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Alcohol Dehydration: Mechanism of Ether Formation Using an Alumina Catalyst

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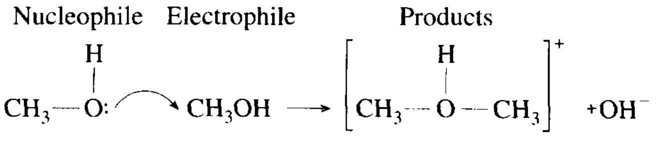
Ether formation during the dehydration of secondary alcohols, namely, 2-butanol, 3-pentanol, and 1-cyclopentylethanol, was investigated. Using the proper reaction conditions, the yield of di-2-butyl ether during the dehydration of 2-butanol on alumina can be as high as 40%. That ether is formed by adding an alcohol to the alkene is ruled out by the results from deuterium tracer studies. Results from experiments using S(+)-2-butanol suggest that the formation of di-2-butyl ether occurs by a S_N2-type mechanism. © 1995 Academic Press, Inc.

INTRODUCTION

Alumina-catalyzed dehydration of alcohols has been known for centuries (1, 2). Despite many years of study, the mechanisms for the formation of the olefin and ether products are still not clear. During the dehydration of an alcohol, both an intramolecular dehydration and an intermolecular dehydration may occur. The relative amounts of these pathways depend on the reaction conditions as well as the reactant and catalyst used. It has been reported (3) that the intermolecular dehydration of two alcohol molecules to form an ether, using alumina as a catalyst, has a lower activation energy than the intramolecular dehydration to produce alkenes. Therefore, at low temperatures the thermodynamically less favorable bimolecular ether may be the kinetically favored product. In the 1960s, several research groups studied the mechanisms for ether formation during dehydration of alcohols on alumina. Knözinger *et al.* (4, 5) studied the dehydration of aliphatic alcohols and found that formation of ether during the dehydration of primary alcohol occurred by a Langmuir–Hinshelwood mechanism. These authors reported that ethers cannot be formed from a secondary alcohol, except for isopropanol, because branched aliphatic ethers are not favored thermodynamically. In contrast to Knözinger *et al.*, DeBoer *et al.* (3) reported that the formation of ether occurred by both Rideal–Eley and Langmuir–Hinshelwood mechanisms. Pillai *et al.* (6, 7) studied the dehydration of methanol, 2-propanol, 1-propanol, and a mixture of methanol and (+) 2-butanol. They concluded that ether is formed by a Langmuir–Hinshelwood mechanism. In the study by Pines and Haag (8), the ether may not be present because of the high reaction temperature of 350°C that they used. However, in the experiments conducted by Knözinger *et al.* (9) and Kannan and Pillai (7), this ether is expected according to the present results; however, these authors did not report the formation of the ether. Shortly following the publication of the mechanism by Pillai and co-workers (6, 7), first Notari (10) and then Figueras *et al.* (11) questioned the validity of the mechanism.

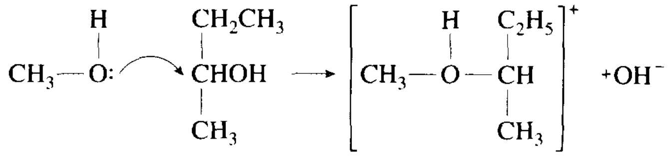
The previous workers, despite the conflicting views and a disagreement in interpreting the mechanism, agreed that ether formation from a secondary alcohol, and 2-butanol in particular, is very difficult. In particular, Knözinger *et al.* (9) reported that the only products from the dehydration of 2-butanol are alkenes and water, even at temperature as low as 200°C. Kannan and Pillai (7) reported that the only ether product from the dehydration of a mixture of 2-butanol and methanol is methyl 2-butyl ether. Thus, almost all of the mechanisms proposed for ether formation is based on results using primary alcohols.

Ether formation from alcohols involves a nucleophilic and an electrophilic species. For the mixed alcohols used by Kannan and Pillai (7), four reactions are possible.



$$\mathrm{CH_3{-}\overset{H}{\overset{|}{O}}{:}\ \curvearrowright\ CH_3OH \longrightarrow \left[CH_3{-}\overset{H}{\overset{|}{O}}{-}CH_3\right]^+ + OH^-}$$

[1]



$$\mathrm{CH_3{-}\overset{H}{\overset{|}{O}}{:}\ \curvearrowright\ \overset{CH_2CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{CHOH}}} \longrightarrow \left[CH_3{-}\overset{H}{\overset{|}{O}}{-}\overset{C_2H_5}{\overset{|}{\underset{\underset{CH_3}{|}}{CH}}}\right]^+ + OH^-}$$

[2]

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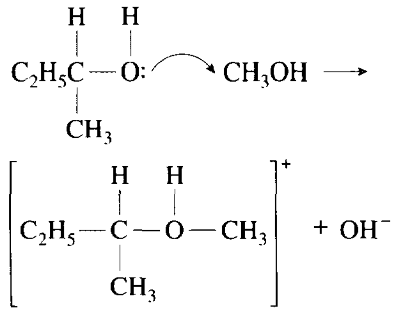
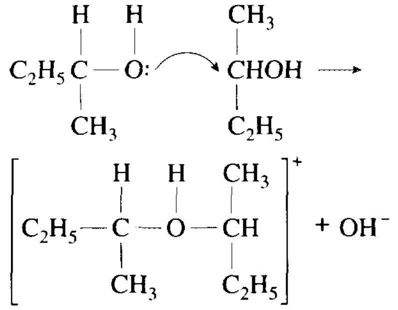
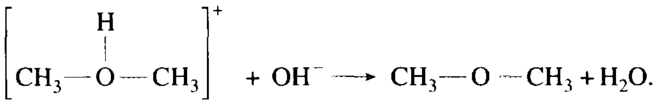


$$C_2H_5\overset{H}{\underset{CH_3}{C}}-\overset{H}{O}{:}\curvearrowright CH_3OH \longrightarrow \left[C_2H_5-\overset{H}{\underset{CH_3}{C}}-\overset{H}{O}-CH_3\right]^+ + OH^- \qquad [3]$$



