

Catalytic Dehydration of Alcohols over Alumina Mechanism of Ether Formation

JAGDISH RAI JAIN* AND C. N. PILLAI†

*From the Department of Chemistry, Indian Institute of Technology,
Madras 36, India*

Received June 6, 1967; revised September 26, 1967

The dehydration of alcohols over alumina to form ethers and olefins was studied from a mechanistic point of view. The rates of both olefin formation and ether formation were independent of the partial pressure of the alcohol, beyond a certain partial pressure. This saturation partial pressure was higher for ether formation than for olefin formation. The conclusion was drawn that both reactions are surface reactions but requiring different types of active sites. Certain reagents, like phenol, when added to the alcohol in small quantities, caused a large increase in the rate of olefin formation and a large decrease in the rate of ether formation. Certain other reagents like pyridine caused decrease in the rates of both ether formation and olefin formation. An explanation is offered for the above observations assuming the presence of both acidic and basic sites on the surface of alumina.

INTRODUCTION

Dehydration of alcohols to form ethers and olefins is an important reaction catalyzed by alumina. Considerable work has been done to elucidate the mechanism of olefin formation (1). It is now reasonably well established that olefins are formed by the adsorption of alcohol on the acidic sites through the oxygen atom of the alcoholic hydroxyl group, thereby polarizing the C-O bond. Breakage of the C-O bond and the abstraction of a β -hydrogen by a nucleophile seems to happen in a concerted manner.

Extension of the above mechanism to ether formation involves the assumption that a second alcohol molecule interacts with the adsorbed molecule visualized above, in a nucleophilic displacement reaction. This picture raises two questions. Does the second alcohol molecule come

from the gas phase or is it also in the adsorbed phase? If the latter is the case, is the surface site on which the second alcohol molecule is adsorbed the same acid site visualized above or is it a different kind of site? The following studies were undertaken to decide to what extent these questions can be answered.

EXPERIMENTAL

Technique. The dehydration studies were carried out in a flow-type system. The catalyst employed was Houdry hard alumina, grade 200A (Houdry Process Corporation, Philadelphia, Pennsylvania), of surface area 165 m²/g and Na₂O content 0.1%, in the form of 1/8-inch pellets. The reactants were displaced into the catalyst tube using mercury at any desired reproducible rate. The products were analyzed by gas chromatography.

Rate vs. partial pressure studies. The relative rates of olefin and ether formation at various partial pressures of alcohol were determined as follows: Mixtures of alcohol with a neutral diluent of various compositions up to 100 mole% of alcohol were prepared. These were individually passed

* Taken from the Ph.D. Thesis of J. R. J., Indian Institute of Technology, Madras, 1966. Present address: Indian Institute of Technology, New Delhi.

† Author to whom communications regarding this paper should be addressed.

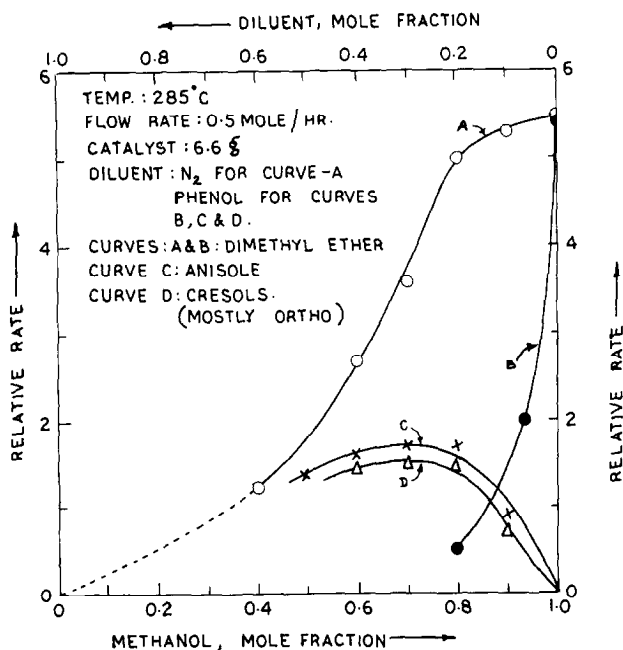


FIG. 1. Dehydration of methanol in the presence of N₂ (Curve A) and in the presence of phenol (Curves B, C, and D).

