Attention was focused on resolving methyl tertiary butyl ether (MTBE) from methyl isobutyl ether (MIBE) and tertiarybutyl-isobutyl ether (TIBE) from diisobutyl ether (DIBE). No C-12 compounds were detected in this sample. MTBE and MIBE show very different mass spectrometric fragmentation patterns and therefore distinction between the two was unambiguous.

The mass spectrum of DIBE showed a perfect fit with the library spectrum and is therefore determined beyond any doubt. Through this mass spectrometric analysis, the other C_8 isomer produced and seen by GC, as described in this report, was recently identified unambiguously as TIBE and not DTBE (ditertiarybutyl ether).

C. ^{1}H NMR to Resolve Whether 1-Butene was a Product

Our main technique to identify reactants and products was gas chromatography. Isobutene was an abundant product when isobutanol was dehydrated over acid catalysts. As shown, other possible dehydration products were *cis*-2-butene, *trans*-2-butene, and 1-butene. By GC analysis with our present method of separation, isobutene could be separated from *cis*-2-butene and *trans*-2-butene but not from 1-butene. To resolve if and how much 1-butene was present as a product over the sulfated zirconia, ^{1}H NMR was utilized to further distinguish the C_4 products.

Products from dehydration of isobutanol over sulfated zirconia were collected in a N_2 (*l*) cooled trap. The product stream was dried with molecular sieves prior to the trap to remove as much water as possible. As standards, individual samples of pure 1-butene, isobutene, *cis*-2-butene, and *trans*-2-butene were collected from their respective gas cylinders.

A 500 MHz Bruker AM500 NMR instrument was utilized for these analyses. The spectra were acquired from 0 to 8 ppm at approximately -20°C. All samples were diluted approximately 1:4 with $CDCl_3$. The pure butene samples were used to calibrate peak positions.

Isobutene has distinctive ^1H NMR peaks at 4.65 and 1.7 ppm (Figure 67), whereas 1-butene has groups of peaks at approximately 5.9, 4.9, 2.1, and 1.0 ppm (Figure 68). The spectra of the pure butenes were compared to the spectrum of the dehydration products of isobutanol (Figure 69).

From the NMR spectra, it was concluded that 1-butene was indeed present in the product stream in a small amount. By integrating the NMR peaks at 5.9 and 4.65 ppm, the quantity of 1-butene could be determined since neither *cis*-2-butene nor *trans*-2-butene have any peaks in this region. It was found that the butene product stream produced by the sulfated zirconia catalyst contained ≤3% 1-butene.

D. Liquid Phase Alcohol Coupling Reactions

The dehydrative coupling of ethanol/isobutanol over the very active Amberlyst-35 catalyst resin, obtained from Rohm & Haas, was carried out in the liquid phase with an autoclave reactorfor comparison with the gas phase reaction and as a basis for suture liquid phase reactions. The reactor (300 cc EZE-SEAL), purchased from Autoclave Engineers, Inc., is capable of running between 25-450°C and 0.1-20 MPa. In the current study, 10 ml ethanol, 90 ml isobutanol and 2.0 grams of the Amberlyst-35 catalyst were charged into the 300 ml reactor. The reactor was then pressurized with 0.5 MPa of nitrogen, which also served as the internal standard for the GC analysis of the gas phase products. The reaction temperature was set at 100 °C, and the magnetic stirring rate was set at 1000 rpm. The liquid and gas phase samples were taken at designated times, and the analyses were performed with a HP5890 series II GC equipped with TCD and FID detectors.

Figure 67. NMR spectrum of pure isobutene in $CDCl_3$.

