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Reactions of Alcohols

VII. Kinetic Studies of the Dehydration of Primary Alcohols to Ethers over Nickel Catalysts in the Presence of Hydrogen*

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Kinetic studies have been made of the conversion of primary alkanols to ethers over catalysts consisting of 6% nickel-kieselguhr and 6% nickel on Cab-O-Sil. The alcohols studied were ethanol, propanol, *n*-butanol, isobutyl alcohol, 2- and 3-methylbutanol, neopentyl alcohol, and 3,3-dimethylbutanol. The experiments were made at 140 to 190° in the presence of varying partial pressures of hydrogen and at combined pressures of hydrogen and alcohols ranging from 1.00 to 0.25 atm. It was found that although hydrogen does not participate in the reaction of conversion of alcohols to ethers, its presence seems to be required to maintain the oxidation of the nickel catalyst and/or to prevent the dehydrogenation of the alcohols to aldehydes which can then undergo a decarbonylation reaction. Kinetic evidence shows that steric effects control the rate of reaction. The following equation represents a satisfactory kinetic model for the reaction:

$$r^0 = kK_A^2P_A^2/(1 + K_AP_A)^4,$$

where r^0 = initial rate; k = rate constant of surface reaction; K_A = adsorption coefficient of alcohol; P_A = partial pressure of alcohol.

In previous papers of this series (*1–6*), it was reported that primary and secondary alkanols form ethers when passed over supported and nonsupported reduced nickel oxide catalysts. The reaction proceeds in the presence of hydrogen at temperatures ranging from 120 to 190°.

The purpose of the present study was to establish the rates of reactions of primary alkanols as functions of partial pressures of the alkanols and of their structures. A review of the literature (*7*, *8*) had shown that most of the kinetic studies in heterogeneous systems were made using alumina as catalyst and it was generally agreed that the formation of ethers follows a bimolecular reaction. The rate of ether formation from the following alcohols was determined, using nickel–kieselguhr as catalyst: ethyl-, propyl-, *n*-butyl-, isobutyl-, 2,2-dimethylbutyl- (neopentyl), 2- and 3-methylbutyl alcohol. A few experiments were also made using nickel on Cab-O-Sil as catalyst. An attempt to use unsupported nickel as catalyst was not successful because of the rapid deterioration of the catalyst.

EXPERIMENTAL PART

1. *Apparatus and Procedure*

The experiments were conducted in a micropulse reactor described previously

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(*9*), and modified for a continuous flow system operation (*1*).

A liquid nitrogen trapping technique was used to collect samples for vpc analysis (*3*, *9*, *10*). The descriptions of the columns and of the quantitative evaluation of the product was given previously (*1*).

The catalyst consisting of nickel oxide on support was reduced *in situ* at 400° for 2 hr in a flow of hydrogen. After the reduction, the temperature was lowered to the temperature at which the kinetic measurements were made. Most of the experiments were made at 160°.

2. Catalysts

a. Unsupported nickel oxide was prepared from 15% aqueous solution of nickel nitrate hexahydrate and ammonia, according to the procedure described previously (*5*).

b. 6% Nickel on kieselguhr. It was prepared from nickel nitrate hexahydrate, kieselguhr, and an aqueous solution of ammonium carbonate monohydrate (*1*, *3*).

c. 6% Nickel on Cab-O-Sil. The catalyst was prepared by the same method as described in (b). The Cab-O-Sil M-5 (Cabot Corporation, Boston, MA) is a commercial silica in the form of fine powder. The catalyst cake obtained from the precipitated nickel carbonate was dried and crushed to 100–200 mesh powder. The nickel carbonate on Cab-O-Sil was decomposed on heating to form nickel oxide, which was then reduced with hydrogen to nickel, according to the established procedure (*2*, *4*).

RESULTS AND DISCUSSION

Stability of the catalysts. Before any kinetic measurements can be made it is imperative to determine the stability of the catalysts over a long period of time towards the conversion of the alcohols to ethers.

