JOURNAL OF CATALYSIS **139**, 406–420 (1993)

Methanol and 2-Methyl-1-Propanol (Isobutanol) Coupling to Ethers and Dehydration over Nafion H: Selectivity, Kinetics, and Mechanism

JOHN G. NUNAN,[1] KAMIL KLIER, AND RICHARD G. HERMAN

Department of Chemistry and Zettlemoyer Center for Surface Studies, 6 East Packer Avenue,
Lehigh University, Bethlehem, Pennsylvania 18015

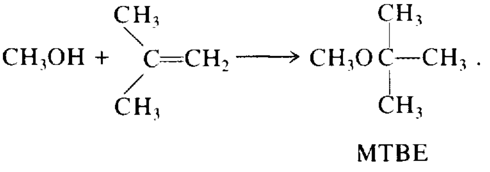
Received June 2, 1992; revised September 9, 1992

The dehydration of a mixture of methanol and isobutanol has been studied over the sulfonic acid Nafion H catalyst. Dehydration products consisted of dimethyl ether (DME), di-isobutyl ether (DIBE), methyl-isobutyl ether (MIBE), butenes, octenes, and traces of methyl-tertiarybutyl ether (MTBE). At low temperatures and high alcohol pressures ($P \gtrsim 150$ kPa), the dehydration product slate was dominated by ether formation with selectivity within the ethers significantly in favor of the mixed ether, MIBE. The rates of ether and butene formation as a function of alcohol pressure could be described by Langmuir–Hinshelwood kinetics in which competitive adsorption of the two alcohols on the surface $-SO_3H$ sites was the dominant feature. The kinetics of isobutanol dehydration to isobutene were consistent with a dual-site mechanism involving the cooperative action of a free surface $-SO_3H$ site and an adjacent adsorbed alcohol molecule. Dehydration to ethers was consistent with the reaction of two adsorbed alcohols, also by a dual-site mechanism. As a consequence, dehydration to symmetric ethers showed saturation-type kinetics as a function of alcohol pressure, while the rate of isobutene formation went through a distinct maximum. Due to the competitive adsorption of methanol and isobutanol, the mixed ether MIBE was formed at a maximum rate with an optimum ratio of partial pressures of the two alcohols. The high selectivity to MIBE was explained by stronger adsorption of isobutanol on the catalyst surface as compared to methanol.

The absence of MTBE and the predominance of products such as MIBE and 2,5-dimethylhexene suggests that dehydration to give "free" carbenium ions that subsequently rearrange to the more stable tertiary intermediate was not occurring. It was proposed that the alcohols react with the $-SO_3H$ groups to give oxonium ions or esters. These intermediates couple to give the product ethers or octenes.

INTRODUCTION

Acid-catalyzed coupling of alcohols with olefins to produce ethers is an important class of reactions that has given rise to fast growing industrial processes, including the synthesis of the octane-enhancing methyl-tertiarybutyl ether (MTBE) (*1*), *viz.*,



$$\mathrm{CH_3OH} + \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}{=}\mathrm{CH_2} \longrightarrow \underset{\substack{\mathrm{CH_3}\\ \mathrm{MTBE}}}{\mathrm{CH_3O}\overset{\mathrm{CH_3}}{\mathrm{C}}{-}\mathrm{CH_3}}. \quad (1)$$

There is interest, both scientific and technological, in alternate routes using two different alcohols as a source of the two alkyl groups of a mixed ether,

$$\mathrm{ROH} + \mathrm{R'OH} \longrightarrow \mathrm{ROR'} + \mathrm{H_2O}. \quad (2)$$

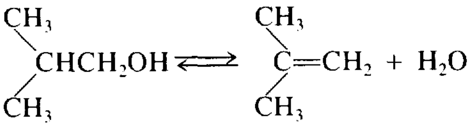
The four-carbon alcohol isobutanol (2-methyl-1-propanol) is a desirable source of a four-carbon alkyl group because it can be synthesized, along with methanol, directly from carbon monoxide and hydrogen over alkali-modified methanol synthesis cata-

---

[1] Current address: Allied Signal, P.O. Box 5016, Des Plaines, IL 60017.

0021-9517/93 $5.00

lysts (*2*). However, the reaction selectivity to mixed ethers is more difficult to control in processes of type (2) because a number of side reactions can occur in the coupling of two alcohols, in contrast to the simple and selective course of reaction (1). We have reported results of coupling methanol and isobutanol over an acid form of Nafion resin, wherein methyl-isobutyl ether (MIBE) and dimethyl ether (DME) were the dominant products at high pressures and isobutene (IB) dominated at low pressures (*3*). Other products were di-isobutyl ether (DIBE), octenes, and higher molecular weight products. The same reactants yielded significant amounts of MTBE over Amberlyst H, a polystyrene-sulfonic resin (*4*), DME over H-mordenite, DME, MIBE and DIBE over H-ZSM-5, and IB over sulfonated zirconia (*5*). Thus it is evident that selectivity is controlled by the catalyst used; however, over a single type catalyst, reaction conditions also play a very important role by regulating the kinetics of various parallel and consecutive partial reactions. In this work, we report a detailed and quantitative study of chemical and physical factors controlling the methanol-isobutanol conversions over Nafion H. The reactions involved are listed below.



$$(CH_3)_2CHCH_2OH \rightleftharpoons (CH_3)_2C{=}CH_2 + H_2O \quad (3)$$

IB

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \quad (4)$$

DME

$$(CH_3)_2CHCH_2OH + CH_3OH \rightleftharpoons (CH_3)_2CHCH_2OCH_3 + H_2O \quad (5)$$

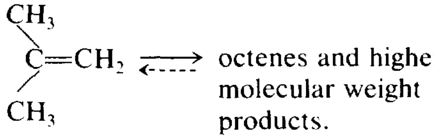
MIBE

$$(CH_3)_2CHCH_2OH + CH_3OH \rightleftharpoons (CH_3)_3COCH_3 + H_2O \quad (6)$$

MTBE

$$2(CH_3)_2CHCH_2OH \rightleftharpoons (CH_3)_2CHCH_2OCH_2CH(CH_3)_2 + H_2O \quad (7)$$

DIBE



$$(CH_3)_2C{=}CH_2 \overset{\longrightarrow}{\dashleftarrow} \text{octenes and higher molecular weight products.} \quad (8)$$

Nafion H, a solid perfluorinated sulfonic acid resin, was chosen for this study because of its thermal stability and for being a proven catalyst for many acid-catalyzed reactions such as alkylation (*6–8*), isomerization (*9, 10*), oligomerization (*11*), hydration (*12*), etherification (*13, 14*), esterification (*15*), carbomethoxylation (*16*), and dehydration (*6, 13*). Further, thermometric titrations of Nafion H by pyridine indicated that the acid strength of the $-SO_3H$ groups is uniform and independent of the degree of ionization (*4*), and therefore kinetic data obtained over this solid acid are amenable to interpretation based on simple physicochemical models. In particular, it is shown in this paper that alcohol coupling to ethers and dehydration of isobutanol to isobutene obey simple rate laws that are characteristic of competitive activation of the reacting alcohols on the acid sites. As a consequence, selectivity to the different products of reactions (3)–(8) is determined in a predictable fashion by concentrations of the reactants and total pressure.

EXPERIMENTAL

The alcohol dehydration reactions were carried out in a stainless steel continuous flow reactor at pressures ranging from 0.10 to 7.29 MPa (1 atm = 101.325 kPa) total pressure, with nitrogen as a carrier gas. The reactants, methanol and isobutanol (purity > 99.9%), were fed as liquids to the inlet line at the top of the reactor using a Gilson HPLC pump, Model 302. The alcohols were vaporized and homogeneously mixed with nitrogen in a preheater section of the reactor before coming in contact with the catalyst bed.