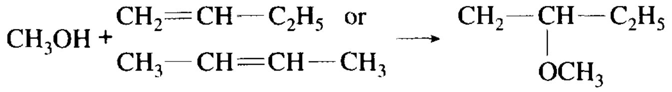
$$C_2H_5\overset{H}{\underset{CH_3}{C}}-\overset{H}{O}{:}\curvearrowright \overset{CH_3}{\underset{C_2H_5}{CHOH}} \longrightarrow \left[C_2H_5-\overset{H}{\underset{CH_3}{C}}-\overset{H}{O}-\overset{CH_3}{\underset{C_2H_5}{CH}}\right]^+ + OH^- \qquad [4]$$

The final step involves the formation of water from the ionic products as, for example,



$$\left[CH_3-\overset{H}{O}-CH_3\right]^+ + OH^- \longrightarrow CH_3-O-CH_3 + H_2O. \qquad [5]$$

Reactions [1–5] are not written as concerted reactions so that emphasis can be placed upon the role of the nucleophile and electrophile. Since methanol is considered to be a better nucleophile and, therefore, a poorer electrophile than 2-butanol, reaction [2] is considered to occur most readily. Similarly, reactions [1] and [4] should be easier than reaction [3]. Another pathway to form the mixed ether, methyl-2-butyl ether, is the reaction between the alcohol and the olefins formed by 2-butanol dehydration.



$$CH_3OH + \begin{matrix} CH_2{=}CH-C_2H_5 \text{ or} \\ CH_3-CH{=}CH-CH_3 \end{matrix} \longrightarrow CH_2-\underset{OCH_3}{CH}-C_2H_5 \qquad [6]$$

Much can be learned about the mechanism of the reaction and the nucleophile leading to the mixed ether through the use of a stereoisomer of a suitable alcohol. Consider the conversion of *S*-(+)-2-butanol. If the mixed ether is formed by reaction [2], the product should be the ether formed by a backside attack (Walden inversion) by the nucleophile. If methanol serves as the nucleophile (reaction [2]) the stereochemistry of 2-butanol should be inverted so that methyl-*R*-(−)-2-butyl should be the only ether formed. If, on the other hand, 2-butanol serves as the nucleophile (reaction [3]) the stereochemistry of the 2-butanol should be retained and the mixed either would be methyl-*S*-(+)-2-butyl ether. For reaction [4], the stereochemistry of the Walden inversion would require (*R,S*)-di-2-butyl ether to be the only ether product.

There is abundant literature to show that di-n-butyl ether is formed during the dehydration of 1-butanol on alumina even at temperatures as high as 260°C (e.g., Ref. (12) and references therein). It is not clear why 2-butanol should be so different from 1-butanol. Our current interest in the mechanistic studies on the dehydration of alcohols with metal oxide catalysts led us to study ether formation from secondary alcohols.

EXPERIMENTAL

Catalysts. Al_2O_3 was precipitated from a solution of aluminum isopropoxide in isopropyl alcohol by the addition of H_2O. The surface area, after calcination at 600°C for 16 h, was 210 m^2/g. Prior to use as an alcohol conversion catalyst, the metal oxide was pretreated under H_2 at 500°C overnight.

Reagents. 1-Cyclopentylethanol was purchased from Lancaster Synthesis Inc. and had a purity of 97%. All other undeuterated reagents and solvents were obtained from Aldrich and had a purity (GC) of 99% or better except for *S*-(+)2-butanol, the optical purity of which is 84% since it contains 16% of *R*-(−)2-butanol.

2-Butanol-d_5 ($CD_3-CH(OH)-CD_2-CH_3$) and 3-pentanol-d_4 [$CH_3CD_2CH(OH)CD_2CH_3$] were synthesized from 2-butanone and 3-pentanone, respectively, by a modified procedure (13) through repeated exchange with D_2O in the presence of Na_2CO_3 and then by reduction of the exchanged ketone to the alcohol with $LiAlH_4$. ^1H NMR, ^2H NMR and GC/MS data indicate that ≥98% of the hydrogens in the 1 and 3 positions of 2-butanol and in the 2 and 4 positions of 3-pentanol had been exchanged with deuterium.

Run procedure. The alcohol conversion was effected in a plug flow reactor fitted with a thermowell extending to the center of the catalyst bed. About 20–30 ml of the reactor volume above the catalyst bed contained Pyrex glass beads to serve as a preheater. The alcohol was fed using a syringe pump. In some runs toluene was added to the feed to serve as an internal standard. In the case of the intermolecular competition experiments, equal amounts of undeuterated and deuterated compounds were used as the feed. Liquid products were collected at 0°C (ice trap) and gas products were collected at −68°C (dry ice-acetone trap).

Analysis. The percentage conversion was determined by GC using a DB-5 column. Reaction products were identified by GC/MS, ^1H NMR, ^{13}C NMR, and 2D NMR. A

TABLE 1
Product Distribution from the Dehydration of a Mixture of Methanol and 2-Butanol on Alumina at 220°C[a]

Product	Mol%		
	Methanol/2-butanol (1 : 1)	Methanol/2-butanol (2 : 1)	Methanol/2-butanol (1 : 2)
Dimethyl ether	3.6 (14.0)[b]	8.8 (21.6)[b]	1.6 (5.9)[b]
Butenes	74.4	59.2	72.9
2-Butyl methyl ether	19.4 (75.5)[b]	30.4 (74.5)[b]	20.3 (74.6)[b]
Di-2-butyl ether	2.7 (10.5)[b]	1.6 (3.9)[b]	5.3 (19.5)[b]

[a] The total conversion in these runs is less then 50%.

[b] Mole percent distribution among ether products.