It was found that reduced nickel oxide which was not deposited on support could not be used for the kinetic study because its activity and selectivity in the reaction of *n*-butanol has been changing continuously with the duration of the experiment (Fig. 1). On the other hand, nickel–kieselguhr showed excellent stability for catalytic activity and selectivity in the conversion of butanol, Figs. 2 and 3. At 160°, the conversion was 20% and the selectivity of the nickel–kieselguhr for the formation of ether was about 99%. At 190° and with longer contact time, the overall conversion was 91% but the selectivity for ether was about 72% with the remainder of the product consisting mostly of propane with smaller amount of butane. At both temperatures throughout 16 hr on stream, the catalyst did not demonstrate any alteration in its reactivity and selectivity.

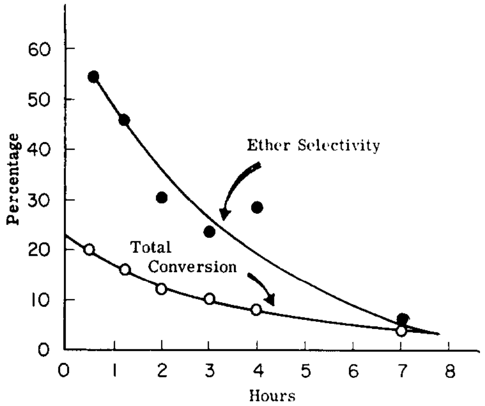


FIG. 1. Activity of unsupported nickel catalyst vs time on stream; experimental conditions: temp, 190°; ratio of *n*-butanol/hydrogen = 1:10; LHSV = 45.

Nickel on Cab-O-Sil also maintained its catalytic activity during the time of test which lasted 6 hr, Fig. 4. At 160°, 20% of *n*-butanol with a selectivity towards di-*n*-butyl ether of 98%. In addition both nickel on kieselguhr and nickel on Cab-O-Sil showed no deterioration of their activity and selectivity during intermittent runs lasting for days and during which time the temperature of the reaction has been varying between 120 and 210°. In order to maintain the stability of the nickel supported catalysts, it is essential that a stream of hydrogen passes over them, otherwise, there is a rapid deterioration of their catalytic activity. However, the latter can be restored by passing hydrogen at 190–220° over the catalyst.

The estimation of kinetic model for ether formation. From the experiments made with *n*-butanol at a combined partial pressure of alcohol and hydrogen equal to 1.0, 0.75, 0.50, and 0.25 atm, it was found that

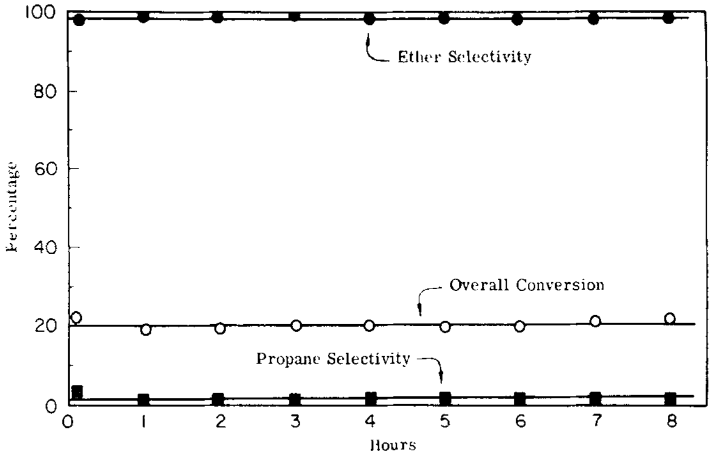


FIG. 2. Activity of 6% nickel on kieselguhr vs time on stream; experimental conditions: temp, 160°; ratio *n*-butanol/hydrogen = 1:10; LHSV = 16.1.

