HIGH OCTANE ETHERS FROM SYNTHESIS GAS-DERIVED ALCOHOLS

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OBJECTIVES OF THE RESEARCH

The objective of the proposed research is to synthesize high octane ethers, primarily methyl isobutyl ether (MIBE) and methyl tertiary butyl ether (MTBE), directly from $H_2/CO/CO_2$ coal-derived synthesis gas via alcohol mixtures that are rich in methanol and 2-methyl-1-butanol (isobutanol). The overall scheme involves gasification of coal, purification and shifting of the synthesis gas, higher alcohol synthesis, and direct synthesis of ethers.

The last stage of the synthesis involves direct coupling of synthesis gas-derived methanol and isobutanol that has been demonstrated by us to occur over superacid catalysts to yield methyl isobutyl ether (MIBE) at moderate pressures and a mixture of methanol and isobutene at low pressures. MIBE is an isomer of MTBE and a process is proposed whereby MTBE from the two alcohols is maximized and MIBE is minimized. This will be achieved by the proper choice of reaction conditions, i.e. intermediate pressures, and of inorganic acid catalysts that are stable at temperatures higher than 200°C, at which the carbonium ion reaction coupling of the two alcohols to MTBE is more effective than the oxonium ion or ester reaction coupling to MIBE.

Both organic and inorganic catalysts will be investigated, and the better catalysts of these classes will be subjected to long term performance studies. The long term performance studies of the combined process will extend to 1000 hr and detailed analytical data for all products will be provided. The project is divided into the following three tasks:

- Task 1. Synthesis of High Octane Ethers from Alcohol Mixtures Containing Predominantly Methanol and 2-Methyl-1-Propanol over Superacid Resins
- Task 2. Inorganic Catalysts for the Synthesis of High Octane Ethers from Alcohols
- Task 3. Long Term Performance and Reaction Engineering for Scale-Up of the Alcohols-to-Ethers Process

The expected result of the proposed research is a novel process for producing ethers, in particular MTBE, in which all five carbons of the unsymmetric C_1-O-C_4 ethers originate from coal-derived synthesis gas.

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SUMMARY OF TECHNICAL PROGRESS

The temperature dependence of ether synthesis, particularly unsymmetric methylisobutylether (MIBE), was carried out over the Nafion-H microsaddles (MS) catalyst. The principal product formed under the rather severe reaction conditions of 1100 psig pressure and temperatures in the range of 123–157°C was the expected MIBE formed directly by coupling the methanol/isobutanol reactants. In addition, significantly larger quantities of the dimethylether (DME) and hydrocarbon products were observed than were obtained under milder reaction conditions.

Deactivation of the Nafion-H MS catalyst was determined by periodically testing the catalyst under a given set of reaction conditions for the synthesis of MIBE and MTBE from methanol/isobutanol = 2/1, i.e. 123°C, 1100 psig, and total GHSV = 248 mol/kg cat/hr. After carrying out various tests over a period of 2420 hr, with intermittent periods of standing under nitrogen at ambient conditions, the yields of MIBE and MTBE had decreased by 25% and 41%, respectively.

In order to gain insight into the role of the surface acidity in promoting the selective coupling of the alcohols to form the unsymmetric ether, the strengths of the acid sites on the catalysts are still being probed by calorimetric titrations in non-aqueous solutions.

TECHNICAL PROGRESS

A. Temperature Dependence of MIBE Synthesis and Catalyst Stability

Purpose

The objective is to determine the effect of temperature on the yields and selectivities of products when methanol and isobutanol are pumped over Nafion-H microsaddles (MS) at high pressure.

Catalyst Loading and Pretreatment

The DuPont Nafion catalyst was described in our earlier technical progress reports (1,2) and was used as received from C.G. Processing, Inc. of Rockland, Delaware. A 1.0039 g portion of the Nafion catalyst was weighed and loaded into the reactor with the usual 10 ml of 3 mm Pyrex beads as diluent. The reactor containing the catalyst was connected to the testing unit and flushed with nitrogen for several hours to remove any residual oxygen or water.