Varian 400 mHz spectrometer was used. The mixture of optically active and inactive isomers was analyzed by an optical active column (Cyclodex-B) and a flame ionization detector.

RESULTS

In a study of ether formation during the dehydration of a mixture of methanol and 2-butanol, Kannan and Pillai (7) reported that only one ether, 2-butyl methyl ether, was formed. In the initial phase of this study, runs were made using the same reaction conditions as used by Kannan and Pillai. The products (Table 1) show that for a methanol : 2-butanol = 1 : 1 molar reaction mixture, all three of the possible ethers were formed. Because dimethyl ether and the butenes have appreciable vapor pressure at the temperature of the first trap (about 0°C) and the other two ethers are liquids, obtaining an accurate mass balance is a demanding task. Based on the products trapped in the 0 and −68°C traps, it is observed that the percentage of the mixed ether remains essentially constant as the methanol/2-butanol ratio varies from 2 : 1 to 1 : 2 (Fig. 1). The percentage of the dimethyl or di-2-butyl ether varies according to the ratio of the corresponding alcohol in the reaction mixture. The formation of an ether requires two alcohol molecules; thus, the amount of dimethyl and di-2-butyl ether formed should depend upon the surface coverage of the corresponding alcohol. For a zero-order dependence on alcohol pressure for alcohol dehydration, as has been observed for numerous studies (for example, 11, 14, 15) the surface concentration of an adsorbed alcohol should depend directly upon the partial pressure of the corresponding alcohol. Likewise, the involvement of an Eley–Rideal mechanism (16) would show a rate that depends upon the partial pressure of the alcohol. The data in Fig. 2 show that this is indeed the case except for the highest partial pressure data point for dimethyl ether formation. The total mole fraction of ethers (23–25%) in the product remains essentially constant from a reactant feed of pure 2-butanol up to a mixture of methanol/2-butanol = 1/1 (Fig. 1), and the mole fraction of the butene also remains constant (75–78%) over the same feed composition range. This implies that adsorbed methanol and adsorbed 2-butanol are about equally effective as nucleophiles.

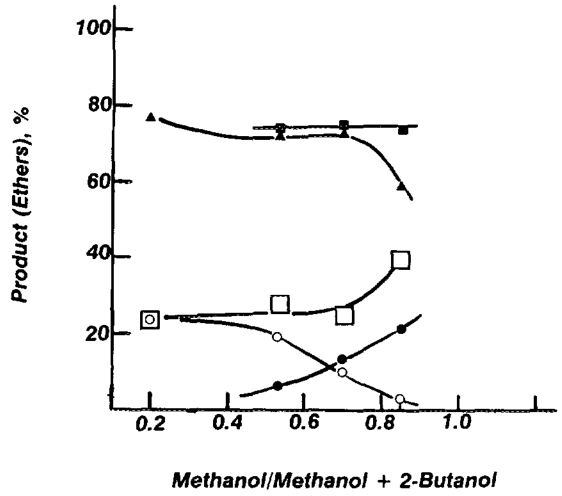


FIG. 1. Distribution of products from the conversion of mixtures of methanol and 2-butanol: ▲, (butenes)/(butenes + ethers) × 100; □, total ether, (ethers/ethers + butenes); ■, methyl-2-butyl ether, percentage of total ethers; ○, di-2-butyl ether, percentage of total ethers; ●, dimethyl ether, percentage of total ethers.

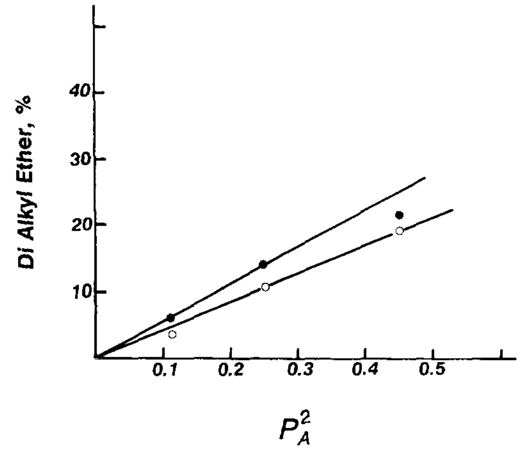


FIG. 2. Dependence of percentage of total ether that is represented by di-2-butyl ether (○) and dimethyl ether (●) upon the partial pressure of the corresponding alcohol.

In conducting the analyses for the present study, a high-resolution DB-5 capillary GC column was used to separate and quantify the dehydration products. Thus, baseline separation was obtained for all of the ether products reported in Tables 1–3. The dominant ether is methyl-2-butyl ether (75 mole%) and, with the GC columns available in the 1960s, it is likely that the failure of Kannan and Pillai (7) to detect all three ethers was due to the relatively poorer analytical capability at the time they conducted their exper-

TABLE 2

The Distribution of Ether Isomers Formed during the Dehydration of S-(+)2-butanol and of a Mixture of Methanol and S-(+)2-butanol Using an Alumina Catalyst[a]

Reagent	*S*(+)2-butanol	*S*(+)2-butanol	*S*(+)2-butanol/ methanol (1 : 1)	*S*(+)2-butanol/ methanol (1 : 2)	*S*(+)2-butanol/ methanol (2 : 1)
Temperature (%)	230	220	220	220	220
Product (mole%)[b]					
R-(−) BME	—	—	—	75	74
S-(+) BME	—	—	—	25	26
(*R*,*R*)-DBE	13.8	13.0	13.7	—	—
(*S*,*S*)-DBE	13.8	13.0	12.8	—	—
(*R*,*S*)-DBE	72.4	74.0	73.5	—	—

[a] S(+)2-butanol used in this study contains 16% R(−)2-butanol.