The total reactor pressure was controlled using a Tescom back pressure regulator Model No. 26-1700. One- to two-gram portions of catalyst having a particle diameter between 0.4 and 1.4 mm were used, and the catalyst was diluted with four times its volume of 3-mm Pyrex beads. The exit gas from the reactor was sampled every 22 min using an in-line automated heated sampling valve and analyzed using an on-line Hewlett–Packard Model 5730A gas chromatograph that was coupled with a Hewlett–Packard Model 3388A integrator/controller unit. Reaction products were separated on Poropak P columns and were identified by comparison of their retention times with those of known standards and also from their mass spectroscopic fragmentation patterns as determined by a Finnigan Model 4000 GC/MS/DS spectrometer. The fragmentation patterns of MIBE (major *m/e* peak at 45) and MTBE (major *m/e* peaks at 57 and 73) are very distinctive for these compounds.

Steady state activities were readily achieved within 2 hr of initiating alcohol injection or after altering a reaction variable such as pressure or temperature. No catalyst deactivation was observed over several hundreds of hours of testing and upon change of reaction conditions, the steady states were established reversibly.

Porous and nonporous forms of the Nafion H resin were used. Both forms had the same ion exchange capacity, i.e., 0.9 meq/g, and were in the fully acid form. The porous form was obtained under the trade name Nafion H-MicroSaddles and is referred to as Nafion H-MS, while the regular or gellular form is referred to simply as Nafion H.

RESULTS

To obtain reliable and interpretable kinetic data, reaction conditions were established so that the reactor was operated in the differential mode. In Fig. 1 is shown the effect of reciprocal space velocity (a reaction parameter proportional to the contact time) on the degree of conversions of methanol, isobutanol, and 2 : 1 methanol : isobutanol mixture. All three plots are linear with zero intercepts, indicating that in the conversion ranges studied neither reverse reactions nor external mass transfer limitations occurred within the cata-

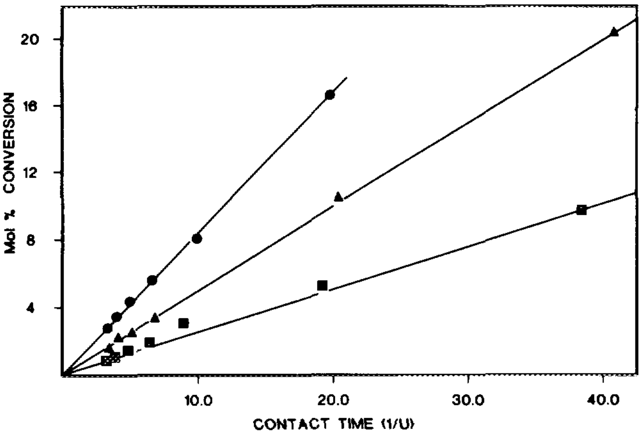


FIG. 1. Plot of the mol% conversion of methanol (■), isobutanol (▲), and alcohol mixture (methanol : isobutanol = 2 : 1) (●) to products vs contact time 1/*U* over the Nafion H catalyst (2.0 g). *T* (methanol) = 373 K; *T* (isobutanol) = 395 K; *T* (alcohol mixture) = 390 K; P_{Tot} = 1.34 × 10^3 kPa, P_M = 143.0 kPa; P_B = 66.5 kPa; P_{Al} mixture = 103.0 kPa. *U* is the gas space velocity in liters (STP) of reactant gas per liter of catalyst per minute.

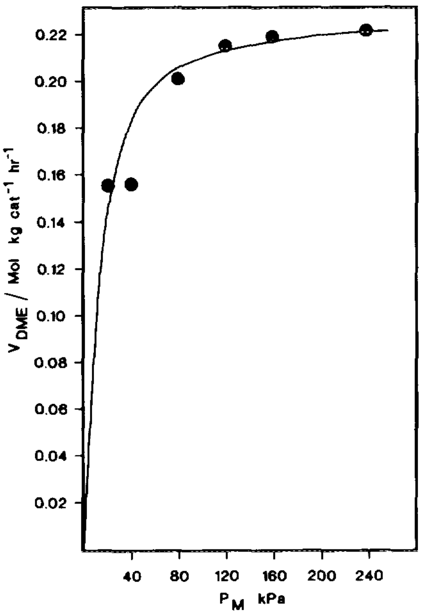


FIG. 2. Effect of methanol partial pressure (p_M) on the steady state rate of formation of dimethyl ether (DME) over 2.0 g Nafion H at 375 K, total pressure of 1.34×10^3 kPa and N_2 + alcohol feed rate 250 mol/kg catalyst/hr. Circles are experimental points and the full line is a theoretical curve according to Eq. (4) in Table 1, using $k_1 = 5.54 \times 10^{-2}$ mol/kg catalyst^{-1} hr^{-1} and $K_M = 2.22 \times 10^{-1}$ kPa^{-1}.

lyst bed, the degree of conversion being a direct measure of the reaction rate. Kinetic data were subsequently obtained within these conversion ranges. For methanol dehydration, DME was the only product by reaction (4), and the rate of DME formation reached a constant value at high methanol pressures, as shown in Fig. 2. For isobutanol dehydration, the products were isobutene, DIBE and octenes, and the rates of formation of these products are shown in Fig. 3. Of particular interest is the dependence of the rate of isobutene formation on the reactant isobutanol pressure, which shows a maximum at 14 kPa. Methanol when present was a retardant of the isobutanol dehydration to isobutene, and this effect is demonstrated by comparing the rates of isobutanol dehydration to isobutene in the absence and presence of methanol.

In another set of experiments, the rate of dehydration of the alcohol mixture was followed as a function of partial pressure of each individual alcohol while maintaining the partial pressure of the second alcohol constant. The rates of MIBE formation represented in Fig. 4 show maxima on the dependences on partial pressures of both methanol and isobutanol, indicating retardation, or self-poisoning, of the MIBE synthesis by either reactant: a stronger self-poisoning by isobutanol and weaker by methanol.

The dehydration of the alcohol mixture over porous Nafion H-MS was studied over a range of pressures and temperatures. The overall pressure dependence of the synthesis is shown in Fig. 5 and the temperature dependence in Fig. 6, both with methanol : isobutanol ratio 2 : 1. The general feature of the pressure dependence, a dramatic increase of selectivity to MIBE and DME with concomitant suppression of isobutene and octene formation (Fig. 5), was also reported in the preliminary communication (*3*). Aside from the dominant mixed ether product MIBE, its isomer MTBE was formed in small amounts. Increase of temperature increased the rates of all product formation, with MIBE and DME still dominant products, but with increased selectivity to butenes and octenes. Within the butenes, the selectivity between isobutene and the linear butenes varied between 75 and 100% isobutene so that the greater the reaction rate, e.g., at low isobutanol partial pressures and high temperatures, the lower the selectivity for isobutene. The octenes formed by reactions (3) and (8) were identified as predominantly 2,5-dimethylhexene at low temperatures and predominately 2,2,4-trimethylpentene at higher temperatures, with a smooth variation of composition of these two isomers at intermediate temperatures within this range. For example, at 409 K the 2,5-dimethylhexene was the only octene detected, while at 430 K it accounted for 28% of the total octene product