Catalyst Testing

The first step in the testing of the catalyst was setting the flow of the helium-nitrogen gas mixture using a wet test meter (Precision Scientific Co.). When the flow was set to within 1% of the desired value, the reactor was pressurized and the flow was once again checked and adjusted if necessary. After the correct flow was obtained at reaction pressure, the reactor heaters were turned on. Once a thermal equilibrium was achieved, one or two blank injections were made to check for a smooth GC baseline. The 2:1 molar methanol/isobutanol solution was then pumped into the H₂/He gas feed at a previously calculated rate using a Gilson Model 302 pump. The Nafion catalyst was tested under the following conditions:

Table I. Catalytic Test Conditions

Reactor Temperature (°C)	123, 137, 147, 157, 123
Reactor Pressure (psig)	1100
Total GHSV (mol/kg cat/hr)	248
Catalyst Weight (kg)	0.0010039
Nitrogen flow (mol/hr)	0.0206
Helium flow (mol/hr)	0.21027
Methanol flow (mol/hr)	0.01222
Isobutanol flow (mol/hr)	0.00611

Results

The catalyst was maintained at each temperature for approximately 48 hr so that a steady state could be verified. The gas chromatographic data, thermal response factors, and internal standard flow rate are used to calculate product yields. Dividing the product yield (mol/hr) by the amount of catalyst used gives the Gas Hourly Space Velocity (GHSV). Average product yields are then calculated from the GHSV of the reactants for steady state injections. The effects of temperature on product yields for the reaction conditions shown in Table I are shown in Figure 1, where DME is dimethylether, C₄ are butenes, tBuOH is tertiary butanol, MTBE is methyl tertiarybutyl ether, and MIBE is methyl isobutyl ether.

Figure 1. Effects of Temperature on the Yield of Products

The long term deactivation of the Nafion-H MS was tested at 123°C with the same pressure and reactant flows rates as shown in Table I. The catalyst had been subjected to many different reaction conditions, e.g. even MTBE decomposition studies, after being loaded into the stainless steel reactor. These included periods of standing under N₂ at ambient temperature and pressure. The times given reflect total time in the reactor, not total reaction time at elevated temperatures and pressures. The results of the deactivation study at high pressure (1100 psig) when the catalyst was 0-24, 360, and 2420 hr in the reactor are shown in Figure 2. The tests in Figure 1 up to 157°C are represented in the first 450 hr in Figure 2. Other tests were conducted and then the catalyst was retested under the initial conditions of the 123°C experiment. It is important to note that the test at 360 hr is probably not under true steady-

state conditions. Fluctuations occurred in the 360 hr test, and the corresponding data points in Figure 2 were obtained by averaging the data at 360 hr. In any case, a comparison of the time at 0 hours and 2420 hours shows deactivations of 50%, 41%, and 25% for DME, MTBE, and MIBE, respectively.

Figure 2. Deactivation of Nafion-H MS
Under Reaction Conditions in Table I.

Activation energies for the different products are calculated by assuming that the yields are proportional to the reaction rate constants. A plot of $\log k$ vs $1/T(K)$ gives straight lines whose slopes can be multiplied by $2.303R$, where R is the gas constant of $1.987 \text{ cal/deg}\cdot\text{mol}$, to give the activation energy. Tables II and III list the calculated apparent activation energies for the major products observed to be formed over the Nafion-H MS catalyst under the rather severe reaction conditions given in Table I.

B. MTBE Pumping Experiment

The temperature dependence study with the Nafion-H MS catalyst was followed by an MTBE pumping experiment to determine the major products formed when MTBE decomposed on the catalyst. This experiment will allow reaction conditions to be optimized in future studies for the synthesis of MTBE. MTBE was injected into the inert gas stream pumped over the Nafion-H MS catalyst at 123°C under 1 atm of pressure at three different GHSV. The results are given in Table IV. It is evident that MTBE very readily decomposed, principally to methanol and isobutene, under these reaction conditions. Calibration of the GC thermal response factors is being carried out to increase the accuracy of the quantitative data.