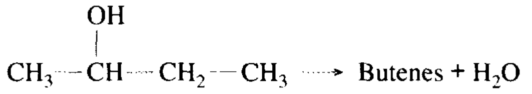
[b] BME, 2-butyl methyl ether; DBE, di-2-butyl ether.

iments. It is noted that Jain and Pillai (6) did report the formation of significant amounts of di-isopropyl ether in the products from the dehydration of isopropanol with an alumina catalyst.

The formation of di-2-butyl ether was effected during the dehydration of *S*-(+)-2-butanol. These results, together with those obtained with a reaction mixture of methanol and *S*-(+)-2-butanol, are compiled in Table 2. As can be seen from the data in Table 2, the (*R*,*S*) isomer accounts for about 73% of the ether and amounts of the (*R*,*R*) and (*S*,*S*) isomers are about equal. The *R*-(−)-2-butanol impurity in the reactant used in this study requires that a maximum of 73% of the (*R*,*S*) ether isomer can be formed if the reaction involves a Walden inversion and that the other 27% of the ether products be comprised of equal amounts of the (*R*,*R*) and (*S*,*S*) isomers that arise from the impurity optical isomer. The probabilities for the formation of ether products from a molar fraction mixture of 0.84 *S*-(+)-2-butanol and 0.14 *R*-(−)-2-butanol are such that the following percentages of ethers should be formed: (*S*,*R*), 2.6% [(0.16)(0.16)100]; (*R*,*S*), 70.6 [(0.84)(0.84)100]; (*R*,*R*), 13.4 [(0.16)(0.84)100]; and (*S*,*S*) 13.4. Since the (*R*,*S*) and (*S*,*R*) ethers are the same compound, this peak should correspond to 73%. These results indicate that di-2-butyl ether is formed almost exclusively during the dehydration of 2-butanol by a backside attack involving a S_N2 mechanism.

Based on the above results, it is reasonable to assume that during ether formation it is the alcohol acting as an electrophile that would undergo inversion of its configuration. If this is true, then a mixture of *S*(+)2-butanol (containing 16% of *R*(−)2-butanol) and methanol would produce 84% of the *R*(−) 2-butyl methyl ether and 16% of S(+)2-butyl methyl ether (Eq. [2]). As can be seen from the data in Table 2, about 75% of *R*-(−)2-butyl methyl ether and about 25% of *S*(+)2-butyl methyl ether were obtained. The reason for the uncertainty in the amounts of the ethers is that the separation of the *R* and *S* isomers of 2-butyl methyl ether with the Cyclodex-B column does not give baseline separation. Thus, the experimental error may be reasonably large, depending on the relative concentration of the two compounds. In spite of this uncertainty, the data show that if any ether products are formed by Eq. [3], they must be less than 10%.

It is difficult to compare the contributions of Eq. [1] and Eq. [4] because the formation of di-2-butyl ether in Eq. [4] must compete with the formation of butenes (Eq. [7]), and the latter is the major pathway under our reaction conditions.



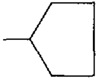
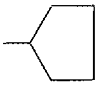
$$CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_2-CH_3 \longrightarrow \text{Butenes} + H_2O \qquad [7]$$

The yields of 2-butyl ethers at different reaction temperatures are summarized in Table 3. At 220°C, about 40–50% of di-2-butyl ethers is included in the total products. In these runs, about 15% toluene was added to the alcohol to serve as an internal standard in order to calculate the total conversion and mass balances. The data in Table 3 may not represent the true activity and selectivity of the catalyst because of the presence of toluene. However, runs made in the absence of toluene on a larger scale in order to prepare about 6 g of pure di-2-butyl ether for identification purposes (17) indicate that the presence of toluene did not make a measurable difference. Also included in this table are the data for ether formation during the dehydration of 3-pentanol and 1-cyclopentyl ethanol. In the case of 3-pentanol, di-3-pentyl ether accounts for about 5 wt.% of the conversion products; in the case of 1-cyclopentyl ethanol, the yield of di-1-cyclopentylethyl ether is about 2.6 wt.% of the products at 200°C. Efforts were not made to obtain the reaction condition to maximize the yield of these latter two ethers. However, from the above results it seems clear that under the proper conditions, ether can be produced during the dehydration of a secondary alcohol with alumina.

The synthesis of di-2-butyl ether in high yields is very difficult. The Williamson method, commonly used for ether synthesis, was unsuitable for the formation of di-2-butyl

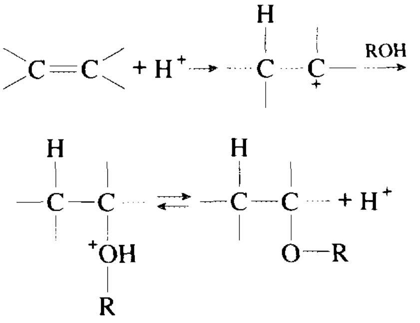
TABLE 3

Ether Formation during the Dehydration of a Secondary Alcohol RCHOHR′ Using an Alumina Catalyst

Reagent		Temperature (°C)	Conversion (Wt%)	Ether Wt% of conversion products	Alcohol conversion rate (mol m^{-2} sec^{-1})
R	R′				
$-CH_3$	$-CH_2CH_3$	220	23	41.7	7.54×10^{-9}
$-CH_3$	$-CH_2CH_3$	230	37	31.4	12.13×10^{-9}
$-CH_3$	$-CH_2CH_3$	240	76	6.8	24.92×10^{-9}
$-CH_3$	$-CH_2CH_3$	250	100	0	—
$-CH_2CH_3$	$-CH_2CH_3$	180	8	5.0	2.72×10^{-9}
	$-CH_3$	200	23	2.6	2.04×10^{-9}
	$-CH_3$	225	72	0.7	6.39×10^{-9}

ether because of the low yield (18). The reaction of 2-butyl alcoholate and di-2-butyl sulfate gives only a 34% yield (18, 19). Therefore, the synthesis of di-2-butyl ether using alumina as a catalyst may even be a useful alternative for the preparation of this ether.