over the catalyst at the required temperature at a constant flow rate (0.5 mole/hr), each for the same length of time. Thus the contact time of the total mixture was kept the same in all the runs. The products

were collected suitably and analyzed. The weight of product formed in 1 hr is taken as a measure of its relative rate of formation. The results are presented in the figures as plots of these relative rates

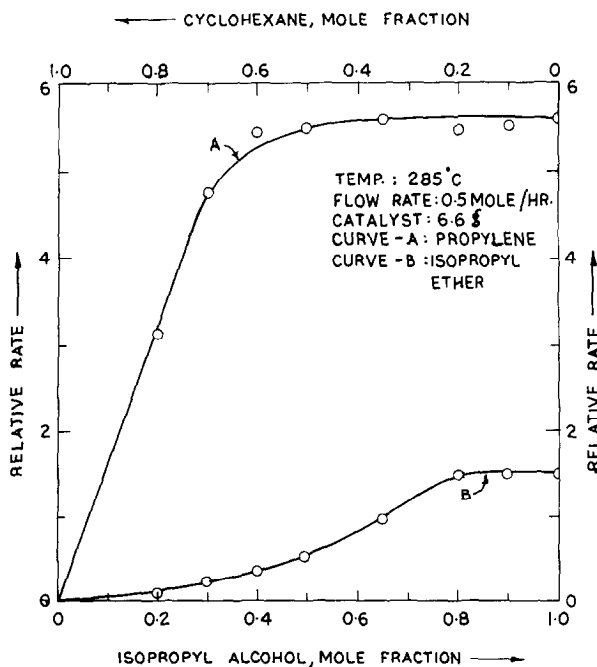


FIG. 2. Dehydration of isopropyl alcohol in the presence of inert diluent, cyclohexane.

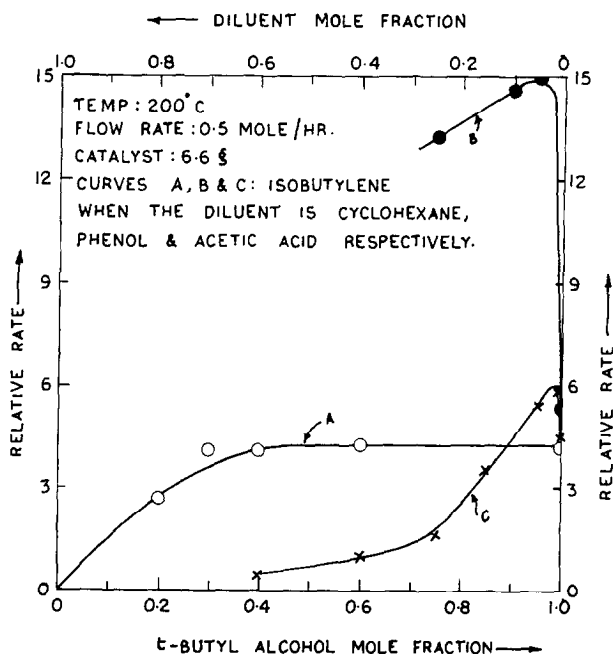


Fig. 3. Dehydration of *tert*-butyl alcohol in the presence of different diluents.

against mole fraction or partial pressure of the reactants. For all the alcohols used, except methanol, cyclohexane was used as the diluent. For methanol, due to its immiscibility with cyclohexane, nitrogen was

used as the diluent. It was found that after an initial drop the catalyst activity remained constant for 4 to 5 hr, provided no regeneration was attempted. All the experiments relating to one series were completed