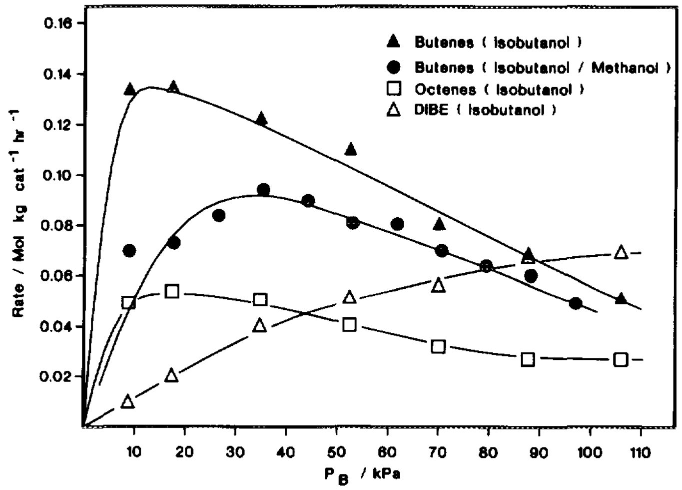


FIG. 3. Rates of formation of isobutene (▲), di-isobutyl ether (DIBE) (△), and octenes (□) from isobutanol over 2.0 g Nafion H as a function of isobutanol partial pressure p_B at T = 396 K, total pressure of 1.34×10^3 kPa, and N_2 + alcohol feed rate 250 mol/kg catalyst/hr. For comparison, the rates of isobutene formation in 2 : 1 methanol : isobutanol mixture are shown as (●), under similar conditions to isobutanol dehydration but with T = 400 K.

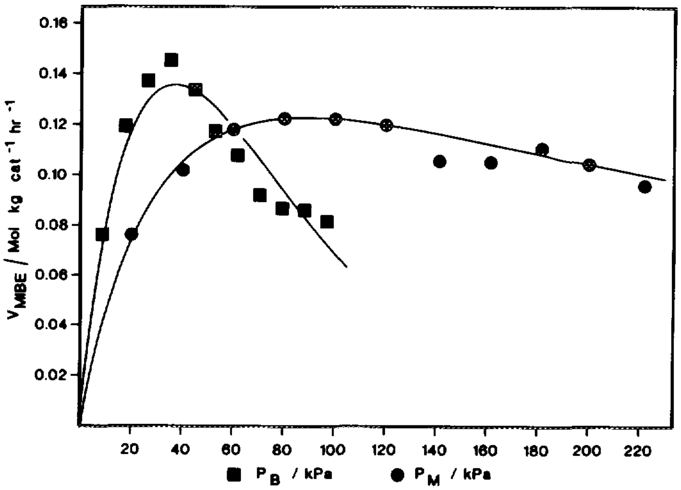


FIG. 4. Rates of methyl-isobutyl ether (MIBE) formation from methanol/isobutanol mixtures as a function of partial pressure of methanol, p_M, with partial pressure of isobutanol kept constant at p_B = 8.82 kPa (●), and of partial pressure of isobutanol, p_B, with constant p_M = 20.16 kPa (■) over 1.0 g Nafion H at 400 K, total pressure 1.34×10^3 kPa, and N_2 + alcohol feed rate 125 mol/kg catalyst/hr. Circles are experimental points and full lines are theoretical curves, using Eq. (5) in Table 1 for the dependence of v_{MIBE} on p_M with k_4 = 2.78 mol/kg catalyst/hr, $K_M = 1.37 \times 10^{-2}$ kPa^{-1}, $K_B = 2.43 \times 10^{-2}$ kPa^{-1}, and Eq. (9) for the dependence of v_{MIBE} on p_B with $K_B'' = 1.0 \times 10^{-6}$ kPa^{-2}, $K_B''' = 1.5 \times 10^{-6}$ kPa^{-3}, and k_4, K_M, and K_B as above.

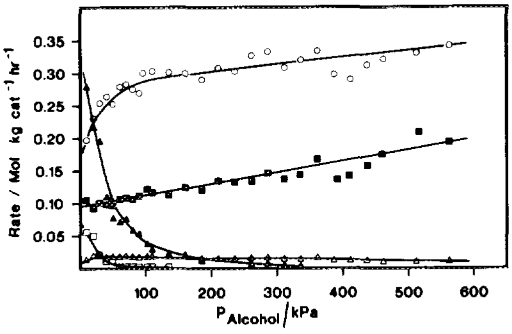


FIG. 5. Variation of product yield with methanol : isobutanol 2 : 1 alcohol mixture partial pressure at a steady-state reaction rate at 389 K over 1.0 g Nafion H MicroSaddles (alcohol feed = 15.59 mol/kg catalyst/hr, N_2 feed = 186 mol/kg catalyst/hr, ○ = MIBE, ■ = DME, ▲ = butenes, △ = DIBE, □ = octenes).

with 2,2,4-trimethylpentene accounting for the remainder.

DISCUSSION

Properties of Nafion H and the Nature of Its Acidity

A correct interpretation of catalysis, both mechanistic and kinetic, over Nafion H cannot be undertaken without an appreciation of the unique physico-chemical properties of this resin. Similar to the sulfonated cross-linked polystyrene resins, the reactions are considered to occur to a greater or lesser extent within the catalyst mass, wherein the reactants, products, and solvent are in equilibrium with the external solution or gas phase (*17, 18*). Access to the resin phase is brought about through resin swelling in the presence of polar molecules such as alcohols or water. However, resin swelling by polar solvents could in principle also change the efficiency of the catalytically active acid sites. Gates and Rodriguez (*19*) have shown that excess water or alcohol can modify the acidity from the more active undissociated sulfonic acid that gives rise to general acid catalysis to the less active solvated proton, giving rise to specific acid catalysis. This hypothesis was substantiated by IR studies (*20*) that showed a network of $-SO_3H$ groups in the anhydrous resin that break up in the presence of polar solvents, first through the insertion of a few molecules in the hydrogen bonded structure, which finally leads to their dissociation and solvation of the protons. Similar effects of polar solvents have been shown to occur over Nafion H using IR (*21*).

Swelling of Nafion H depends on the nature of the polar solvents used. Alcohols lead to greater swelling than water at room temperature (*22*), with the degree of swelling decreasing in the order methanol > ethanol > 1-propanol ≈ 2-propanol > 1-butanol, but within this range the differences are quite small. Further, a phenomenon known as exchange site clustering occurs in Nafion H resins (*23*). The exact nature of these ion clusters is not known, but it has been suggested that exchange sites, counterions, and polar molecules, such as sorbed water or

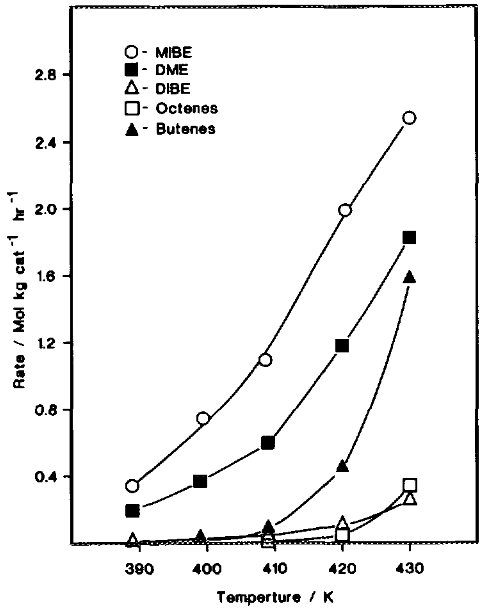


FIG. 6. Effect of temperature on the observed reaction rates over 1.0 g of the Nafion H MicroSaddles catalysts with methanol : isobutanol 2 : 1 at total pressure of = 7.58 × 10^3 kPa (alcohol feed = 15.59 mol/kg catalyst/hr; N_2 feed = 186 mol/kg catalyst/hr; ○ = MIBE, ■ = DME, ▲ = butenes, ○ = octenes, △ = DIBE).