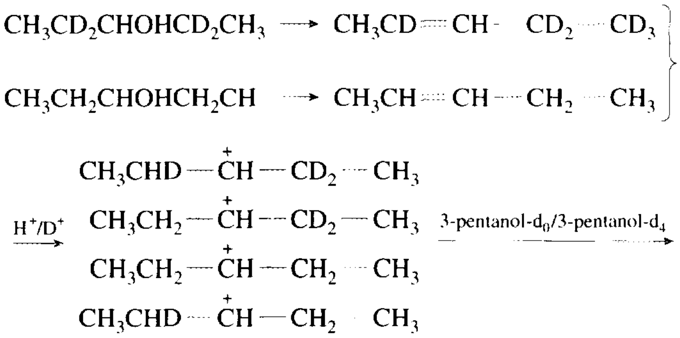
There is always the possibility of an ether being formed by the addition of an alcohol to an olefin because the latter are the major products during dehydration of alcohol. When this reactions is acid-catalyzed, the mechanism for the addition involves an electrophile, with H^+ as the attacking species.



[8]

The carbocation resulting from the protonation of the alkene then adds to the oxygen of an alcohol molecule. The formation of di-3-pentyl ether or di-2-butyl ether can be estimated from the products from the conversion of an equimolar mixture of 3-pentanol-d_4 [$CH_3CD_2CH(OH)CD_2CH_3$] and 3-pentanol-d_0 or of 2-butanol-d_5 [$CD_3CH(OH)CD_2CH_3$] and 2-butanol-d_0.

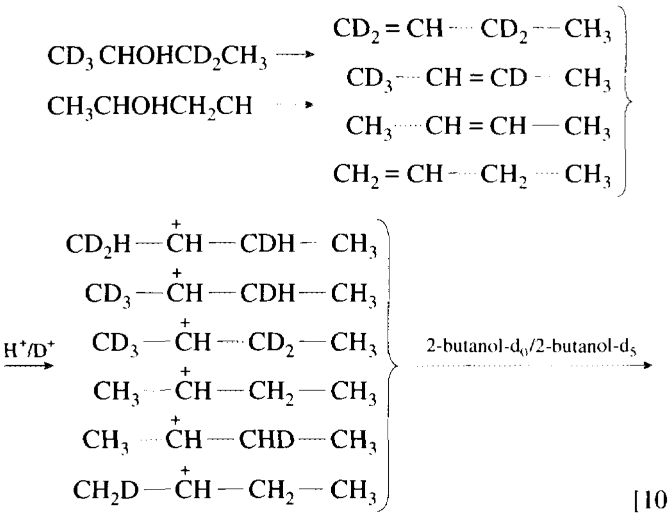
For the conversion of the 3-pentanol mixture, seven of the nine possible deuterium labeled ethers should be formed (Eq. [9]). Likewise, for the conversion of the 2-butanol mixture, seven of the eleven possible deuterium labeled ethers should be formed (Eq. [10]).



$$\left.\begin{array}{l} \mathrm{CH_3CD_2CHOHCD_2CH_3} \longrightarrow \mathrm{CH_3CD{=}CH{-}CD_2{-}CD_3} \\ \mathrm{CH_3CH_2CHOHCH_2CH} \longrightarrow \mathrm{CH_3CH{=}CH{-}CH_2{-}CH_3} \end{array}\right\}$$

$$\xrightarrow{\mathrm{H^+/D^+}} \begin{array}{l} \mathrm{CH_3CHD{-}\overset{+}{C}H{-}CD_2{-}CH_3} \\ \mathrm{CH_3CH_2{-}\overset{+}{C}H{-}CD_2{-}CH_3} \\ \mathrm{CH_3CH_2{-}\overset{+}{C}H{-}CH_2{-}CH_3} \\ \mathrm{CH_3CHD{-}\overset{+}{C}H{-}CH_2{-}CH_3} \end{array} \xrightarrow{\text{3-pentanol-}\mathrm{d_0}\text{/3-pentanol-}\mathrm{d_4}}$$

di-3-pentyl ether- d_0,-d_1,-d_3,-d_4,-d_5,-d_7,-d_8 [9]



$$\left.\begin{array}{l} \mathrm{CD_3CHOHCD_2CH_3} \longrightarrow \\ \mathrm{CH_3CHOHCH_2CH} \longrightarrow \end{array} \begin{array}{l} \mathrm{CD_2{=}CH{-}CD_2{-}CH_3} \\ \mathrm{CD_3{-}CH{=}CD{-}CH_3} \\ \mathrm{CH_3{-}CH{=}CH{-}CH_3} \\ \mathrm{CH_2{=}CH{-}CH_2{-}CH_3} \end{array}\right\}$$

$$\xrightarrow{\mathrm{H^+/D^+}} \left.\begin{array}{l} \mathrm{CD_2H{-}\overset{+}{C}H{-}CDH{-}CH_3} \\ \mathrm{CD_3{-}\overset{+}{C}H{-}CDH{-}CH_3} \\ \mathrm{CD_3{-}\overset{+}{C}H{-}CD_2{-}CH_3} \\ \mathrm{CH_3{-}\overset{+}{C}H{-}CH_2{-}CH_3} \\ \mathrm{CH_3{-}\overset{+}{C}H{-}CHD{-}CH_3} \\ \mathrm{CH_2D{-}\overset{+}{C}H{-}CH_2{-}CH_3} \end{array}\right\} \xrightarrow{\text{2-butanol-}\mathrm{d_0}\text{/2-butanol-}\mathrm{d_5}}$$

[10]

di-2-butyl ether- d_0,-d_1,-d_4,-d_5,-d_6,-d_9,-d_{10}

The data in Fig. 3 do not conform with the distributions given in Eq. [9] and [10]. The major products from these runs are di-3-pentyl ether-d_0, -d_4, and -d_8 in the case of