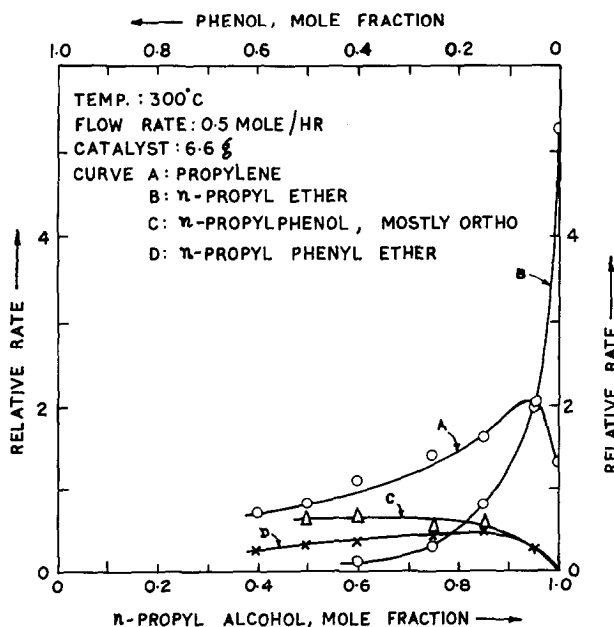


Fig. 4. Dehydration of *n*-propyl alcohol in the presence of phenol.

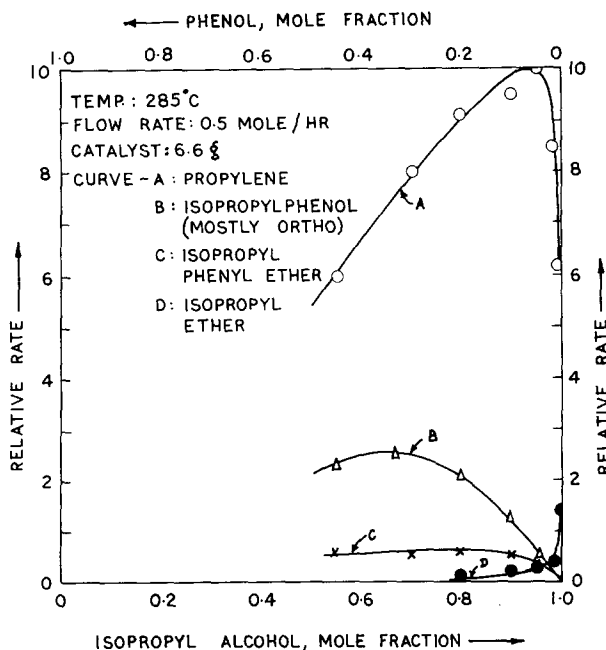


Fig. 5. Dehydration of isopropyl alcohol in the presence of phenol.

in this time. At the end of each series the first experiment was repeated to make sure that the activity had remained constant. The results regarding the dependence of the rates of formation of dimethyl ether on the partial pressure of methanol,

those of diisopropyl ether and propylene on the partial pressure of isopropyl alcohol, and that of isobutylene on the partial pressure of *tert*-butyl alcohol are plotted in Figs. 1, 2, and 3, respectively.

Dehydrations in the presence of reactive

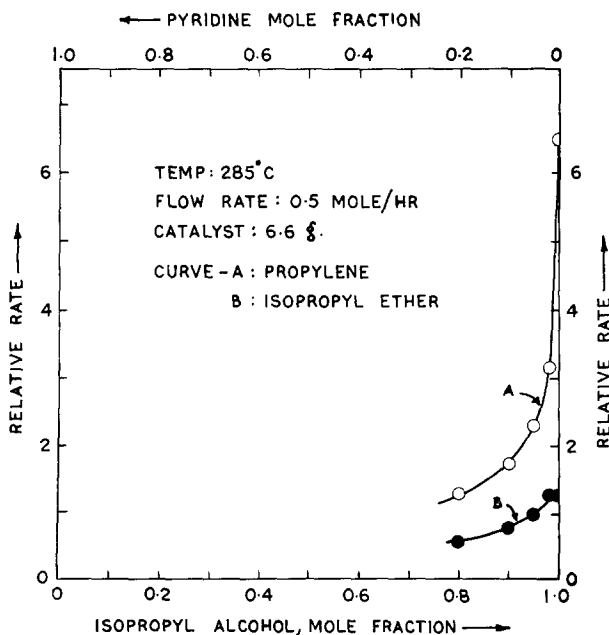


Fig. 6. Dehydration of isopropyl alcohol in the presence of pyridine.