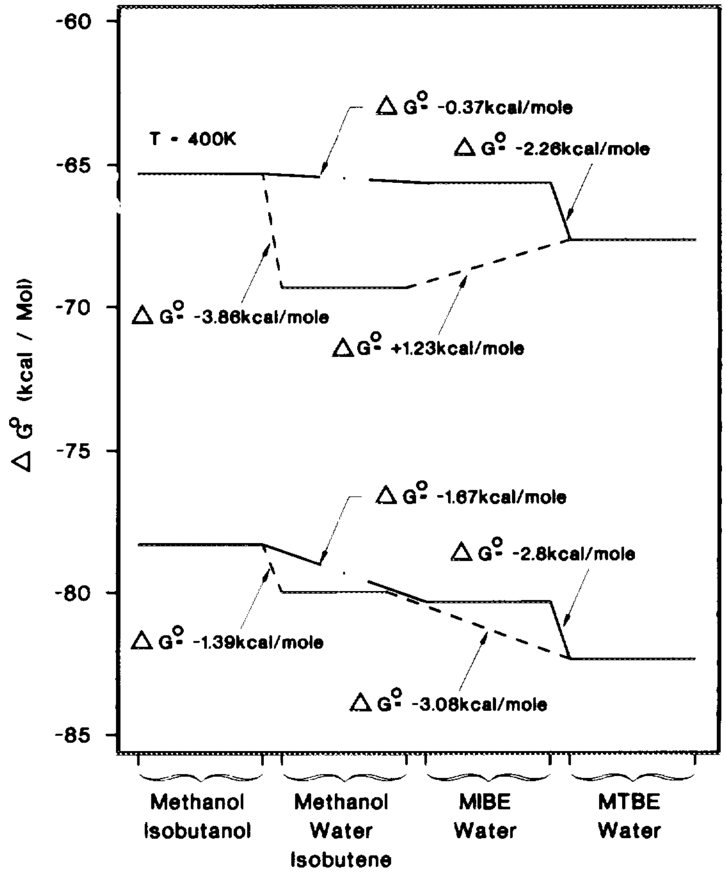


FIG. 7. Standard free energies for dehydration reactions in the methanol–isobutanol (2-methyl-1-propanol) mixtures. Sources are Lewis, G. N., and Randall, M., "Thermodynamics," McGraw–Hill, New York, 1961; Freifelder, D., "Principles of Physical Chemistry," Jones & Bartlett, Boston, 1982; and "T.R.C. Thermodynamics Tables for Hydrocarbons and Non-Hydrocarbons," Texas Research Institute.

alcohols, exist as separate microphases in the polymer.

In the reactions studied, the partial pressures of all the reactants and products were below their saturated vapor pressure. The lowest saturated vapor pressure was that of isobutanol, 202 kPa at 400 K, and in some experiments partial pressures of isobutanol were used that, even though lower than the saturated vapor pressure, were high enough for capillary condensation to occur. The degree of intraporous condensation and swelling could not be determined under the present experimental conditions, temperatures 380–400 K and alcohol pressures 0–600 kPa, and it was not *a priori* known whether the complex physical properties associated with swelling would influence the intraporous reactions. However, the high reaction rates observed indicate that the acid sites of the catalyst were readily accessible. Since Nafion H was used in most of the present kinetic studies, it is highly probable that swelling by the reactants had occurred to open up the pores in which the sulfonic groups are located. Further, the simple linear relationship between the conversion to various products and the contact time (Fig. 1) indicates that the system established steady states that corresponded to a well-behaved differential kinetics regime.

TABLE 1

Kinetic Laws for Dehydration Reactions of Methanol and 2-Methyl-1-Propanol

Reaction	Rate law	Linear form of rate law
(4)	$v_{\mathrm{DME}} = k_1\theta_{\mathrm{M}}^2 = \dfrac{k_1K_{\mathrm{M}}^2p_{\mathrm{M}}^2}{(1 + 2K_{\mathrm{M}}p_{\mathrm{M}} + K_{\mathrm{B}}p_{\mathrm{B}})^2}$	$\sqrt{\dfrac{1}{v_{\mathrm{DME}}}} = \sqrt{\dfrac{1}{k_1}}\left[\dfrac{(1 + K_{\mathrm{B}}p_{\mathrm{B}})}{K_{\mathrm{M}}p_{\mathrm{M}}} + 2\right]$
(7)	$v_{\mathrm{DIBE}} = k_2\theta_{\mathrm{B}}^2 = \dfrac{k_2K_{\mathrm{B}}^2p_{\mathrm{B}}^2}{(1 + 2K_{\mathrm{B}}p_{\mathrm{B}} + K_{\mathrm{M}}p_{\mathrm{M}})^2}$	$\sqrt{\dfrac{1}{v_{\mathrm{DIBE}}}} = \sqrt{\dfrac{1}{k_2}}\left[\dfrac{(1 + K_{\mathrm{M}}p_{\mathrm{M}})}{K_{\mathrm{B}}p_{\mathrm{B}}} + 2\right]$
(3)	$v_{\mathrm{IB}} = k_3\theta_{\mathrm{B}}\theta_{\mathrm{E}} = \dfrac{k_3K_{\mathrm{B}}p_{\mathrm{B}}}{(1 + K_{\mathrm{B}}p_{\mathrm{B}} + K_{\mathrm{M}}p_{\mathrm{M}})^2}$	$\sqrt{\dfrac{p_{\mathrm{B}}}{v_{\mathrm{IB}}}} = \sqrt{\dfrac{1}{k_3K_{\mathrm{B}}}}[1 + K_{\mathrm{B}}p_{\mathrm{B}} + K_{\mathrm{M}}p_{\mathrm{M}}]$
(5)	$v_{\mathrm{MIBE}} = k_4\theta_{\mathrm{M}}\theta_{\mathrm{B}} = \dfrac{k_4K_{\mathrm{M}}p_{\mathrm{M}}K_{\mathrm{B}}p_{\mathrm{B}}}{(1 + K_{\mathrm{M}}p_{\mathrm{M}} + K_{\mathrm{B}}p_{\mathrm{B}})^2}$	$\sqrt{\dfrac{p_{\mathrm{M}}p_{\mathrm{B}}}{v_{\mathrm{MIBE}}}} = \sqrt{\dfrac{1}{k_4K_{\mathrm{M}}K_{\mathrm{B}}}}[1 + K_{\mathrm{M}}p_{\mathrm{M}} + K_{\mathrm{B}}p_{\mathrm{B}}]$

Because the $-SO_3H$ groups were shown to be equivalent by enthalpimetric titrations that were carried out in suspensions at room temperature (*4*), it is deemed reasonable to assume that they were also equivalent under the catalytic reaction conditions employed here. Based on the above observations, the physico-chemical model adopted here is one in which mass-transfer phenomena play no role in influencing the kinetics even when intraporous condensate is present, and in which all acid sites are equivalent in their catalytic action. Since alcohols are the reactants and water is the reaction product in all our reactions, it is believed that the "dry" general acid sites are converted under the reaction conditions to specific acid sites comprising solvated protons (*19*) or adducts with alcohols such as oxonium salts or esters.