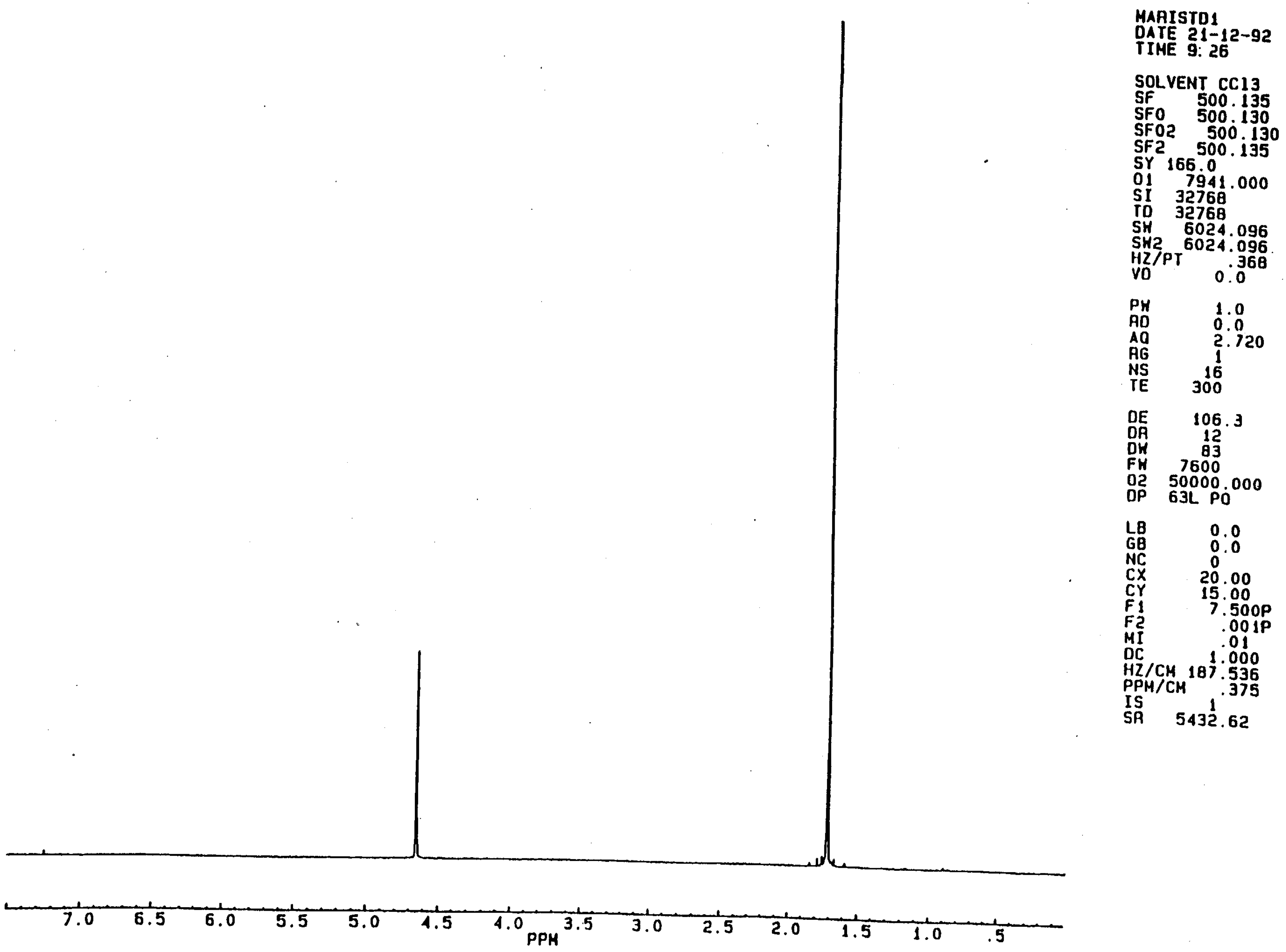


Figure 68. NMR spectrum of pure 1-butene in $CDCl_3$.