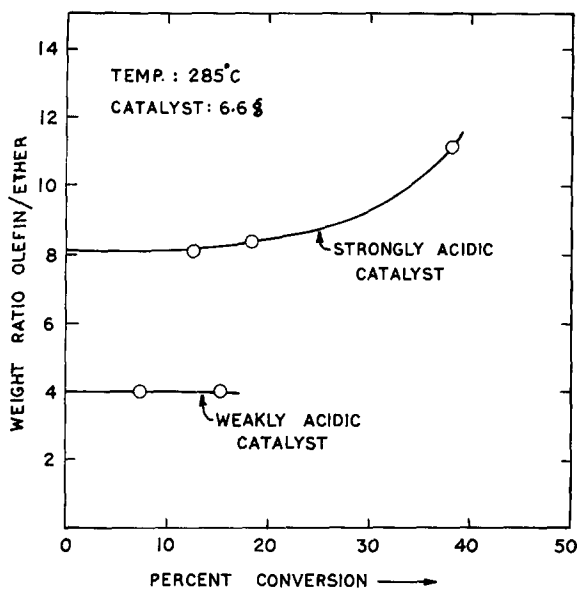


Fig. 7. Dehydration of isopropyl alcohol. Dependence of olefin/ether ratio on the acidity of the catalyst.

or polar diluents. Dehydrations in the presence of diluents such as phenol, acetic acid, pyridine, and benzene were also carried out in a similar manner. In the case of the first two diluents, in addition to the

normal dehydration products, products arising from the reactions of the diluents themselves were also formed. Thus alkyl phenyl ethers and alkyl phenols in the presence of phenol and alkyl acetate in the

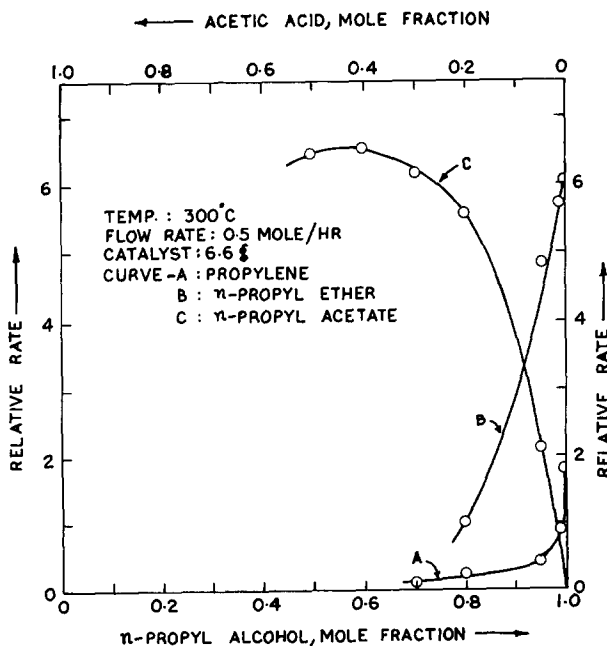


Fig. 8. Dehydration of *n*-propyl alcohol in the presence of acetic acid.

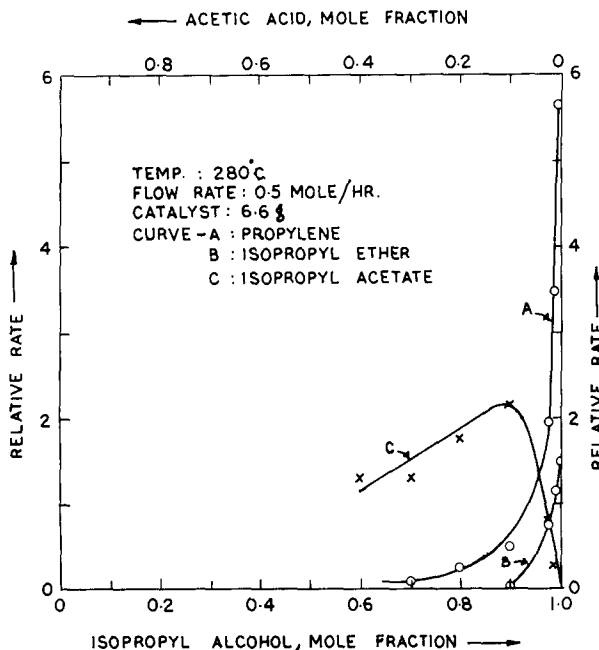


Fig. 9. Dehydration of isopropyl alcohol in the presence of acetic acid.

presence of acetic acid were also detected. The results are presented in Figs. 1 to 6, 8 and 9.