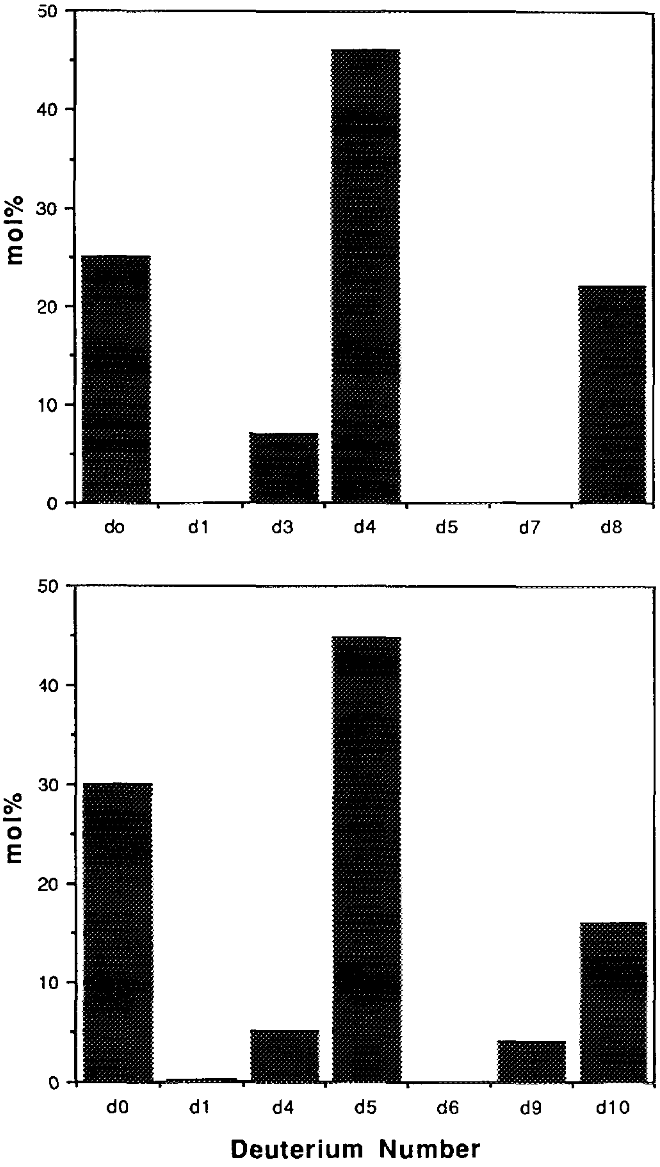


FIG. 3. Relative amount of ether isomers in the dehydration of a 1 : 1 mixture of 3-pentanol-d_0 and 3-pentanol-d_4 (top) and of 2-butanol-d_0 and 2-butanol-d_5 (bottom).

the runs with the 3-pentanol mixture and di-2-butanol ether-d_0, -d_5, and -d_{10} in the case of the runs with the 2-butanols. The amounts of the other deuterium components in the ether products are very small and are within the experimental error. The deuterium distributions are the results that clearly show that H^+/D^+ electrophilic attack on an alkene product is not involved in the ether formation process under the conversion conditions used in the present study. Most importantly, the prediction by this mechanism involving the alkene products of the formation of 50% of the (*S*,*S*) di-2-butyl ether and 50% of the (*R*,*S*) di-2-butyl ether during the conversion of *S*-(+)-2-butanol is in contradiction with the experimental data. Therefore, this mechanism can be eliminated from consideration.

For the conversion of an equal molar mixture of 3-pentanol-d_0 and 3-pentanol-d_4, the ratio of the deuterium labeled ether should be $d_0 : d_4 : d_8 = 1 : 2 : 1$ if ether formation follows a statistical distribution. The products shown in Fig. 3 are very close the expected distribution. The distribution of the labeled ethers from the conversion of the equimolar 2-butanol-d_0 and 2-butanol-d_5 mixture should be $d_0 : d_5 : d_{10} = 1 : 2 : 1$. The data shown in Fig. 3 are in reasonable agreement with this distribution, although they do not conform to the expected isotope distribution as well as the ethers produced from the 3-pentanols.

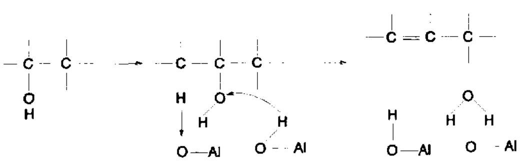
DISCUSSION

The use of high-resolution GC capillary columns permits us to obtain data that clearly show that the conversion of a mixture of methanol and 2-butanol using an alumina catalyst produces dimethyl and di-2-butyl ethers in addition to methyl-2-butyl ether. Under certain conditions, when 2-butanol is converted alone, di-2-butyl ether may account for more than 40 wt.% of the total products.

The present studies were conducted with a total alcohol pressure of 1 atm.; under these conditions, alcohol dehydration is a zero-order reaction (11, 14, 15). This implies that the surface is saturated with adsorbed alcohol. The probability of one alcohol being adsorbed from a gaseous mixture under these zero-order conditions is directly proportional to the partial pressure of the alcohol. Thus, the probability of two molecules of the same alcohol being on adjacent sites becomes proportional to the square of the partial pressure of the alcohol. For the conversion of a mixture of methanol and 2-butanol, the amounts of dimethyl or di-2-butyl ethers that are formed should be directly related to the square of the partial pressure of the alcohol. The experimental data conform to this expectation (Fig. 2).

The data for the conversion of *S*-(+)-2-butanol alone and in a mixture with methanol clearly show that the formation of the ether occurs by a mechanism that involves a backside approach, the Walden inversion. Thus, the data are consistent with a S_N2 mechanism.