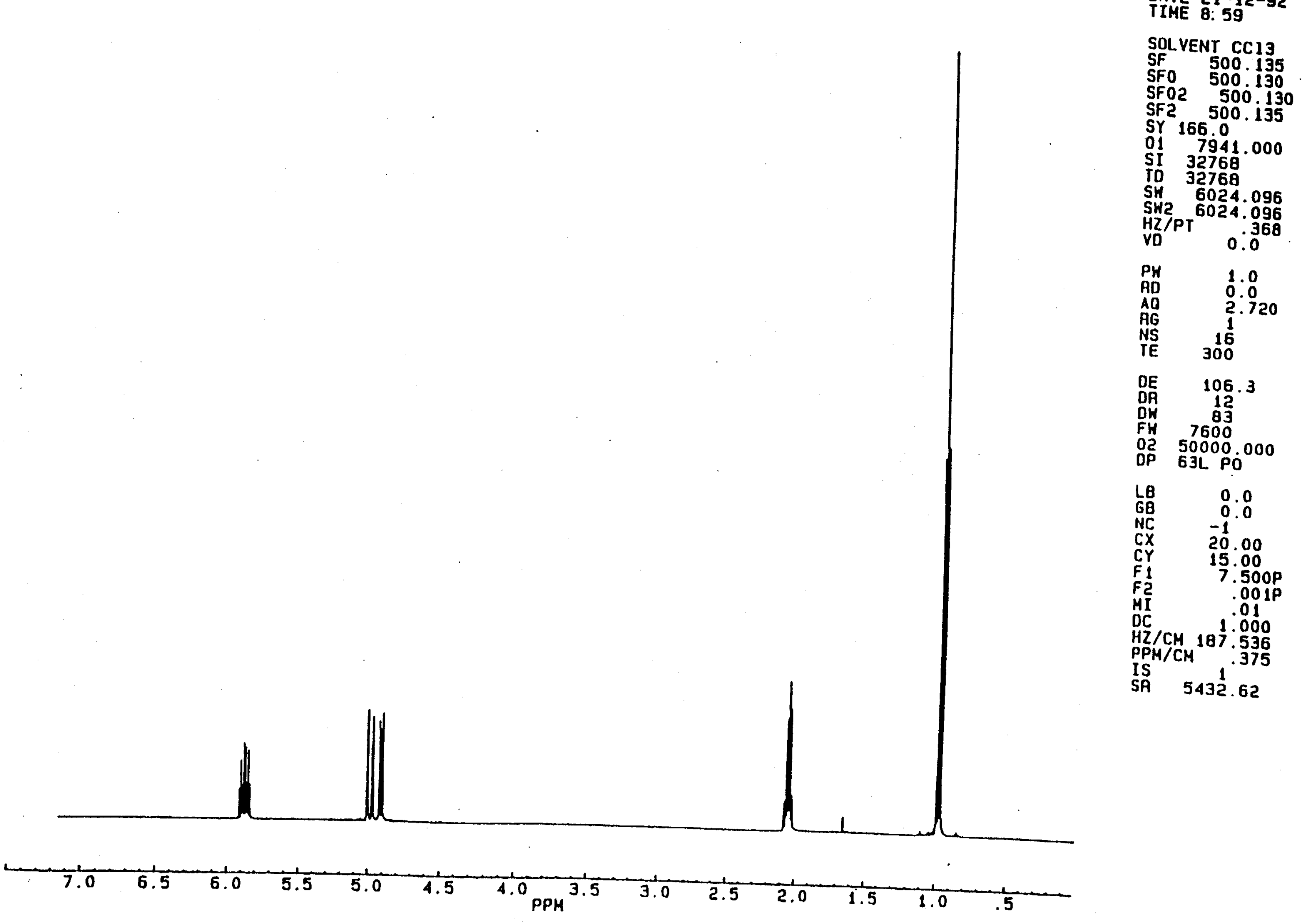
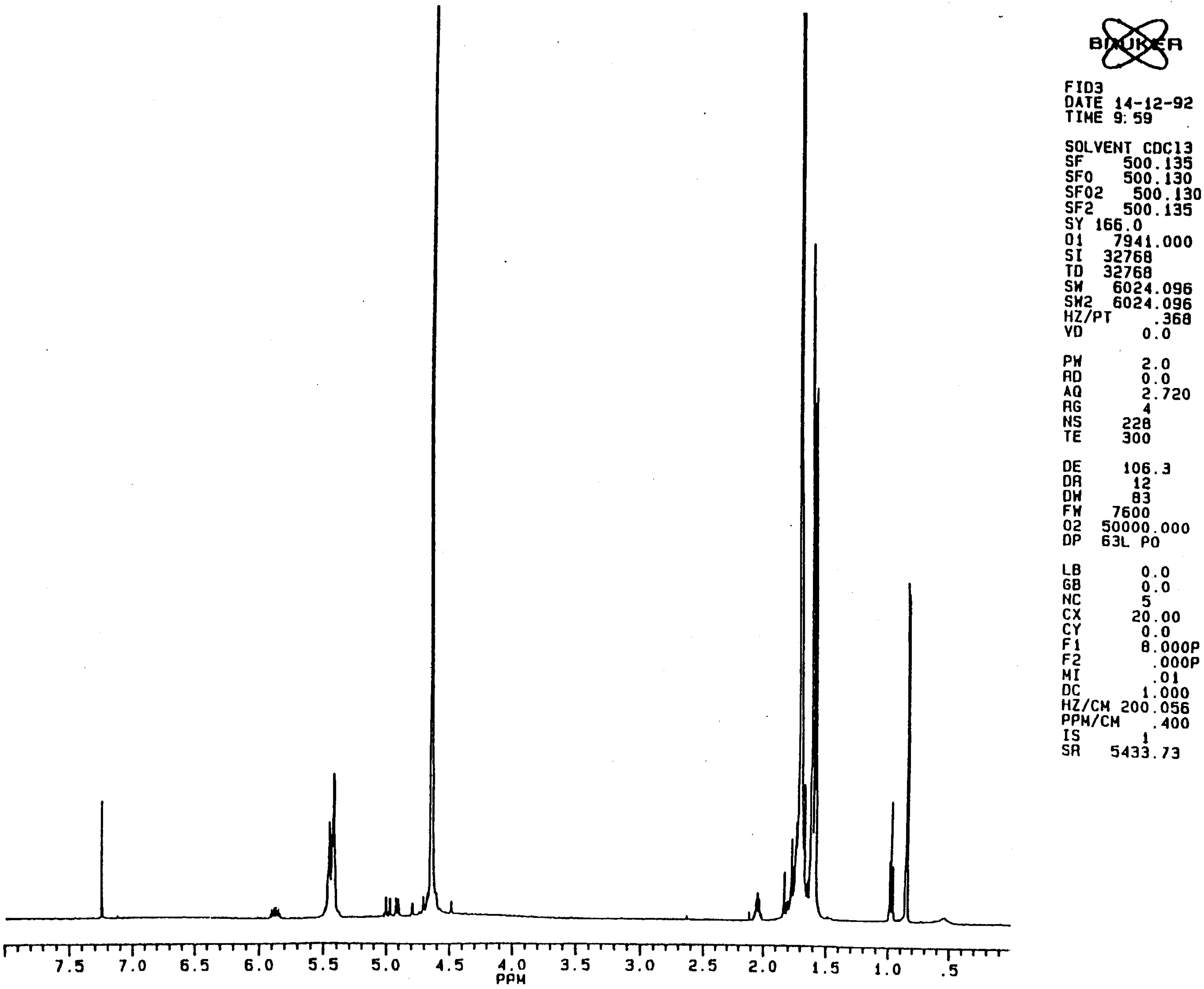