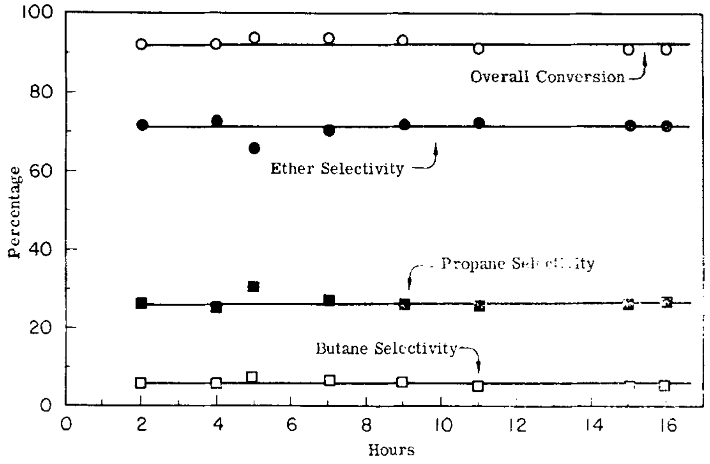


FIG. 3. Activity of 6% nickel on kieselguhr vs time; experimental conditions: temp, 190°; ratio of *n*-butanol/hydrogen = 1:10; LHSV = 4.

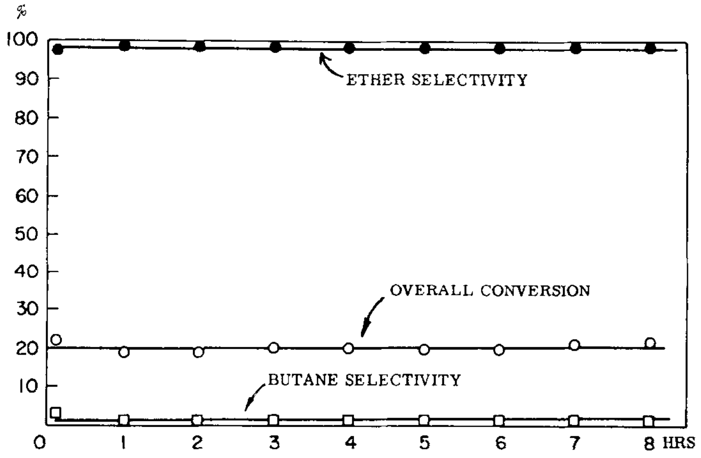


FIG. 4. Activity of 6% nickel on Cab-O-Sil vs time on stream; experimental conditions: temp, 160°; ratio of *n*-butanol/hydrogen = 1:10; LHSV = 4.

lowering of pressure had no influence on the reaction rate of alcohols to ethers. Lowering of pressure was achieved by diluting the vapors of the reactants with helium which is not adsorbed on the catalyst. From the above observation, it was concluded that hydrogen does not participate in the reaction and that the formation of ether proceeds through a bimolecular reaction.

The function of hydrogen seems to be to maintain the oxidation state of the nickel surface and/or to prevent the formation of aldehydes. The latter through a condensation reaction might lead to side-products which could deposit on the surface of the catalyst. It has been shown previously that a critical concentration of nickel oxide in the nickel containing catalyst is essential for an optimum yield of ethers (*3*).

In the derivation of rate equations, the Langmuir-Hinshelwood concept was applied, which was further developed by Hougen and Watson (*11*). It was assumed that alcohols were adsorbed on the catalytic surface with and/or without dissociation and that surface reaction or adsorption could be considered as rate determining step, while the desorption of the product was considered not to be a rate determining factor in the reaction.

Various assumed kinetic models for the dehydration of alkanols to ethers were evaluated (Table 1) to determine the model which best agrees with the experimental data. The procedure used for the evaluation of the data was the same as described by Hanĉil and co-workers (*12*). For the treatment of the kinetic data, Marquardt's procedure (*13, 14*) of nonlinear regression analysis was used. From the computation it was found that the kinetic model 3, Table 1, represented by the following equation, is in best agreement with the experimental data:

$$r^0 = kK_A{}^2P_A{}^2/(1 + K_AP_A)^4. \qquad (1)$$

Equation (1) is based on the assumption that the controlling step for the formation of ethers is surface reaction of two adsorbed molecules of alcohols, with two additional active sites present on the surface. This equation is in good agreement with the experimental dependence of the rate of ether formation on partial pressure of alcohols. The experimental and calculated dependence of the initial rates of reaction as a function of partial pressure of alcohols, $r^0 = f(P_A)$, for *n*-butyl alcohol and isobutyl alcohol over nickel–kieselguhr is given in Fig. 5 and that of *n*-butyl alcohol over nickel–Cab-O-Sil in Fig. 6.