Effect of the acid strength of the catalyst on the olefin/ether ratio. For this study a strongly acidic catalyst and a weakly acidic catalyst were prepared according to the procedures reported by Pines and Haag (2), by the hydrolysis of aluminum nitrate and by the decomposition of sodium aluminate by carbon dioxide, respectively. The former was more acidic than the latter in the sense that it was six times more active for cyclohexene isomerization than the latter at 410°C. The olefin/ether ratios on these two catalysts at different contact times using isopropyl alcohol are plotted in Fig. 7.

DISCUSSION

It can be seen from Figs. 2 and 3 that the rates of olefin formation from isopropyl and *tert*-butyl alcohols are dependent on the partial pressure of the alcohols only up to about 0.3 atm. The rates are constant above this partial pressure. Clearly this represents the saturation partial pressure as far as the olefin-forming sites are con-

cerned and olefin formation is a true surface reaction.

The rates of ether formation from methanol (Fig. 1) and from isopropyl alcohol (Fig. 2) also reach constant values, but at much higher partial pressures. It can be concluded that ether formation is also a surface reaction but the sites responsible for ether formation are saturated only at higher partial pressures than the sites responsible for olefin formation.

Thus we come to the conclusion that there are two types of active sites on the surface of alumina. The first, those which are saturated at lower partial pressures and are responsible for olefin formation, are probably the well recognized acidic sites of alumina. These will be referred to as A sites in this paper. A clue regarding the nature of the second type of sites is obtained from the studies in the presence of phenol.

Effect of Phenol

The spectacular effect of phenol on the activity of alumina is seen in Figs. 1, 3, 4, and 5. When 5 mole% phenol is added to isopropyl alcohol the rate of olefin

formation is increased by more than 50%. The rate of ether formation, on the other hand, is decreased to less than half (Fig. 5). Similar enhancement of the rates of olefin formation and reduction of the rates of ether formation are seen in the case of other alcohols also.

The reduction in the rate of ether formation in the presence of phenol is not solely due to any increase in the rate of decomposition of ether, since phenol reduces the rate of formation of even dimethyl ether though no decomposition products of dimethyl ether are formed. On the other hand, this effect of phenol could very well be due to the competition of phenol with the alcohol for the surface of the catalyst. At low partial pressures of phenol this competition is not for the A sites since the rate of olefin formation is not decreased. Thus, under these conditions, phenol gets preferentially adsorbed on the second type of sites which may be called the B sites. This preferential adsorption of phenol suppresses dialkyl ether formation but alkyl phenyl ether and alkyl phenols are readily formed. This gives a clue to the mechanism of ether formation, namely, that it involves the interaction of a molecule, alcohol or phenol, adsorbed on the B site with the alcohol molecule adsorbed on the A site. This argument is developed further in the next section.

The increase in the rate of olefin formation in the presence of phenol is not solely due to the reduced competition from ether formation since this increase is seen even in the case of *tert*-butyl alcohol which does not form any ether even in the absence of phenol. It is likely that this increased activity for olefin formation in the presence of phenol is due to an increase in the acidity of the surface brought about by the adsorption of phenol.

Sites Responsible for Ether Formation

The data given here are consistent with a mechanism for ether formation involving two adsorbed alcohol molecules. The following two possibilities may be considered regarding the nature of these sites: (1) Both alcohol molecules are adsorbed on the

same kind of sites, B, these being different from the sites responsible for olefin formation. This scheme may be designated the B-B scheme. (2) The two adsorbed alcohol molecules responsible for ether formation are adsorbed on two different kinds of sites, namely, A and B. This may be designated the A-B scheme.