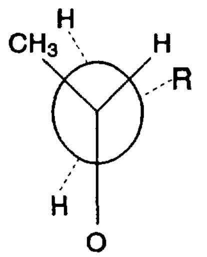
The mechanism for the conversion of alcohols has been considered by many investigators. By analogy with the homogeneous catalyzed dehydration with sulfuric acid that involves a proton, Brønsted acidity has been utilized in the reaction scheme. This approach may be illustrated by the application of the "principle of least motion," widely utilized in organic chemistry, to catalytic reactions by Eucken and Wicke (19). This principle simply states that a reaction will take place readily when the motion of the nuclei participating in the molecular rearrangements, dehydration with elimination of water in this example, is held to a minimum. This was illustrated by Eucken and Wicke

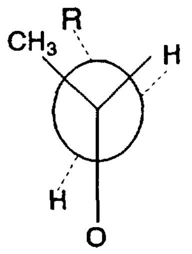

[11]

SCHEME 1. (Redrawn from Ref. (20).)

(20) for the mechanism for alcohol dehydration on γ-Al_2O_3 (see Scheme 1). Depending upon the timing, this mechanism may involve a "cation-like" or an "anion-like" intermediate or it may represent a concerted mechanism in which the β-hydrogen is lost in synchronization with the hydroxyl group. Considering the conversions of alcohol over a wide range of catalysts, Davis (21, 22) considers the conversion to follow a concerted mechanism in which the timing of OH and H loss depends upon the catalyst.

Alumina provides a unique selectivity for alcohol dehydration since about 90% of the alkene products formed during the conversion of a 2-ol, e.g., 2-octanol, are the two less stable alkene isomers, about equally divided between the 1-alkene and *cis*-2-alkene. Pines and Manassen (23) involved an interaction of the proton with the forming double bond to account for the dominant amount of the *cis*-2-alkene. Davis (e.g., (21, 22)) attributed this selectivity to the geometry of a catalytic site, presumed to involve a coordinately unsaturated aluminum ion. Another constraint upon the reaction intermediate (transition state structure) that is formed during alcohol dehydration is the operation of an antielimination mechanism. It is well documented that alkene formation by thermal decomposition of the acetate ester occurs predominately by a syn-elimination with about equal amounts of the *cis*-2- and *trans*-2-alkene, or even a predominance, of the trans-2-isomer (e.g., (24)). The pyrolysis mechanism therefore follows the pathway expected, based upon steric repulsion effects, as illustrated by structures I–IV. The repulsion of the R and CH_3 groups in structure II would favor structure I, and therefore the *trans* isomer. This is not the case for alcohol dehydration by an antielimination to produce predominantly *cis*-2-alkene in favor of *trans*-2-alkene since this requires the Newman projection with the greatest steric interaction (III) rather than the less crowded intermediate (IV) that would lead to the *trans*-2-isomer. Structure III should be favored over IV only when a bulky group that is provided by the catalyst is situated so that it provides an interaction to overcome the crowding of the R (or the CH_3) group in structure III.


I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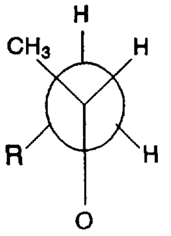
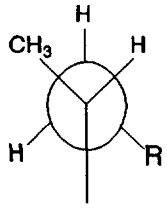
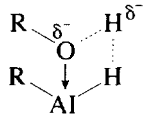
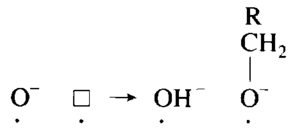

III


IV

The structures of alcohols adsorbed on alumina that result from several infrared and gravimetric studies (25–30) have been concisely summarized recently by DeCanio *et al.* (31). The studies are considered to show that one of the three types of species that result from the adsorption of short-chain alcohols is produced by alcohol chemisorption onto a coordinatively unsaturated aluminum ion (Lewis acid site) producing species designated as *A* in Ref. (31).


A

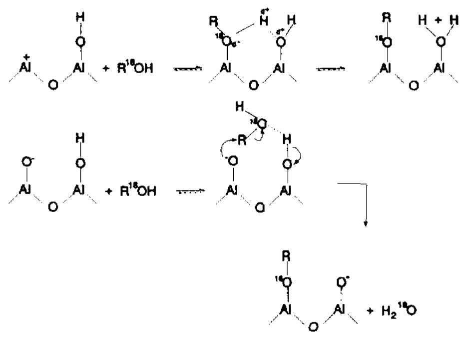
Structure *A* is similar to the one provided much earlier, for example, by Notari (10).



$$\overset{\cdot}{O^-}\quad \overset{\cdot}{\square} \rightarrow \overset{\cdot}{OH^-}\quad \overset{\overset{R}{CH_2}}{\overset{|}{\overset{\cdot}{O^-}}} \qquad [12]$$

This structure has likewise been utilized for the acid–base pair in the alumina model advanced by Knozinger and Ratnasamy (32), where □ in the above structure represents a coordinately unsaturated Al^{3+} ion.

DeCanio *et al.* (31) used TPD and mass spectroscopic techniques to define the products formed when either $[^{18}O]$methanol or $[^{18}O]$ethanol was adsorbed on alumina prior to conducting the TPD experiment. With either alcohol, they obtained the corresponding ether containing either ^{18}O or ^{16}O. The ether containing ^{18}O was the first to appear during a TPD experiment for either alcohol. For adsorbed ethanol or 1-propanol the ratio of ether to alkene in the desorbed products was about 1 to 33; however, this



SCHEME 2. (Redrawn from Ref. (31).)

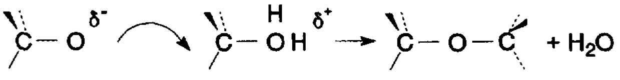
ratio was about 1 to 2,000 when 2-propanol was adsorbed and then subjected to the TPD experiment.