The calculated rate constants for the formation of ethers k and the adsorption coefficients of alcohols K_A are given in Table 2.

The calculated activation parameters for the formation of di-*n*-butyl- and dissobutyl ether from the corresponding alcohols over

TABLE 1

EQUATIONS FOR ASSUMED KINETIC MODELS FOR THE DEHYDRATION OF ALKONOLS TO ETHERS[a]

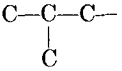
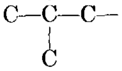
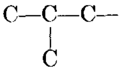
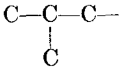
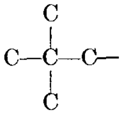
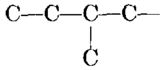
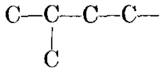
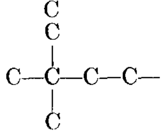
No.	Mode of adsorption (dissociation)	Rate controlling step	No. of centers	Model r^0 =
1	Without	Surface reaction	2	$kK_A{}^2P_A{}^2/(1 + 2K_AP_A)^2$
2[b]		Adsorption	1	$k_{ads}P_A/(1 + 2K_AP_A)$
3		Surface reaction	4	$kK_A{}^2P_A{}^2/(1 + 2K_AP_A)^4$
4	With	Surface reaction	4	$kK_A{}^2P_A{}^2/[1 + (K_AP_A)^{1/2}]^4$
5[b]		Adsorption	1	$k_{ads}P_A/[1 + (K_AP_A)^{1/2}]$
6	Without	Surface reaction	3	$kK_A{}^2P_A{}^2/(1 + K_AP_A)^3$
7	With	Surface reaction	3	$kK_A{}^2P_A{}^2/[1 + (K_AP_A)^{1/2}]^3$

[a] r^0 = initial reaction rate; k = rate constant of surface reaction; k_{ads} = rate constant of adsorption; K_A = adsorption coefficient of alcohol; P_A = partial pressure of alcohol.

[b] It is assumed that the absorption of only one molecule of the alcohol participating in the ether formation is involved in the rate determining step. Therefore $P_{A_1} = P_{A_2} = \frac{1}{2}P_A$, and $K_{A_1} \neq K_{A_2}$.

TABLE 2

CALCULATED RATE CONSTANTS FOR THE FORMATION OF ETHERS AND ADSORPTION COEFFICIENTS OF ALCOHOLS[a]

Alcohol ROH R =	Temp (°C)	Catalyst[b]	Initial rate constant (*k*)[c]	Adsorption coefficient of alcohols (K_A)[d]
C—C—	160	Ni-K	1.091	5.04
C—C—C—	160	Ni-K	0.738	5.20
C—C—C—C—	140	Ni-K	0.819	6.53
C—C—C—C—	140	Ni-C	0.846	4.63
C—C—C—C—	160	Ni-C	1.312	3.04
C—C—C—C—	190	Ni-C	7.333	2.42
 $C-\underset{\underset{C}{\vert}}{C}-C-$	160	Ni-K	0.419	6.97
 $C-\underset{\underset{C}{\vert}}{C}-C-$	160	Ni-C	0.943	2.38
 $C-\underset{\underset{C}{\vert}}{C}-C-$	175	Ni-C	2.390	2.24
 $C-\underset{\underset{C}{\vert}}{C}-C-$	190	Ni-C	3.711	2.12
 $C-\overset{\overset{C}{\vert}}{\underset{\underset{C}{\vert}}{C}}-C-$	160	Ni-K	0.102	4.46
 $C-C-\underset{\underset{C}{\vert}}{C}-C-$	160	Ni-K	0.354	5.38
 $C-\underset{\underset{C}{\vert}}{C}-C-C-$	160	Ni-K	0.813	7.54
 $C-\overset{\overset{C}{\vert}}{\underset{\underset{C}{\vert}}{C}}-C-C-$	160	Ni-K	0.406	5.10

[a] Calculated from the equation, $r^0 = kK_A{}^2P_A{}^2/(1 + K_AP_A)^4$.

[b] Ni-K, 6% nickel on kieselguhr; Ni-C, 6% nickel on Cab-O-Sil.

[c] mole hr^{-1} g^{-1} (catalyst).