Thermodynamic Considerations

In general, the absolute values of the standard free energies, $\Delta G°$, of reactions (1)–(8) are not large, and within the temperature range employed, the reaction equilibria can be shifted from right to left or *vice versa* by changes of concentrations, temperature, and pressure. The $\Delta G°$ values for the key reactions involved in the set (1)–(8) are represented in Fig. 7 for two temperatures, 298 and 400 K. At 400 K and above, the synthesis of MTBE from methanol and isobutene (1) becomes a thermodynamically uphill process, while if methanol and isobutanol are the reactants in reactions (5) and (6), the paths to the mixed ether isomers MTBE and MIBE are exoenergetic. Further, MIBE, that is readily formed over Nafion H (*3*), is a thermodynamically less favorable product than MTBE. Elevated pressure will favor the ether-forming reactions (4)–(7) over the dehydration of isobutanol to isobutene (3) in which the molar volume increases when going from the left to the right.

Kinetic Models and Quantitative Treatment

From the data presented in Figs. 2–6, the following general patterns emerge: (a) the dehydration of methanol to DME (4) and dehydration of isobutanol to DIBE (7) follow "saturation" kinetics wherein the rate of formation of these symmetrical ethers first increases with the alcohol pressure and then becomes constant at higher alcohol pressures; (b) the dehydration of isobutanol to isobutene (3) shows a maximum with the isobutanol pressure, demonstrating self-poisoning of this reaction at high pressures; and (c) the coupling of methanol and isobutanol to the mixed ether MIBE (5) shows a maximum when the partial pressure of either alcohol is varied, indicating a competitive activation of these two alcohols. All of these kinetic features can be cast into quantitative relationships utilizing the following assumptions: (i) the reactants are in equilibrium

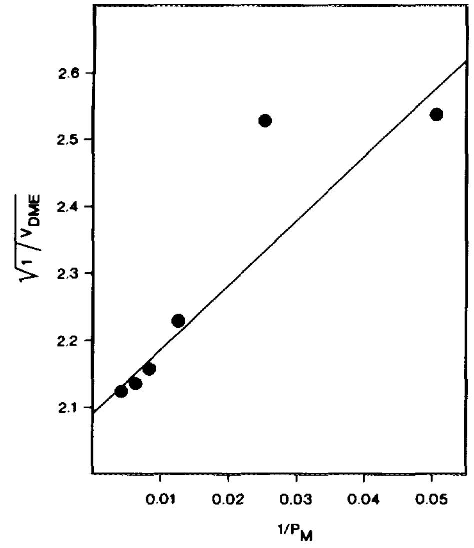


FIG. 8. Langmuir–Hinshelwood linear plot for a bimolecular surface reaction in the case of methanol dehydration to DME over 2.0 g Nafion H at 375 K with total pressure 1.34 × 10^3 kPa and N_2 + alcohol feed 250 mol/kg catalyst/hr. The slope and intercept give $k_1 = 5.54 \times 10^{-2}$ mol/kg catalyst/hr and $K_M = 2.22 \times 10^{-1}$ kPa^{-1}, using Eq. (4) of Table 1. The experimental data and conditions are those of Fig. 2.

with the acid sites of the Nafion H catalyst, (ii) all acid sites are equivalent, and (iii) the reaction rate is proportional to the surface concentrations of the reacting species. The partial pressures of methanol and isobutanol are denoted p_M and p_B, respectively, and the surface concentrations of empty protonated sites θ_E, adsorbed activated methanol θ_M, and adsorbed activated isobutanol θ_B. Further, the rates of DME, DIBE, isobutene, and MIBE formation are denoted as v_{DME}, v_{DIBE}, v_{IB}, and v_{MIBE}, respectively. The kinetic laws following from assumptions (i)–(iii) are summarized for reactions (3)–(5) and (7) in Table 1.

Other rate laws have been explored but those listed in Table 1 give the most satisfactory account of the experimentally observed kinetics, with one modification for the dependence of MIBE formation on the isobutanol pressure that is discussed below. In particular, steady-state kinetics of the Michaelis–Menten type, adapted for dual-site reactions, was explored. This led to fairly complex expressions for the reaction rates and the assumption that surface intermediates are at a steady state but not in equilibrium with their gas-phase source molecules was found unnecessary. The present Langmuir–Hinshelwood kinetics is a special case in which the gas molecules are in a rapid equilibrium with their adsorbed species, and provides a satisfactory account of the observed rates. The linear forms of the rate laws, also listed in Table 1, are graphically represented in Figs. 8–11.

In each of these graphs, the slope and intercept were used to determine the appropriate kinetic constant k_i, equilibrium constants K_M and K_B, or a combination of the constants from which k_i, K_M, and K_B could be retrieved. For example, in the DME synthesis with no isobutanol present (p_B = 0), plotted in Fig. 8, the intercept $2/\sqrt{k_1}$ and the slope $k_1^{-1/2}K_M^{-1}$ gave the

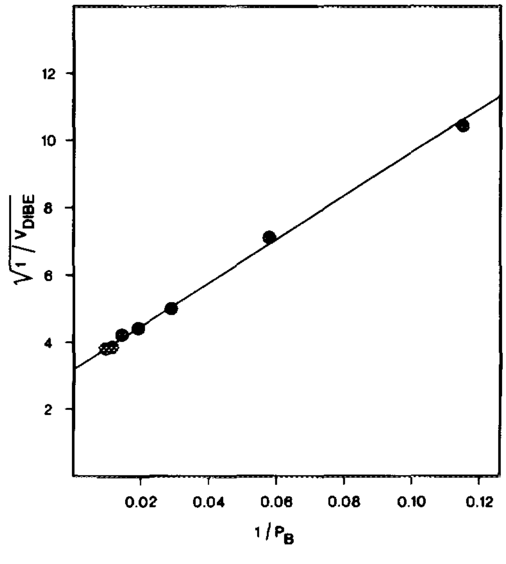


FIG. 9. Langmuir–Hinshelwood linear plot for a bimolecular surface reaction in the case of isobutanol (2-methyl-1-propanol) dehydration to DIBE over 2.0 g Nafion H at 396 K with total pressure 1.34 × 10^3 kPa and N_2 + alcohol feed 250 mol/kg catalyst/hr. The slope and intercept give $k_2 = 7.9 \times 10^{-1}$ mol/kg catalyst/hr and $K_B = 2.4 \times 10^{-2}$ kPa^{-1}, using Eq. (7) of Table 1.

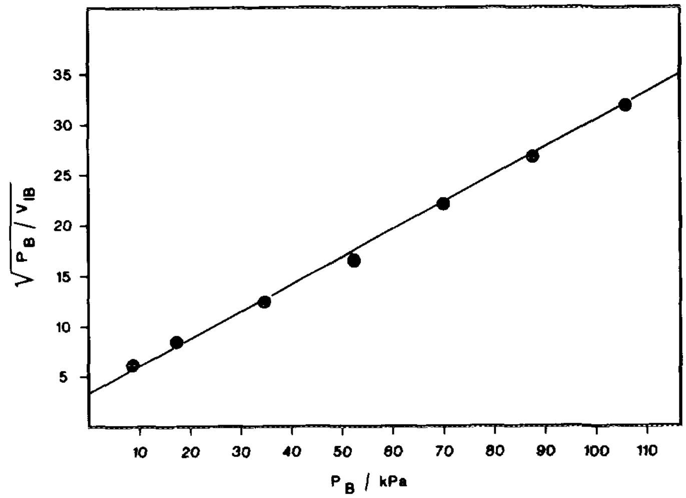


FIG. 10. Langmuir–Hinshelwood linear plot for the dehydration of 2-methyl-1-propanol (isobutanol) to butenes over 2.0 g Nafion H catalyst at 396 K, total pressure of 1.34×10^3 kPa and N_2 + alcohol feed rate 250 mol/kg catalyst/hr. The slope and intercept give $k_3 = 7.72 \times 10^{-1}$ mol/kg catalyst/hr and $K_B = 7.35 \times 10^{-2}$ kPa^{-1}, using Eq. (3) of Table 1. The experimental data and conditions are those of Fig. 3.