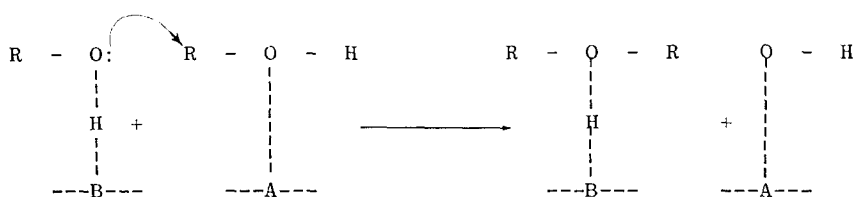
A choice between the two schemes can be made on the basis of the results of the reactions with phenol. In the reaction between methanol and phenol, Fig. 1, the rate of anisole formation reaches a maximum when the mole fraction of phenol is about 0.3. If the B-B scheme is accepted, this represents the composition where half the available B sites are occupied by phenol and the other half by methanol. Under these conditions, the rate of dialkyl ether formation should have been one-fourth the original value, whereas actually it is much less; the amount of dimethyl ether formed was too small to measure. This clearly rules out the B-B mechanism. The A-B scheme is entirely consistent with the above results. Phenol is preferentially adsorbed on the B sites and concentration of alcohol on the B sites is reduced to very low values before the concentration on the A sites is affected. Hence when the rate of anisole formation is maximum, practically no dialkyl ether is formed.

This kind of analysis of the effect of phenol on ether formation is not possible in the case of *n*-propyl and isopropyl alcohols (Figs. 4 and 5) since, at maximum, alkyl phenol formation exceeds alkyl phenyl ether formation.

The A-B scheme is also more consistent with the expected polarizations of the adsorbed species if A and B are taken to be acidic and basic sites and the scheme enables us to build a reasonable model for the behavior of these sites.

Mechanism of Ether and Olefin Formation

We have already made the proposal in a preliminary communication (3) that the two types of sites present on alumina are acidic and basic sites. The following mechanism was proposed for ether formation:



In the above scheme, --B-- and --A-- represent, respectively, the basic (nucleophilic) and the acidic (electrophilic) sites on the surface.

The chemisorption of the alcohol on the acidic site polarizes the C-O bond and makes the hydroxyl a better leaving group. To what extent the breaking of the C-O bond has taken place in the adsorbed complex will depend upon the structure of the alcohol, strength of the acid site, and temperature. Thus it is possible that with tertiary alcohols at high temperatures and in the presence of strong acid catalysts, the bond breaking may be complete and the adsorbed species may be a true carbonium ion. However, with primary and secondary alcohols, stereochemical evidences reported by Pines and co-workers (1) clearly indicate that the bond breaking is not complete.

Chemisorption of alcohol on a basic site, represented as a hydrogen bonding to the surface, increases the nucleophilicity of the oxygen of that alcohol molecule. Such an alcohol molecule, which may be considered to be an incipient alkoxide anion, can effect a nucleophilic displacement on the positively polarized carbon atom of the alcohol adsorbed on the acidic site to form ether. Thus ether formation may be visualized as a nucleophilic displacement reaction taking place in the adsorbed phase. The alternate fate of the alcohol molecule adsorbed on the acidic site is to lose a β -proton to form olefin. Thus, the adsorbed phase is similar to a polar medium where olefin-forming elimination reactions and ether-forming substitution reactions are taking place simultaneously and competing with each other.

Adsorption of alcohol to the surface oxide ions, which could be the basic sites, through hydrogen bonding, finds a parallel in the proposed nature of chemisorption

of water on alumina by de Boer *et al.* (4) and the spectroscopic evidence for the adsorption of formic acid to form formate ions (5) and the adsorption of acetylene through the acidic hydrogen (6).