[d] atm^{-1}.

nickel–Cab-O-Sil are given in Table 3. The calculations were made using the standard expressions and the FORTRAN program SVARRH and the rate constant values given in Table 2. The energy of activation for di-*n*-butyl- and diisobutyl ether were about the same 17 and 18 kcal, respectively. The entropy of activation, however, was lower for di-*n*-butyl ether and this could be ascribed to the structural parameter of the alcohol. It is interesting to note that the energies of activation for the formation of ethers over alumina catalysts are much higher, 25.9 ± 0.6 kcal for diethyl ether (*15*) and 25.1 ± 0.6 kcal for di-*n*-propyl ether (*16*).

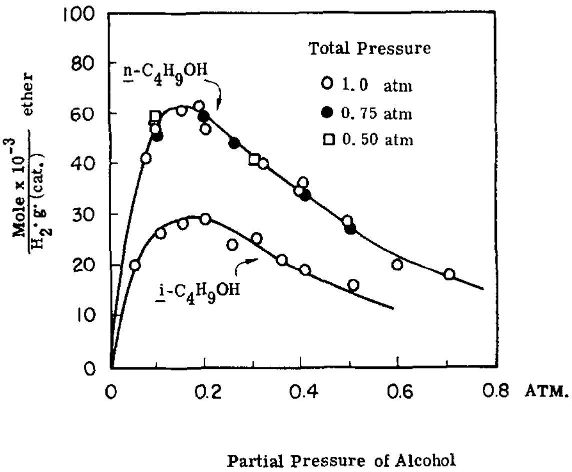


FIG. 5. Initial rate of ether formation vs partial pressures of alcohols; catalyst: 6% Ni on kieselguhr; temp of reaction, 160°.

Reaction of di-n-butyl ether. Dibutyl ether does not undergo any noticeable reaction when passed over nickel on Cab-O-Sil at 190° in the presence of hydrogen. The inertness of the ether towards hydrogenolysis can be ascribed to its low level of

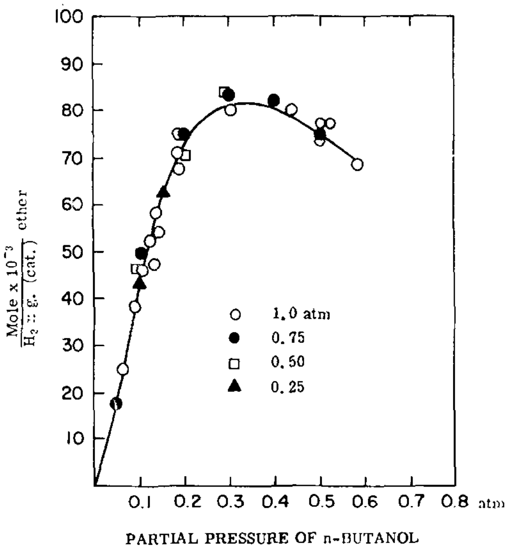


FIG. 6. Initial rate of formation of di-*n*-butyl ether vs partial pressure of *n*-butanol; catalyst: 6% Ni on Cab-O-Sil; temp of reaction, 160°.

TABLE 3
ACTIVATION PARAMETERS FOR THE FORMATION OF ETHERS ON NICKEL/CO-O-SIL

	Butanol	Isobutyl alcohol
Energy of activation, E_a(kcal/mole)	16.8 ± 2.4	18.2 ± 1.9
Enthalpy of activation, $\Delta H\ddagger$(kcal/mole)	16.2 ± 2.4	17.2 ± 1.9
Entropy of activation, $\Delta S\ddagger$(cal/°C mole)	−7.05	−5.72

absorptivity on the catalyst. This was confirmed by determining the reaction rates for the conversion of n-butanol to its ether in the presence of various partial pressures of added di-n-butyl ether (Table 4). The adsorption coefficient for the ether was calculated using the following equation:

$$r^0 = \frac{kK_A{}^2P_A{}^2}{(1 + K_AP_A + K_EP_E)^4} \qquad (2)$$

(K_E and P_E correspond, respectively, to adsorption coefficient and partial pressure of ether).