Table II. Apparent Activation Energy using the

$$\text{Arrhenius Equation } \log k = \frac{-E_a}{2.303R} \frac{1}{T} + \log A$$

Plotting $\log k$ versus $\frac{1}{T}$ provides a line whose slope = $\frac{-E_a}{2.303R}$.
Solving for activation energy gives $E_a = -2,303R$ (slope).
 R , the gas constant, = $1.987 \frac{\text{cal}}{\text{deg mol}}$

X - Axis		Y - Axis					
		DME	tBuOH	MTBE	MIBE	DTBE	DIBE
T (K)	1/T	log Yield	log Yield	log Yield	log Yield	log Yield	log Yield
430	0.002326	0.273	- 1.005	- 0.883	0.468	- 1.059	- 0.307
420	0.002381	- 0.031	- 1.449	- 0.956	0.280	- 1.166	- 0.725
410	0.002439	- 0.295	-	- 1.355	0.0796	- 1.521	- 0.872
396	0.002525	- 0.562	-	- 1.926	- 0.167	- 1.882	- 1.128
Slope Log vs 1/T		- 4151	- 8019	- 5467	- 3187	- 4320	- 3888
$E_{\text{activation}}$ in Kcal/mol		19.0	36.7	25.0	14.6	19.8	17.8

Table III. Apparent activation Energy using the

$$\text{Arrhenius Equation } \log k = \frac{-E_a}{2.303R} \frac{1}{T} + \log A$$

Plotting $\log k$ versus $\frac{1}{T}$ provides a line whose slope = $\frac{-E_a}{2.303R}$.
 Solving for activation energy gives $E_a = -2.303R$ (slope).
 R , the gas constant, = $1.987 \frac{\text{cal}}{\text{deg mol}}$

X - Axis		Y - Axis				
		isoButene	1-Butene	2-Butene	isoOctene1	isoOctene4
T (K)	1/T	log Yield	log Yield	log Yield	log Yield	log Yield
430	0.002326	- 0.034	- 0.834	- 1.095	-0.3158	- 0.7712
420	0.002381	- 0.385	- 1.680	- 1.897	- 1.849	- 1.813
410	0.002439	- 1.088	-	-	-	
396	0.002525	- 2.356	-	-	-	
Slope	Log vs 1/T	- 11863	- 15279	-14582	- 27690	- 18815
E _{activation} in Kcal/mol		54.3	69.9	66.7	126	86.1

Table IV. Results of MTBE Pumping Experiment

Yield at different GHSV, 123°C and 1 atm (101.327 kPa)

Catalyst: Nafion-H MS

Catalyst weight: 0.0010039 kg

Compound	GHSV 230 (mol\kg cat\hr)	GHSV 496 (mol\kg cat\hr)	GHSV 1748 (mol\kg cat\hr)
MTBE in	6.11	12.22	46.55
MTBE out	0.73	0.20	1.93
Water	0.98	0.39	0.30
DME	0.84	0.22	0.26
MeOH	5.39	10.21	44.17
Isobutene	7.55	7.90	43.08
1-butene	0	0	0
2-butene	0	0	0
n-butane	0.03	0	0
MIBE	0	0	0
Isooctene1	3.38	0.41	0.33
Isooctene2	1.18	0.14	0.12
Isooctene3	0.47	0.06	0.01
Isooctene4	0.80	0.08	0
Isooctene5	2.13	0.25	0.11
C-12	3.07	0.42	1.03
C-12	0.68	0	0.01

C. Thermodynamic Considerations for Ether Synthesis from Alcohols: MIBE vs. MTBE

In earlier research described in a paper by Nunan et al. (3) and in the previous technical progress reports (1,2), it was demonstrated that MIBE (methyl isobutyl ether) can be obtained as a major product over a Nafion-H resin at high pressures and moderate temperatures (123°C) from a 2:1 molar mixture of methanol and isobutanol. This invention pointed out that a "new" acid catalyzed chemistry is occurring at the acidic sulfonic groups at the surface of the Nafion resin. Kinetic studies obtained for the same catalyst system (4) showed that the chemistry is mainly characterized by the following features: (a) a bimolecular process at the catalyst surface is occurring, i.e. the ether is formed after interaction of two separate surface-held intermediate complexes, (b) the interaction between the sulfonic acid groups and the adsorbing alcohols is competitive and a preference for isobutanol exists, and (c) the nature of the adsorbed transition state complex is of primordial importance in determining which ether will be formed. If the complex were carbonium-like, MTBE would be expected to be formed via an initial dehydration of isobutanol to isobutene and subsequent reaction of the isobutene with methanol. If instead the transition state complexes would be oxonium or ester complexes, then MIBE would be formed from isobutanol and methanol. The exact nature of the transition state complexes in the formation of MIBE is yet still to be proven. More recent catalytic tests (2) with the Nafion-H resin showed that MTBE could also be found in very small concentrations in the product stream. Initial results (1), obtained with the Amberlyst-15 resin as catalyst under similar conditions, showed that MIBE and MTBE were both present as products but in a more equal amount.