DeCanio *et al.* (31) state that the two isotopomeric [containing ^{16}O or ^{18}O] ether products originate from two different alkoxide species, one incorporating an ^{18}O and the other ^{16}O. They suggest that the presence of the two alkoxides indicate that alkoxide is formed following two routes, one involving a direct reaction at a Lewis site (Eq. [13], Scheme 2, that results in deprotonation of the complexed alcohol and the formation of ^{18}O-labeled alkoxide) and the other involving a reaction with a nucleophilic surface base site (Eq. [14], Scheme 2, bottom, resulting in ^{18}O displacement and the formation of ^{16}O-labeled alkoxide). The latter pathway was considered to involve interaction with an adjacent acid site since the hydroxide is a poor leaving group. These authors cited data from poisoning experiments to support Scheme 2. They (31) state that the mechanism suggested by Figueras *et al.* (11) for the reaction of methanol on alumina is consistent with the appearance of the [^{16}O]ether.

The application of the conclusions of DeCanio *et al.* (31) to our data is questionable. They (31) conclusively show that physisorbed alcohol is not present on the alumina surface at the temperatures at which ethers form. This, according to them, indicates that either formation cannot involve a reaction between alkoxide and physisorbed alcohol, in contrast to the suggestions of Jain and Pillai (7) and Knözinger *et al.* (33). Alcohol dehydration is a zero-order reaction at 1 atm alcohol pressure but becomes first-order at the low pressures where DeCanio *et al.* (31) conducted their experiments. Thus, their (31) data do not show that the formation of ether from a physisorbed alcohol, or, for that matter, from a gaseous alcohol molecule in an Eley–Rideal mechanism (16), is not allowed at the pressures used in the present study. Under conditions where the reaction is zero order in alcohol, the surface sites will be saturated, and this was not the case at the lower pressure studies (31). In addition, secondary reactions are more likely to occur when operating at low surface coverage; this may explain the low ether:alkene ratio that was observed (31) during the TPD experiments with 2-propanol.

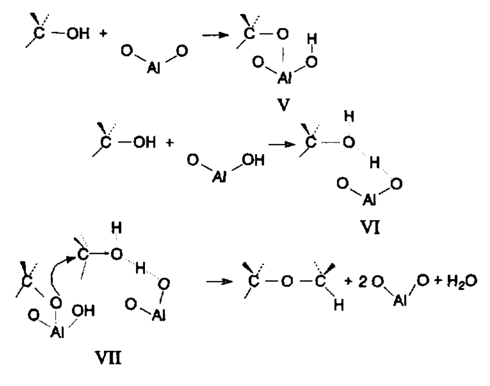
Surface-bound alkoxides were proposed in Ref. (31) to be formed by two routes: (a) dissociative adsorption of Lewis acid sites and (b) nucleophilic attack by a surface oxide on an alcohol that is probably activated toward C–O cleavage. The operation of the nucleophilic attack by the bottom pathway of Scheme 2 appears questionable. If reaction [14] occurs, the reaction cannot be reversible. If it was reversible, the reactant would undergo inversion, and this was not observed even at 50% and higher conversion levels. More importantly, if ether formation involves R—^{16}O-Al, where R has undergone inversion during its formation, the ether cannot be formed by a S_N2 mechanism since, if this were to occur, the ether formed would either have no evidence for inversion (*S,S* ether from the S isomer) or both alkyl groups would have undergone inversion (*R,R* ether from the S isomer). Furthermore, if inversion occurs during the reaction represented by Eq. [14] to give the ether, then the $RO^{\delta-}$ group must react with some positively charge species, e.g., $ROH_2^{\delta+}$, by a frontal approach that does not involve inversion. The ratio of the products from the mixture of (*R*) and (*S*) isomers used in this study are in agreement with a S_N2 mechanism. For the above reasons, it is difficult to accept the view that inversion occurs during the reaction represented by Equation [14].

From the viewpoint of organic mechanisms, and ignoring the nature of the catalytic site, the following intermediates for the 2-butanol reaction would involve a good nucleophile and a good leaving group.



[15]

The mechanisms outlined in Scheme 2 do not utilize species such as the electrophile in Eq. [15]. However, the structure for the electrophile is certainly utilized to explain dehydra-

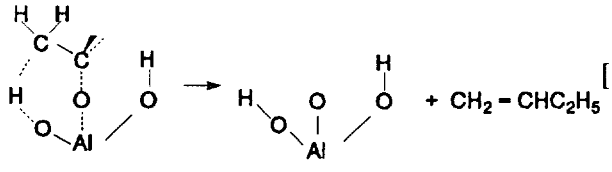


SCHEME 3

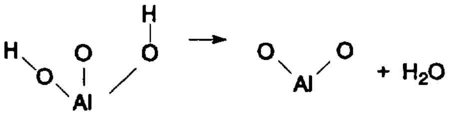
tion using homogeneous catalysts. Thus, a more reasonable mechanism for ether information could be expressed as shown in Scheme 3.

Scheme 3 permits ether formation using a coordinately unsaturated site (Lewis acid) as represented by Notari (10) or Knozinger *et al.* (33), a base site, and a Brønsted site that is generated during the reaction. One of the adsorbed alcohol molecules is converted to a good electrophile while the other develops as a good leaving group. Structure VII, in which the concerted nucleophilic substitution and expulsion of the water leaving group involves a six-atom ring, provides a structure that is favored by many reactions, such as acetate pyrolysis (24).

The structure preceding structure V in Scheme 3 corresponds to structure *A* (25) after the hydroxyl proton has transferred to an oxygen anion. This structure is one that could be visualized to operate during alcohol dehydration to form alkenes. Thus, for alkene formation the oxygen anion would abstract a β-hydrogen, again in a concerted mechanism with the coordinated oxygen serving as the leaving group (Eqs. [19] and [20]).



[19]



[20]

Scheme 3 is preferred by us since: (a) it can utilize a common intermediate to produce either the ether or an alkene, (b) an alcohol can adsorb to serve as either a nucleophile or electrophile, (c) the mechanism allows for the correct stereochemistry for ether formation, and (d) the mechanism allows for the formation of mixed ethers with a feed that consists of two alcohols.

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