The calculated value of $K_E = 0.355 \pm 0.035$ atm^{-1} shows that, in comparison with the alcohols, ether is very weakly adsorbed on the catalyst and therefore once formed it is desorbed from the catalyst.

Influence of structure of alcohols on the rates of ether formation. The Taft equations 3 and 4 (*17–20*) were used to express the influence of the structure of alcohols on the rate of ether formation:

$$\log k/k_0 = \rho^*\sigma^* \text{ for polar effect,} \qquad (3)$$

or

$$\log k/k_0 = \delta E_s \text{ for steric effect.} \qquad (4)$$

The ratio k/k_0 is a ratio reaction rate constant or equilibrium constant reaction related to some standard reaction. In the present case, the standard reaction is the formation of dibutyl ether from n-butanol. The Taft equations are valid assuming that all primary alkanols are dehydrated to ethers by the same reaction mechanism and that the influence of the catalyst on the reaction of alcohols is constant. This means that all the primary alkanols are adsorbed on the catalytic sites in the same manner. The values derived from the Taft equations are given in Table 5. Linear regression analysis by means of a computer was used for the calculation of linear correlation of the relative rates of the reaction of alkanols, as a function of polar and steric effects of the substituents.

There is a good straight-line correlation between steric effects and the rate constant for ether formation, Fig. 7. There was, however, no linear correlation between polar effects and reactivity, Fig. 8. The results show that a methyl substituent on the β carbon atom lowers the reaction rate more than a substituent on the γ carbon, e.g., 2-methylbutyl- vs 3-methylbutyl alcohol and isobutyl alcohol vs n-butyl alcohol. Neopentyl alcohol reacts much slower than the other alcohols. The only exception was observed in the case of 3,3-dimethylbutyl alcohol.

Mechanism of reaction. It was previously shown that reduced nickel oxide in the presence of hydrogen is an excellent catalyst for the conversion of primary alcohols to the corresponding ethers and that the reaction is due to the presence of intrinsic acidic sites (*1–6*). It was also shown that

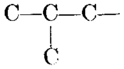
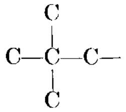
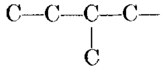
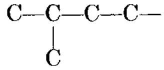
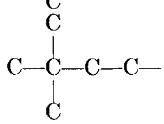
TABLE 4
REACTION RATE AND ADSORPTION COEFFICIENT OF DIBUTYL ETHER OVER NICKEL ON CAB-O-SIL[a]

Partial pressures (atm)			Reaction rate [moles hr^{-1} g^{-1} (catal.) × 10^{-3}]	Adsorption coefficient of ether K_E(atm^{-1})
Alcohol[b]	Ether[c]	Hydrogen		
0.185	0.094	0.721	302	0.390
0.700	0.0203	0.397	402	0.320

[a] Temp, 190°.
[b] n-Butanol.
[c] Dibutyl ether.

TABLE 5

SUMMARY OF THE DATA FOR THE TAFT EQUATIONS

Alcohol ROHR =	k/k_0	$\log k/k_0$	σ^{*a}	E_s^b
C—C—C—C—	1.000	0	−0.130	−0.39
C—C—	1.332	+0.2465	−0.100	−0.07
C—C—C—	0.401	−0.0449	−0.115	−0.36
 $\mathrm{C-\underset{C}{C}-C-}$	0.516	−0.2904	−0.125	−0.93
 $\mathrm{C-\overset{C}{\underset{C}{C}}-C-}$	0.124	−0.8338	−0.140	−1.74
 $\mathrm{C-C-\underset{C}{C}-C-}$	0.432	−0.3641		-0.96^c
 $\mathrm{C-\underset{C}{C}-C-C-}$	0.993	−0.0029		−0.35
 $\mathrm{C-\overset{C}{\underset{C}{C}}-C-C-}$	0.496	−0.3044		−0.34

[a] Ref. (*18*) p. 222 and 228 or Ref. (*20*).

[b] Ref. (*17b*).