Both reaction mechanisms, as outlined later in the report, probably occur at the surface of the Nafion-H and Amberlyst-15 resins. Since the experimental testing conditions were equal for both catalysts (see Reference 2), one can

conclude that the nature of the local environment around the acidic sulfonic groups plays a role in determining which process will be favored.

Since one of the major commercial uses of non-petroleum derived C₅ ethers, as being investigated in this research, would be as additives to gasoline to maintain or improve the high octane rating of this gasoline, it is essential that their octane enhancement behavior be known. An extensive study describing the effect of the addition of oxygenates on the research octane number of a regular gasoline was published in 1986 by Spindelbalker et al. (5). Different alkylbutylethers, including MIBE and MTBE, were included in this study as represented in Table V.

Table V: Effect of Small Additions of Alkylbutylethers on the Research Octane Number of a Gasoline Basestock with 82.4 RON.

<u>Type of Butylether</u>	<u>% added</u>	<u>Δ RON</u>
2-Ethoxy-butane	5	-1.0
	10	-2.0
2-Ethoxy-2-methyl-propane (= Ethyl t-butyl ether)	5	+0.5
	10	+2.1
1-Methoxy-butane	5	-3.1
	10	-5.7
2-Methoxy-butane	5	-1.1
	10	-2.4
1-Methoxy-2-methylpropane (= Methyl isobutyl ether)	5	-1.0
	10	-1.9
2-Methoxy-2-methylpropane (= Methyl t-butyl ether)	5	+1.3
	10	+3.4

The results represented in this table showed that the only type of branched alkylbutylether with a positive effect on the RON were the ones characterized by the presence of a t-butyl group. While MTBE was a powerful octane enhancer, the addition of MIBE led to a small decrease of the RON. This indicates that MTBE

is a preferred product over MIBE, and catalysts and reaction conditions should be sought whereby the yield of MTBE is maximized.

Two ways can be proposed to achieve this goal: (a) by concentrating on the isomerization reaction of MIBE to MTBE after the initial highly active synthesis of MIBE and (b) by enhancing the selective dehydration of isobutanol to isobutene followed by selective isobutene coupling with methanol to form MTBE. The efficiency and occurrence of the second pathway, the dehydration step procedure, already seems to be strongly controlled by the type of catalyst when one compares the previously described behavior of Nafion-H and Amberlyst-15. Therefore, an intensive study to characterize the acid sites was undertaken as outlined in the previous reports and as continued in this report.

It is also important to know whether the right experimental conditions are being used to achieve or optimize the synthesis of MTBE via one or both of the above mentioned pathways. The importance of the right experimental conditions was proven by recent studies in the field of MTBE synthesis from isobutene and methanol over catalysts like Amberlyst-15 (6,7), which indicated that the decomposition of MTBE to isobutene and methanol is an important factor at higher temperatures. Therefore, a detailed thermodynamic study was initiated and this is discussed in this section of the report. The continuation of the research on the acid strength determination of these resins is also discussed in this report.

The following specific problems concerning the choice of the right experimental conditions for ether synthesis over acid resin catalysts were formulated and studied.

- (1) What is the overall *thermodynamic* effect of the reactor temperature and pressure on the different reactions occurring during the C₅ ether synthesis from isobutanol and methanol?
- (2) Which reactions are exothermic and which are endothermic?
- (3) Is it possible to make predictions about the selective conversion of

isobutanol and methanol into MTBE by applying basic thermodynamic principles for a specific set of experimental conditions?