The Effect of Bases

The effect of basic molecules like pyridine is to compete with the alcohol molecules for the acidic sites and thereby inhibit both olefin and ether formation. (See Fig. 6.) Even a very weak base like benzene was shown to have a similar effect, though less pronounced. One interesting point to note in this connection is that the inhibiting effect of the base is felt more on the rate of olefin formation than on ether formation. This clearly indicates the existence of acid sites of different degrees of acidity on alumina. The ability of bases to inhibit the catalytic activity of alumina is well known. Nitrogen bases have been shown to inhibit the activity of alumina for olefin isomerization and for the dehydration of alcohols, the inhibiting effect on the former reaction being much more pronounced than on the latter (7). The reason given for this is that olefin isomerization requires stronger acid sites than are necessary for alcohol dehydration. The effect of the base is felt more on the stronger acid sites and hence more on the olefin isomerization. Extending the same argument to the present situation it may be concluded that of the two reactions, olefin formation and ether formation, the former requires stronger acid sites than the latter. This point was verified by determining the olefin/ether ratios over two catalysts of different acid strengths. The ratios at various conversions, obtained by changing the contact times, are plotted and extrapolated to zero conversion in Fig. 7. It can be seen that the ratio is twice as

large for the strongly acidic catalyst as for the weakly acidic one.

The Effect of Acetic Acid

It was expected that acetic acid would have an effect similar to that of phenol. As expected, it was found that acetic acid inhibits ether formation (Figs. 8 and 9). However the effect on olefin formation is different for *tert*-butyl alcohol on the one hand and for *n*-propyl and isopropyl alcohols on the other hand. In the former case (Fig. 3), the rate of olefin formation is increased by acetic acid in much the same manner as by phenol. But in the latter cases (Figs. 8 and 9), olefin formation was inhibited by acetic acid. In these cases esterification of the alcohol by the acetic acid is a major competing reaction which obscures the effect of acetic acid on the direct dehydration process.

Other Products

In the case of the reactions using phenol, both phenyl alkyl ethers and alkyl phenols were formed. The formation of these products is consistent with the mechanism proposed here. No diphenyl ether was detected. This compound was not formed even when phenol alone was passed over alumina. With acetic acid and alcohols esters were formed, except for *tert*-butyl alcohol. The mechanism of esterification is being further investigated by us.

CONCLUSIONS

(1) Both olefin formation and ether formation over alumina are surface reactions.

(2) The surface of alumina contains both acidic (electrophilic) and basic (nucleophilic) sites. Adsorption of alcohol molecules on acidic sites gives rise to species with positively polarized α -carbon atoms. Such a species can eliminate a β -proton to give olefin. Adsorption of alcohol molecules on basic sites by hy-

drogen bonding through the hydrogen of the hydroxyl group generates incipient alkoxide anions. Nucleophilic displacement by these on the α -carbon atom of the alcohol adsorbed on the acidic sites gives rise to ether.

(3) Relatively stronger acidic sites are required for olefin formation than are required for ether formation.

(4) Basic reagents like pyridine inhibit both olefin and ether formation by excluding alcohol molecules from the acidic sites. Acidic molecules like phenol and acetic acid inhibit ether formation by excluding alcohol molecules preferentially from the basic sites. At the same time the adsorption of these reagents on the surface causes the acidity of the surface to increase. Depending on the structure of the alcohol used, the rate of olefin formation may show an increase in the presence of these reagents.

ACKNOWLEDGMENTS

The authors wish to express their thanks to Dr. J. C. Kuriacose and to Professor M. V. C. Sastri for many valuable discussions and to the Central Leather Research Institute, Madras, for providing facilities for gas-chromatographic analysis.

REFERENCES

1. PINES, H., AND MANASSEN, J., *Advan. Catalysis* **16**, 49-93 (1966).
2. PINES, H., AND HAAG, W. O., *J. Am. Chem. Soc.* **82**, 2471 (1960).
3. JAIN, J. R., AND PILLAI, C. N., *Tetrahedron Letters* **11**, 675 (1965).
4. DEBOER, J. H., FORTUIN, J. M. H., LIPPENS, B. C., AND MEIJS, W. M., *J. Catalysis* **2**, 1 (1963).
5. HIROTA, K., KUWATA, K., OKAI, T., AND ANAI, S., *Actes Congr. Intern. Catalyse, 2^e, Paris, 1960* **1**, 809 (1961).
6. YATES, D. J. C., AND LUCCHESI, P. J., *J. Chem. Phys.* **35**, 243 (1961).
7. PINES, H., AND PILLAI, C. N., *J. Am. Chem. Soc.* **83**, 3274 (1961).