Figure 69. NMR spectrum of isobutanol dehydration products in $CDCl_3$.



The products present in the liquid phase mixture include diethylether (DEE), ethylisobutyl ether (EIBE), ethyltertiarybutyl ether (ETBE), tertiarybutyl-isobutylether (TIBE), diisobutylether (DIBE), and a small amount of isobutene (IB). The isobutene was principally detected in the gas phase. However, since the gas phase product analysis was not very reliable, isobutene was determined based on the production of water and the rest of the liquid products. The isobutene value reported here should represent the maximum quantity of isobutene that could be formed. The results are listed in Table 25 in terms of reactant conversions and product selectivities, where Sel.(%EtOH) and Sel.(%iBuOH) are the product selectivities calculated on the basis of ethanol and isobutanol, respectively. The product space time yields obtained in this liquid phase batch reactor are in comparable amounts to that from the continuous flow reactor. For example, the space time yield of EIBE produced in the liquid phase at 100°C is 0.18 mol/kg cat/hr, as compared with the 0.6 mol/kg cat/hr from the continuous flow gas phase reactor (obtained at 110°C).

Table 25. Conversion and selectivity of the liquid-phase ethanol/isobutanol batch reaction at 100 °C as a function of time.

Time (hr):	4.0	9.0	21.5	31.5
EtOH Conversion (%)	1.8	3.8	8.3	11.4
iBuOH Coversion (%)	0.7	1.5	2.4	2.8
Sel.(%EtOH) DEE	46.0	42.4	42.8	39.5
Sel.(%EtOH) EIBE	46.0	50.8	51.2	54.4
Sel.(%EtOH) ETBE	7.2	6.2	6.8	6.1
Sel.(%iBuOH) IB	33.0	40.4	29.5	12.8
Sel.(%iBuOH) EIBE	20.0	18.6	25.2	30.6
Sel.(%iBuOH) ETBE	5.4	2.5	3.0	3.4
Sel.(%iBuOH) TIBE	38.6	34.2	40.1	46.7
Sel.(%iBuOH) DIBE	3.0	4.3	2.2	6.5

IX. Conclusions

A wide range of organic resin catalysts and inorganic oxide and zeolite catalysts have been investigated for activity and selectivity in directly coupling alcohols, principally methanol and isobutanol, to form ethers and in the dehydration of isobutanol to isobutene in the presence of methanol. All of these catalysts are strong acids, and it was found that the organic and inorganic catalysts operate in different, but overlapping, temperature ranges, i.e. mainly 60-120°C for the organic resins and 90-175°C for the inorganic catalysts. For both types of catalysts, the presence of strong acid centers is required for catalytic activity, as was demonstrated by lack of activity of fully K^+ ion exchanged Nafion resin and zirconia prior to being sulfated by treatment with sulfuric acid.