values $k_1 = 5.54 \times 10^{-2}$ mol/hr–kg catalyst and $K_M = 2.22 \times 10^{-1}$ kPa^{-1} at 375 K. Similarly, for the DIBE synthesis with no methanol present, $k_2 = 7.9 \times 10^{-1}$ mol/hr–kg catalyst and $K_B = 2.40 \times 10^{-2}$ kPa^{-1} at 396 K from the slope and intercept of Fig. 9. The dehydration of isobutanol to isobutene in the absence of methanol ($p_M = 0$), Fig. 10, gives $k_3 = 7.72 \times 10^{-1}$ mol/hr–kg catalyst and $K_B = 7.35 \times 10^{-2}$

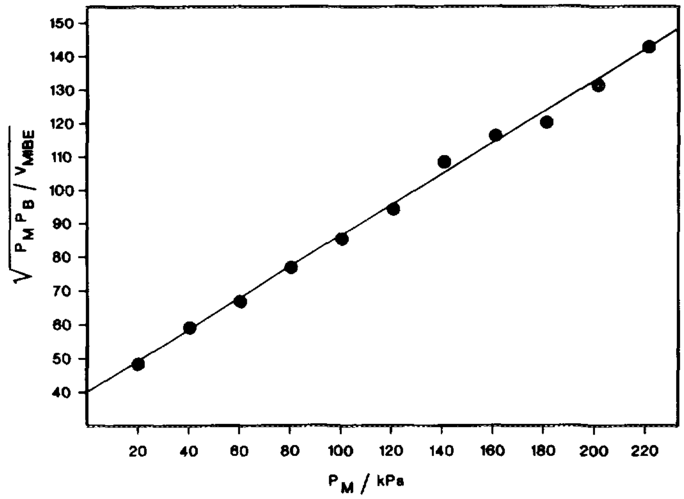


FIG. 11. Langmuir–Hinshelwood linear plot for the dehydrocondensation of methanol and 2-methyl-1-propanol (isobutanol) to MIBE over 1.0 g Nafion H catalyst at 400 K, total pressure of 1.34×10^3 kPa and N_2 + alcohol feed rate 125 mol/kg catalyst/hr at a constant pressure of isobutanol, $p_B = 8.82$ kPa, and varying partial pressure of methanol p_M. The slope and intercept give combinations of rate and equilibrium constants $\sqrt{K_M/(k_4 K_B)} = 0.45$ and $(1 + K_B p_B)/\sqrt{k_4 K_M K_B} = 40.0$, where k_4 is in mol/kg catalyst/hr and K_M, K_B are in kPa^{-1}.

kPa^{-1} at 396 K. The MIBE synthesis with constant pressure of isobutanol ($p_B = 8.82$ kPa) while varying the pressure of methanol, Fig. 11, yields $\sqrt{K_M/(k_4K_B)} = 4.5 \times 10^{-1}$ $\mathrm{mol}^{-1/2}$ $\mathrm{hr}^{1/2}$–kg $\mathrm{catalyst}^{1/2}$ and $(1 + K_Bp_B)/\sqrt{k_4K_MK_B} = 40.0$ $\mathrm{mol}^{-1/2}$ $\mathrm{hr}^{1/2}$–kg $\mathrm{catalyst}^{1/2}$ $\mathrm{kPa}^{-1/2}$ at 400 K.

When the MIBE synthesis was carried out with methanol pressure constant ($p_M = 20.16$ kPa) and pressure of isobutanol varied, as represented in Fig. 4, the kinetic equation for the MIBE synthesis of Table I was found not to be valid and the plot of $\sqrt{p_Bp_M/v_{\mathrm{MIBE}}}$ vs p_B was not linear. This was attributed to additional retardation of the MIBE synthesis by side reactions that became kinetically significant at high pressures of isobutanol. A good account for this additional retardation was obtained by adding terms proportional to the second and the third power of isobutanol pressure in the denominator of the expression for v_{MIBE},

$$v_{\mathrm{MIBE}} = \frac{k_4K_Mp_MK_Bp_B}{(1 + K_Mp_M + K_Bp_B + K''_Bp_B^2 + K'''_Bp_B^3)^2}, \tag{9}$$

with $K''_B = 1.0 \times 10^{-6}\ \mathrm{kPa}^{-2}$ and $K'''_B = 1.5 \times 10^{-6}\ \mathrm{kPa}^{-3}$ at 400 K. The values of K''_B and K'''_B are such that the effects of the additional retardation $(K''p_B^2 + K'''p_B^3)$ are negligible at $p_B \leq 30$ kPa but become important at higher p_B. Thus, the retardation $(K''p_B^2 + K'''p_B^3)$ need not be considered in the experiment represented in Fig. 10, where $p_B = 8.82$ kPa, and the linearized kinetic law for v_{MIBE} of Table 1 is satisfied. The refined kinetic relation (9) is used for v_{MIBE} with varying p_M, and in fact the full line in Fig. 4 is the theoretical curve according to Eq. (9) with $k_4 = 2.78$ mol/hr–kg catalyst, $K_M = 1.37 \times 10^{-2}$ kPa^{-1}, $K_B = 2.43 \times 10^{-2}\ \mathrm{kPa}^{-1}$, $K''_B = 1.0 \times 10^{-6}\ \mathrm{kPa}^{-2}$, and $K'''_B = 1.5 \times 10^{-6}\ \mathrm{kPa}^{-3}$. The variation of v_{MIBE} with p_M, in Fig. 4, is represented by the theoretical relationship (9), full line, with the same values of k_4, K_M, and K_B, and with $(K''_Bp_B^2 + K'''_Bp_B^3)$ negligible.

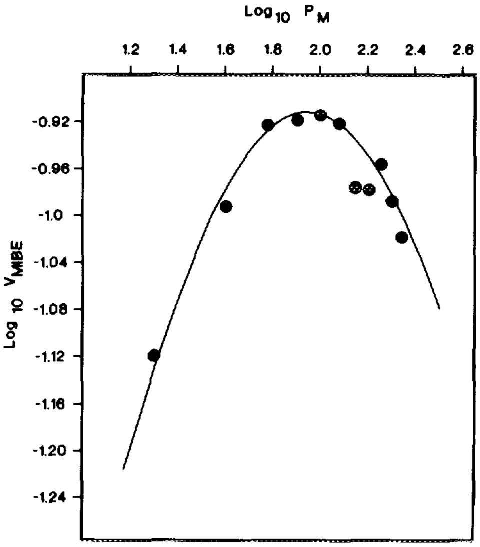


FIG. 12. The rate of MIBE formation, v_{MIBE}, as a function of methanol partial pressure p_M, where the (●) data points = log–log representation of experimental data from Fig. 4 and the full line curve is the theoretical prediction using Eq. (5) of Table 1 with $k_4 = 2.78$ mol/kg catalyst/hr, $K_M = 1.37 \times 10^{-2}\ \mathrm{kPa}^{-1}$, $K_B = 2.43 \times 10^{-2}\ \mathrm{kPa}^{-1}$, and $p_B = 8.82$ kPa.

The competitive adsorption of the two alcohols in MIBE synthesis is most markedly demonstrated in the log–log representation of the kinetics v_{MIBE} in Figs. 12 and 13. In these figures, experimental data are shown as individual points and theory utilizing Eq. (9) with the above set of constants by full lines.