1. Detailed Description of the Methodology

The following scheme, shown in Figure 3, can be drawn to describe the main reactions that can occur during the reaction of isobutanol and methanol over acidic catalysts. In this simple scheme, the two assumptions made were: (a) the only dehydration product of isobutanol considered is isobutene, although one could expect that n-butenes could also be formed in the dehydration process (7), and (b) secondary reactions such as the formation of octenes, etc. are not considered in this first reaction scheme.

HIGH OCTANE MTBE FROM ISOBUTANOL (ISOBUTENE) AND METHANOL

Figure 3. Synthesis of MTBE, DME and MIBE from Alcohols.

As indicated by this scheme, the five different reactions that can occur simultaneously are:

The reaction labels [i] will be used further in the tables to refer to a specific reaction. In the following paragraphs, a detailed thermodynamic study of these reactions is represented to obtain a better view of the effect of temperature and pressure on the reaction equilibria. Two standard reference works, respectively written by Lewis and Randall (8) and Freifelder (9), were used as references for the thermodynamic calculations.

2. Effect of the Temperature

2.1. Exothermicity or Endothermicity?

The enthalpies, free energies, and entropies at room temperature and 1 atm for the different reactions were obtained using the thermodynamic values of the different compounds as they are given by the TRC Thermodynamic Tables for Non-Hydrocarbon and Hydrocarbon Compounds (see Table VI) (10).

Table VI. Standard Enthalpies ΔH_i° , Standard Free Energies ΔG_i° and Entropies ΔS_i° for the reactants and products in Figure 3 (standard conditions are $T = 298.15^\circ\text{C}$ and 1 atm).

Compound	ΔH_i° (kcal/mol)	ΔG_i° (kcal/mol)	ΔS_i° (cal/mol $^\circ\text{C}$)
Methanol	-48.05	-38.8	-31.0
Isobutanol	-67.62	-39.33	-94.9
Isobutene	-4.04	+13.88	-60.1
DME	-43.98	-26.9	-57.3
MIBE	-63.4	-25.2	-128.1
MTBE	-67.7	-28.0	-133.2
H ₂ O	-57.8	-54.6	-10.7

The enthalpies of the reactions ($p_i\Delta H_{\text{products}} - r_i\Delta H_{\text{reactants}}$) of Figure 3 are given in Table VII. All the reactions are exothermic except the dehydration of isobutanol to isobutene and H₂O (Reaction [2]).

Table VII. Enthalpy of Reaction in kcal/mol

<u>Reaction</u>	<u>Enthalpy of Reaction (kcal/mol)</u>
[1]	-5.53
[2]	+5.78
[3]	-15.61
[4]	-4.3
[5]	-5.68

Figure 4 represents a more general overview of the enthalpy changes that can occur during the synthesis of MTBE or MIBE from methanol and isobutanol. As shown, MTBE + H₂O are the thermodynamic favored products for the reaction scheme outlined in Figure 3. Considering the enthalpy changes, an increase in temperature will have a disadvantageous effect on the two reaction pathways to MTBE, i.e. the MIBE synthesis and its eventual subsequent isomerization and the MTBE synthesis from isobutene and methanol. More detailed calculations via the relationship of Van 't Hoff should still be performed.

2.2. The Free Energy ΔG_i and the Equilibrium Constant (K) of a Reaction as a Function of Temperature.

Through the thermodynamic relation of $\Delta G_i = \Delta H_i - T\Delta S_i$, it is possible to determine which effect the temperature has on the free energy of a particular reaction and consequently on its thermodynamic equilibrium constant K. Assuming that the enthalpy and entropy do not change significantly with a change in temperature, the values given in Table VIII for the free energies changes (ΔG_i) can be obtained.

Table VIII. Free Energies Changes for the Ether Synthesis Reactions.