[c] Estimated on the basis of linear correlation of steric effects of alcohols.

the formation of ethers is a concerted *trans*-elimination reaction in which intrinsic acidic and basic sites of the catalyst participate (*4*). The present kinetic studies indicate that four active sites of the catalyst are involved. To accommodate this observation we propose the following explanation:

1. Adsorption of two molecules of alcohol on the intrinsic and acidic sites of the partially reduced nickel oxide catalyst. The basic sites being the oxygen part and the acid sites the metal part of the catalyst; for simplicity they will be designed as A^+ and B^-.

2. The removal of the hydroxyl and hydrogen part of the alcohols is accompanied by the formation of a molecule of ether.

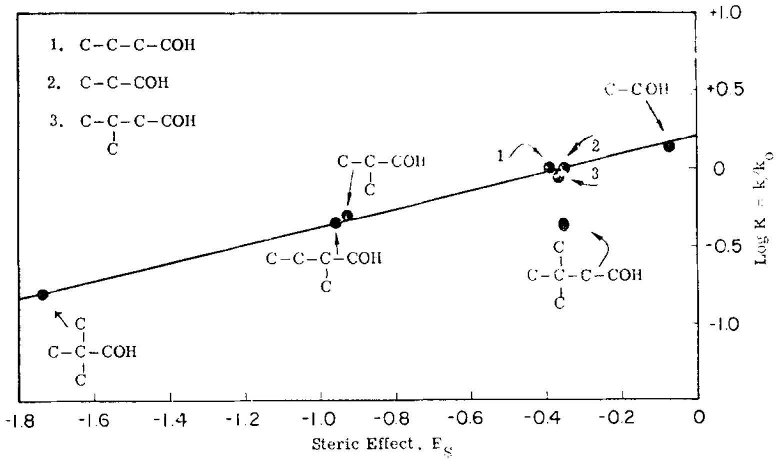


FIG. 7. Logarithms of rate constant ratios of formation of ethers vs steric effect of the alcohols.

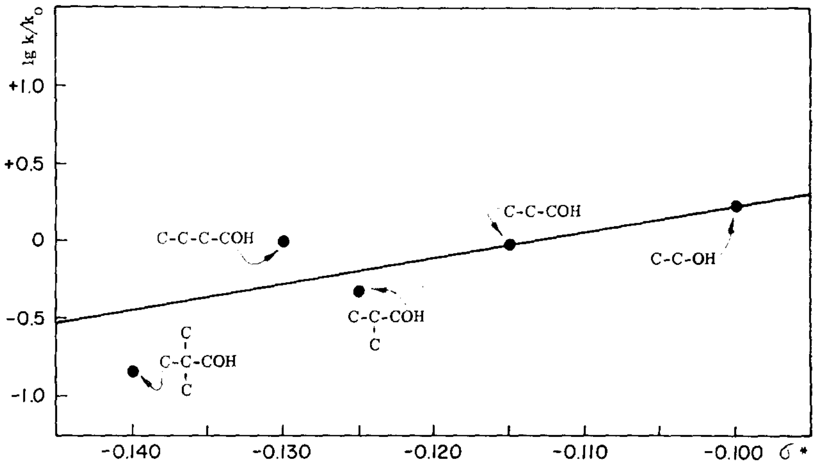
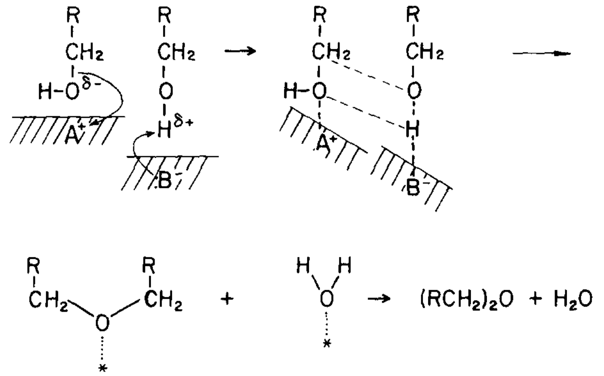


FIG. 8. Logarithms of rate constant ratios of formation of ethers vs polar effect of the alcohols.

3. Two active catalytic sites participate in the adsorption of a molecule of water and a molecule of ether.

4. Desorption of the desorbed molecules:



The rate of reaction depends on the structure of the alcohols and it is governed by steric consideration. Introduction of methyl groups in the β carbon of the alcohols lowers the rate of ether formation.

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