The origin of the additional retardation term $(K''p_B^2 + K'''p_B^3)$ may be physical in nature as a result of isobutanol condensation at the higher pressures. Alternatively, retardation may result from packing of isobutanol molecules into two- and three-molecule or oxonium ion-molecule clusters which form a barrier to accessibility of the sulfonic group sites in their center.

Selectivities

The most significant selectivity feature of the present reaction system is the predominance of the mixed ether MIBE. The absence of the mixed ether MTBE in the reaction product suggests that the olfein product of

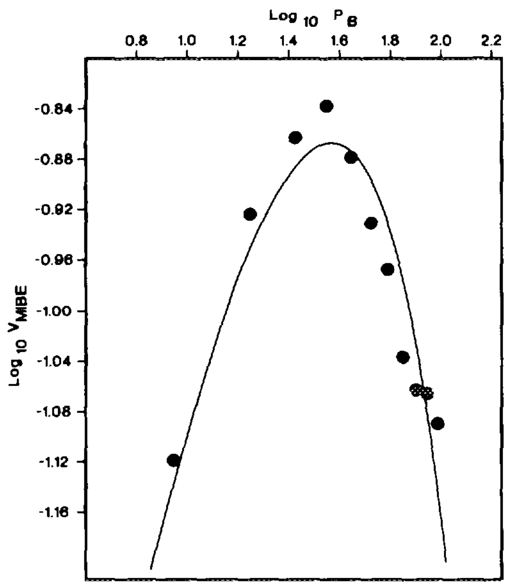


FIG. 13. The rate of MIBE formation, v_{MIBE}, as a function of isobutanol partial pressure p_B, where the (●) data points = log–log representation of experimental data from Fig. 4 and the full line curve is the theoretical prediction using Eq. (9) with k_4 = 2.78 mol/kg catalyst/hr, $K_M = 1.37 \times 10^{-2}$ kPa^{-1}, $K_B = 2.43 \times 10^{-2}$ kPa^{-1}, $K_B'' = 1.0 \times 10^{-6}$ kPa^{-2}, $K_B''' = 1.5 \times 10^{-6}$ kPa^{-3}, and p_M = 20.16 kPa.

isobutanol dehydration, i.e., isobutene, is not an intermediate in ether formation since isobutene reacts with methanol over Nafion H to give MTBE (*14*). In fact, the reaction of isobutene with methanol was carried out over the Nafion H catalyst under reaction conditions similar to that used for the alcohol coupling reaction and MTBE was found to be the only mixed ether product (>99.9% selectivity). The high selectivity of the mixed ether MIBE as compared to DME or DIBE is also noteworthy. If the mixed ether forming reaction were to proceed with equal reactivities of the isobutanol and methanol at the methanol : isobutanol ratio of 2 : 1 used, the product composition should consist of MIBE : DME : DIBE = 4 : 4 : 1. However, the product composition in Fig. 5 was found to be closer to 19 : 9 : 1 at alcohol pressures > 160 kPa, significantly in favor of the mixed ether MIBE. The results indicate that one of the alcohols is preferentially adsorbed and activated. Under the present set of the conditions, the alcohol preferentially adsorbed and activated is isobutanol. This is supported by the kinetic analysis, which showed that K_B was greater than K_M. The fact that isobutanol is adsorbed preferentially on the acid sites agrees with the greater basicity of heavier alcohols over methanol. For example, the proton affinities of *n*-butanol, *t*-butanol, and methanol are 828, 791, and 753 kJ mol^{-1}, respectively (*24*). Data for isobutanol are lacking but since this is a primary C_4 alcohol, its proton affinity is expected to be close to that of *n*-butanol, some 75 kJ mol^{-1} greater than that of methanol. In the sulfonic resin the protons of the SO_3H groups are not free, and the above trend in the proton attachment will be tempered by covalent bonding and SO_3H-backbone interactions, but nevertheless the greater basicity of isobutanol is a plausible reason for the observed $K_B > K_M$.

Even though the kinetic equations in Table 1 and the modified MIBE kinetics [9] were obtained by the analysis of data over Nafion H, they also elucidate the pressure dependence of the product formation patterns over Nafion H-MS, shown in Fig. 5. Thus, at low alcohol partial pressures (p_M = 4.9 kPa, p_B = 2.4 kPa), high selectivity to butenes as compared to MIBE was observed. This arises at this alcohol pressure because the fraction of the unoccupied acid sites is significant. Under these reaction conditions the dual-site mechanism for isobutanol dehydration, in which isobutene formation from adsorbed isobutanol is assisted by a free acid site, will be dominating and the primary product will be isobutene. At higher alcohol partial pressures, the fraction of acid sites occupied by alcohol molecules approaches unity, and the selectivity moves toward ether formation with the mixed ether, MIBE, dominating. The ratio of MIBE/DME was nearly independent of the total alcohol pressure when p_B/p_M was kept constant, but it slightly decreased at elevated pressures due to the additional retardation of the MIBE synthesis by higher power terms in p_B, cf. Fig. 5.

Temperature Dependence of the Alcohol Dehydration Reactions

The temperature dependence of the individual kinetic and equilibrium constants was not studied in detail, primarily because of the limited temperature range employed. It is nevertheless evident from Fig. 6 that the effective activation energies for olefin formation over Nafion H-MS are higher than those for ethers, and therefore selectivity to ethers decreases with increasing temperature. The differences are not large, however, within the range of stability of the Nafion resin, and at all temperatures below 430 K and the high pressures employed, the ethers are dominant products.

Reaction Mechanism

The most striking mechanistic feature of the present reaction system is the predominance of reaction products, which are not typically associated with acid catalysis involving carbenium ion intermediates that are free to rearrange to their more stable tertiary forms. Coupling of methanol and isobutanol over a wide range of other catalysts gave substantial amounts of MTBE in the product mixture (5). This is consistent with the formation of the tertiarybutyl carbenium derived from rearrangement of the primary isobutyl carbenium ion from interaction of isobutanol with an acid site. Reaction of methanol and isobutene over the Nafion H catalyst led to the formation of only MTBE, thus ruling out isobutene as an intermediate in the ether forming reaction under the present reaction conditions. The absence of linear butenes and the predominance of 2,5-dimethylhexene in the product mixture under mild reaction conditions further tends to rule out the formation of the primary isobutyl carbenium ion, which would be free to rearrange to the more stable tertiary form. Thus, reaction pathways must be considered where the formation of the tertiarybutyl carbenium ion does not readily occur.

The kinetic analysis presented above further suggests that two acid sites are utilized in the dehydration process to either isobutene or ethers. In the coupling of two methanol molecules to DME or two isobutanol molecules to DIBE, or one methanol and one isobutanol to MIBE, both alcohol molecules have to be activated. The nature of the adsorbed active state of the alcohols is unclear beyond exclusion of the tertiary carbenium ion. It could involve strongly physisorbed alcohol molecules bound to the acid sites *via* hydrogen bonding, oxonium ions formed as $-SO_3H + ROH \rightarrow -SO_3^{\ominus}H_2OR^{\oplus}$, or sulfonic esters formed as $-SO_3H + ROH \rightarrow -SO_3R + H_2O$. The second alcohol R′OH could react with the oxonium ion in a concerted S_N2 process with elimination of water and regeneration of the acid site, $H_2OR^{\oplus} + R'OH \rightarrow ROR' + H_3O^{\oplus}$. Alternatively, the alcohol R′OH could attack the ester $-SO_3R$, also with regeneration of the acid site, $-SO_3R + R'OH \rightarrow -SO_3H + ROR'$. However, neither of these two mechanisms is consistent with the observed kinetics if the alcohol R′OH is supplied from vapor phase. Therefore, a mechanism involving two surface-bound alcohols must be considered. Several possibilities arise, one of which is the reaction of oxonium with ester, $-SO_3^{\ominus}H_2OR^{\oplus} + -SO_3R' \rightarrow 2\text{-}SO_3H + ROR'$.