Reaction	ΔH_r (kcal/mol)	ΔS_r (cal/mol C)	ΔG_i (kcal/mol) Temperature (K)		
			298.15	400	500
[1]	-5.53	-12.9	-1.67	-0.37	0.92
[2]	5.78	24.1	-1.41	-3.86	-6.27
[3]	-15.61	-42.1	-3.05	1.23	5.44
[4]	-4.3	-5.1	-2.77	-2.26	-1.75
[5]	-5.68	-6.0	-3.90	-3.28	-2.68

FIGURE 4

Reaction enthalpies of ether synthesis reaction pathways

Figure 5 gives a schematic overview of the changes in free energy during the synthesis of MIBE and MTBE at the two temperatures of 298.15 and 400K. At room temperature, all the considered reactions are exo-energetic. However, an increase in the temperature has a variable effect, e.g. the synthesis of MIBE from methanol and isobutanol (reaction [1]) becomes less exo-energetic at 400K, and Table VIII shows that at 500K, this reaction has become endo-energetic. The same trend exists for the MTBE synthesis from isobutene and methanol (reaction [3]), where the reaction has already become endo-energetic at 400K. On the other hand, the three remaining reactions (isobutanol dehydration, MIBE isomerization, and DME synthesis) are always exo-energetic in the studied temperature-range. Whereas Figure 5 gave a schematic overview of the reaction pathways with the respective energy changes and energy levels, Figure 6 represents the evolution of the endo- or exo-energeticity of each reaction as a function of the temperature.

The calculation of the standard free energies for the different reactions at different reactions can also be transformed into specific equilibrium constants. Table IX gives an overview of these equilibrium constants and their evolution as a function of temperature is represented in Figure 7.

Table IX. Equilibrium Constants for the Ether Synthesis Reactions

Reaction	Temperature (K)		
	298.15	400	500
[1] MIBE synthesis	16.57	1.59	0.396
[2] Isobutanol dehydration	10.80	128.52	550.26
[3] MTBE synthesis	172.06	0.210	0.004
[4] MIBE isomerization	107.25	17.17	5.82

FIGURE 5

Free energy of ether synthesis reaction pathways

FIGURE 6 Free energy changes for specific reactions in ether synthesis

FIGURE 7

Equilibrium constants for specific reactions in ether synthesis

The calculated thermodynamic data make it possible to make the following conclusions: (1) an increase in the temperature will disfavor the carbonium-ion pathway because of the appearance of a endo-energetic sub-reaction, and (2) under all temperature conditions (and in the case of a thermodynamic control of the occurring reactions) no limitations can be found that would prevent the isomerization of MIBE to MTBE. The reality that this isomerization can not be observed over the Nafion-catalyst indicates that kinetic factors play an important role in this reaction.

2.3. Effect of the Total Pressure on the Reaction Equilibria.

Initial studies were carried out to obtain information about the effect of the total pressure on the reaction equilibria, and only the following two reactions of the previously shown reaction scheme (Figure 1) would be influenced when studied independently.

The extent of these reactions as a function of pressure, obtained by using the earlier calculated equilibrium constants and activity coefficients (see Table IX), are represented in Figures 8 and 9.

Figure 8. Effect of the Total Pressure on the Dehydration of Isobutanol, Reaction [2], at Different Temperatures (X = degree of conversion).

Figure 9. Effect of the Total Pressure on the Decomposition of MTBE, the Reverse of Reaction [3], at Different Temperatures (X = degree of conversion).

Figures 6 and 7 were calculated for single reaction systems and show the pronounced effect of pressure and temperature on these two reactions. However, more studies would be certainly required in which all the main reactions are considered at the same time since they would influence each other. For example, the presence of methanol in the feed would influence the degree of decomposition of MTBE at reaction equilibrium. In addition, the calculations can be improved by considering the effect of non-ideal gas behavior and introducing fugacity coefficients into the calculations.

D. Determination of Acid Strength of Acid Polymers

In earlier reports, the methodology of enthalpimetric titration calorimetry and the initial experimental results obtained for Amberlyst-15 and Nafion-H-MS resins were presented (1,2). It was strongly emphasized that the choice of the solvent was of primary importance to obtain information about the acid strength of acid polymers. A comparison and discussion of the experimental data are given in this section of the report.

