[b] Calculated from Table 1. B = C—C—C—C.

EXPERIMENTAL PART

Apparatus and Procedure

The experiments were made in a flow system using a microreactor which was adapted for that purpose (*4*, *6*).

The catalyst was prepared by precipitating in aqueous solution of $Ni(NO_3)_2\ 6H_2O$ with ammonium carbonate in the presence of dispersed Cab-O-Sil as described previously (*6*). The catalyst was reduced *in situ* in the presence of a flow of hydrogen. The temperature was raised slowly until it reached 400° and the catalyst was then maintained at this temperature for 2 hr.

The analysis of the ethers were made by vpc and a column filled with 15% Carbowax 20M on 60/80 Gas Pack W and maintained at 150°.

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