An interesting feature of the kinetic analysis is that the dehydration of isobutanol to isobutene was also consistent with a dual site mechanism, one site that activates the alcohol and a second empty acidic site that acts in a cooperative fashion in the dehydration step. Once again, oxonium or ester intermediacy can be invoked. In the oxonium pathway, the free acid site may act as an acceptor of water from the surface oxonium of isobutanol, e.g., $-SO_3^{\ominus}[H_2OCH_2CH(CH_3)_2]^{\oplus} + -SO_3H \rightarrow -SO_3H + -SO_3^{\ominus}H_3O^{\oplus} + CH_2{=}CH(CH_3)_2$. In the ester path, the acid site of the Nafion H may act as a catalyst for the decomposition of the isobutyl ester, $-SO_3CH_2CH(CH_3)_2 + -SO_3H \rightarrow -SO_3H + -SO_3^{\ominus}C^{\oplus}(CH_3)_3 \rightarrow 2\text{-}SO_3H + CH_2{=}C(CH_3)_2$. In either case the primary carbenium ion ${}^{\oplus}CH_2CH(CH_3)_2$ could be the precursor that rearranges to the tertiary carbenium ion $(CH_3)_3C^{\oplus}$, which forms isobutene by a subsequent loss of proton.

The details of the mechanistic paths outlined here are difficult to distinguish experimentally, even with the use of the most sophisticated spectroscopies such as CP-MASS NMR, Raman, or diffuse reflectance FTIR. Currently the various oxonium–carbenium–ester pathways are being examined by *ab initio* quantum chemical calculations on model systems involving short segments of the Nafion H backbone as carriers of the catalytically active $-SO_3H$ groups.

SUMMARY

Even though the mechanistic details remain unresolved, the present study does provide an insight into the dual-site mechanisms involved and a quantitative account of selectivities to several key products of the solid-acid-catalyzed dehydration reactions in the methanol–isobutanol system. The results of kinetic studies of coupling methanol with isobutanol over Nafion H yield the following conclusions:

(i) Dehydration of a mixture of methanol and isobutanol over the Nafion H catalyst leads to selective formation of the mixed ether MIBE. Only traces of MTBE were detected and the reaction products at low temperatures were consistent with oxonium ion or ester chemistry rather than the expected carbenium ion chemistry.

(ii) The kinetics and selectivities of ether and isobutene formation could be described by simple laws, formally of the Langmuir–Hinshelwood type.

(iii) The formation of MIBE, reaction (5), requires two sites occupied by the two different alcohols. The consequence of this behavior is that there is a maximum rate at an optimum ratio of partial pressures of the two alcohols. Quantitative evaluation of the observed rates shows that isobutanol is approximately two times more strongly held by the acid sites of Nafion H than methanol.

(iv) Dehydration of isobutanol to isobutene, reaction (3), requires two acid sites, one of which binds isobutanol and one that supplies an acid catalyzing function for the isobutanol dehydration. The consequence of this kinetic behavior is that at high pressures, isobutanol poisons its own dehydration and the kinetic order becomes negative with isobutanol concentration. Methanol also exhibits a retarding effect on isobutanol dehydration by competitive adsorption and blocking of the acid sites.

(v) The formation of DME, reaction (3), and DIBE, reaction (7), requires two sites occupied by the respective alcohol, methanol for DME and isobutanol for DIBE. The consequence of this behavior is that at high pressures, the kinetics become "saturated" and the rates of DME or DIBE reach constant values.

The dual-site character of all the catalyzed reactions involved imposes a requirement that the acid sites be highly concentrated on the surface of any prospective heterogeneous catalyst. Further, pressure is recognized as an important variable controlling the selectivity to ethers (high pressures) or isobutene (low pressures), and the mixed ether MIBE is favored by preferential adsorption of isobutanol.

ACKNOWLEDGMENT

This research was partially supported by the U.S. Department of Energy Contract DE-AC22-90PC90044.

REFERENCES

1. Chase, J. D., and Galvez, B. B., *Hydrocarbon Process* **60** (3), 89 (1981); Chase, J. D., in "Catalytic Conversions of Synthesis Gas and Alcohols to Chemicals" (R. G. Herman, Ed.), p. 307. Plenum, New York, 1984.

2. Nunan, J. G., Bogdan, C. E., Klier, K., Smith, K. J., Young, C.-W., and Herman, R. G., *J. Catal.* **116,** 195 (1989).

3. Nunan, J. G., Klier, K., and Herman, R. G., *J. Chem. Soc. Chem. Commun.*, 676 (1985).

4. Klier, K., Herman, R. G., Bastian, R. D., DeTavernier, S., Johansson, M., Kieke, M., and Feeley, O. C., *in* "Proc. Liquefaction Contractors' Review Meeting" (G. J. Stiegel and R. D. Srivastava, Eds.), pp. 20–49. U.S. Department of Energy–Pittsburgh Energy Technology Center, 1991.

5. Klier, K., Herman, R. G., Johansson, M. A., and Feeley, O. C., *Prepr. Am. Chem. Soc. Div. Fuel Chem.* **37** (1), 236 (1992).

6. Olah, G. A., Kaspi, J., and Bukala, J., *J. Org. Chem.* **42,** 4187 (1977).
7. Kaspi, J., Montgomery, D. D., and Olah, G. A., *J. Org. Chem.* **43,** 3147 (1978).
8. Olah, G. A., Meidar, D., Mahhotra, R., Olah, J. A., and Narang, S. C., *J. Catal.* **61,** 96 (1980).
9. Olah, G. A., and Kaspi, J., *Nouv. J. Chim.* **2,** 585 (1978).
10. Beltrame, P., Beltrame, P. L., Carniti, P., and Nespoli, G., *Ing. Eng. Chem. Prod. Res. Dev.* **19,** 205 (1980).
11. Hasegawa, H., and Higashimura, T., *Polym. J.* **11,** 737 (1979).
12. Cares, W. R., U. S. Patent 4,065,512 (Dec. 17, 1977); Kim, L., U. S. Patent 4,165,440 (Aug. 21, 1979).
13. Kaspi, J. and Olah, G. A., *J. Org. Chem.* **43,** 3142 (1978).
14. Olah, G. A., British Patent 2,082,177 (Mar. 3, 1982); Oyama, K., and Kihara, K., British Patent 2,075,019 (Nov. 11, 1981).
15. Olah, G. A., Keumi, T., and Meidar, D., *Synthesis*, 929 (1978).
16. Waller, F. J., *in* "Catalytic Conversions of Synthesis Gas and Alcohols to Chemicals," (R. G. Herman, Ed.), p. 193. Plenum, New York, NY 1984.
17. Polanskii, N. G., *Russ. Chem. Rev.* **39,** 244 (1970).
18. Helfferich, F., *J. Am. Chem. Soc.* **76,** 5567 (1954).
19. Gates, B. C., and Rodriguez, W., *J. Catal.* **31,** 27 (1973).
20. Thornton, R., and Gates, B. C., *J. Catal.* **34,** 275 (1974).
21. Falk, M., *Am. Chem. Soc. Symp. Ser.* **180,** 139 (1982).
22. Yeo, R. S., *Polymer* **21,** 432 (1980).
23. Gierke, T. D., and Hsu, H. S., *Am. Chem. Soc. Symp. Ser.* **180,** 283 (1982).
24. Long, J., and Munson, B., *J. Am. Chem. Soc.* **95,** 2427 (1973).