1. Enthalpimetric Titrations of Amberlyst-15

Thermometric titrations of vacuum-dried (110°C, 5 hr) Amberlyst-15 samples (0.5–1.0 g) were repeated and performed in cyclohexane and in acetonitrile, which were predistilled to remove traces of H₂O and acetic anhydride. Pyridine was used as the titrating base. The titrations were carried out past the endpoint based on our knowledge of the proton concentration. The titrant was added batch-like (in 0.5 to 1 ml amounts), and the heat releases were monitored as a temperature change of the solvent slurry. A typical example of one of these titrations is represented in Figure 10. Each of the temperature increases could exactly be determined using the software package connected with the Sanda Facts 2000 Thermotitrator, and subsequently the ΔT values were converted into enthalpy values for the specific acid-base reaction, as discussed previously (1,2).

The results of the titrations of Amberlyst-15 in different solvents with pyridine are represented in Figure 11. The results in Figure 11 give the following information: (1) the acid base titration could be performed with an endpoint reached and (2) the acid strength of the sulfonic acid groups in the Amberlyst-15 resin showed a heterogeneous distribution.

Figure 10. Titration of an Amberlyst-15 Resin in Cyclohexane

2. Titration of Nafion H-MS Resin in Fluorinated APF-140 Solvent

Some of the enthalpimetric measurements (2) showed that use of a solvent having a similar overall chemical composition (perfluorinated hydrocarbons) as the Nafion resin enhanced the transport of the base into the pores of the resin and allowed a subsequent acid-base interaction to occur. The inconvenience of this fluorinated solvent is that it allows only a very limited solubility of bases, and only partially fluorinated bases such as 2,4-difluoroaniline would form stable solutions. Pyridine, which is one of the principal bases used for enthalpimetric titrations, formed an unstable suspension with the APF-140 solvent. The reduced basicity of the fluorinated bases (lower pK_{BH^+} value) rendered the measurements more difficult.

Only one base was used in conjunction with this solvent, namely 2,4-difluoroaniline with a $pK_{BH^+} < 0$, which means that this base is very weak. This fact, together with the still limited solubility of the base in APF-140 (0.15 g/50 ml) made it difficult to carry out the enthalpimetric measurements. If temperature increases occurred, they were always very small and close to the sensitivity of the instrument, and extreme caution had to be undertaken (thermal equilibrium of titrant and titrate solutions!). Moreover, the results were

FIGURE 11

Titration of Amberlyst-15
in different organic solvents

varying from one experiment to another and in some cases, no heat increases could be detected. Therefore, it was decided to return to the methodology used by Arnett et al. (11), in which acetonitrile was used as the solvent. With Amberlyst-15, acetic anhydride was also used as a solvent.

In a typical experiment, about 2 g of the vacuum-dried (150°C, 24 hr) Nafion sample was placed into 20 ml of predistilled acetonitrile or acetic anhydride and allowed to swell. The titrations were again carried out past the endpoint based on our knowledge of the proton concentration. The titrant was added batch-like (in 0.5 to 1 ml amounts) and the heat releases were monitored as a temperature change of the acetonitrile solution. The results were treated in the same way as for the Amberlyst-15 titrations for converting the ΔT values into "enthalpy" values for the specific acid-base reaction. No correction was yet made to include the endothermic dissociation of the acetonitrile-sulfonic acid complex. The results for the Nafion H-MS titrations are represented in Figure 12.

The results in Figure 12 gave the following information: (1) the acid-base titration could be performed in acetonitrile until equilibrium is reached but could not be completed in acetic anhydride where only about 75% of the acid sites could be titrated, (2) the calculated acid strength of Nafion-H as measured by the enthalpy/mole of the acid-base reaction is larger in acetic anhydride than in acetonitrile (whether this difference should only be attributed to the endothermic dissociation of the acetonitrile-sulfonic acid group complex is yet unclear), and (3) the acid strength of the sulfonic groups in the Nafion-MS catalyst seemed to have a very homogeneous distribution when titrated in acetonitrile in contradiction with the results obtained for the Amberlyst-15 resin. In acetic anhydride, some difference can be seen in the acid strength as represented by the enthalpy values but this is not so pronounced as for the Amberlyst-15 resin, as can be seen by the comparison represented in Figure 13.

FIGURE 12

Titration of Nafion-H-MS
in various organic solvents

FIGURE 13

Thermometric Titrations of Acid Polymers

(Solvent = Acetic Anhydride)

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