Testing the organic resin catalysts in a gas phase continuous downflow reactor with a methanol/isobutanol = 1/1 reactant mixture in a He/N_2 carrier gas at ambient pressure and 90°C demonstrated that the overall catalytic activity followed the order of Amberlyst-35 > Amberlyst-36 > Amberlyst-15 ≈ Purolite C-150 > BioRad AG 50W X-2 > Amberlyst-1010 > Nafion-H MS. The resins showed differing selectivity patterns as a function of temperature, but the most selective catalyst was observed to be the fluorocarbon sulfonic acid polymer Nafion-H that exhibited over 60% selectivity toward MIBE, with decreasing quanitities of DME, DIBE, butenes, and MTBE as side products. It was demonstrated with the Nafion-H and Amberlyst-35 resins that increasing the partial pressures of the reactant alcohols (with the total reactor pressure in the 0.1-1.3 MPa range) depressed the catalyst productivity toward butenes while enhancing the productivities (and selectivities) of the ethers formed, principally MIBE and DME.

Mechanistic studies carried out over the Nafion-H resin catalyst at 90°C by using ^{18}O-labelled methanol showed that MIBE and MTBE are formed by two different pathways that do not contain a common intermediate. In particular, in the reaction of $CH_3{}^{18}OH$ + $(CH_3)_2CHCH_2{}^{16}OH$, the products (with >90% isotopic purity) were observed to be ^{16}O-MIBE, ^{18}O-MTBE, and ^{18}O-DME. These isotopic results, along with reaction studies centered on providing insight into the kinetics of the reaction pathways, are consistent witn MIBE being formed by a S_N2-type of reaction, but where high concentrations of either reactant cause self-poisoning of the catalyst, i.e. saturation of the active acid centers. This is a feature of a dual site reaction mechanism, which also applies to the scheme of dehydration of isobutanol to isobutene that subsequently reacts with methanol to form MTBE.

The inorganic catalysts were generally less active than the resin catalysts, and higher reaction temperatures were required to achieve significant dehydration of the alcohols. The overall order of activities for the dehydration reactions over the inorganic solid acids was SO_4^{2-}/ZrO_2 > H-ZSM-5 zeolite > H-mordenite > SiO_2/Al_2O_3 > H-montmorillonite >> γ-Al_2O_3. Of special note are the findings that from a methanol/isobutanol = 1/1 reactant mixture,

1. **H-mordenite** was active in selectively dehydrated methanol with near total conversion to dimethylether (DME) while not converting isobutanol to products at temperatures ≤150°C, and

2. the **SO_4^{2-}/ZrO_2** catalyst was very active, with near total conversion, in dehydrating isobutanol to isobutene at 175°C without significantly activating methanol.

The former observation could be the basis for a process for separating isobutanol from methanol while at the same time producing DME. The latter experimental result could be the basis for a 2-step process for the selective conversion of methanol/isobutanol to MTBE, wherein the first step would be carried out over the SO_4^{2-}/ZrO_2 catalyst, e.g. at 175°C, and the second step would couple the isobutene with the unreacted methanol over a resin catalyst at lower temperature, e.g. Amberlyst-15 or -35 resin at 60-90°C.

Molecular modelling *via* computer graphics of the selective activation and conversion of methanol to DME, in the presence of isobutanol, over H-mordenite indicates that the active acid sites are located in the side pockets of the zeolite structure and not in the large channels. Thus, the active acid centers are not accessible to isobutanol because the pockets are perpendicular to the larger channels, and the isobutanol molecule does not have room to rotate to interact with the acid centers nor to interact with activated methanol in the pockets. It appears that poisoning of the accessible acid centers in the larger channels by the basic isobutanol molecule must also occur at low reaction temperatures because experimentally isobutanol begins to be activated and to form isobutene and MIBE (if methanol is present) at ≈150°C.

Extensive testing and characterization of the active SO_4^{2-}/ZrO_2 catalyst that selectively dehydrates isobutanol to isobutene has been carried out. It was shown that this catalyst was much more active for dehydration of isobutanol to isobutene than for dehydration of ethanol, n-propanol, and n-butanol to olefins. Elevated pressures tended to inhibit the isobutanol dehydration reaction, but high space time yields of isobutene could be obtained by using high isobutanol feed rates and high reaction temperature, e.g. >11 mol isobutene/kg catal/hr at 225°C. The presence of small quantities of water in the reactant alcohol mixture had no effect on the activity in converting isobutanol to isobutene.

It was found that the sulfating treatment signficantly increased the surface area of the zirconia, and XPS analysis indicated that the surface contained 1 S/2 Zr (≈0.5 monolayer coverage), which agreed with the chemical analysis of the catalyst. Therefore, the sulfate groups are located on the surface of the catalyst, and titration showed that there was 1 H^+/SO_4^{2-} group in an aqueous environment. Using pyridine as a probe for acid sites, XPS analysis using resolved positions of the N 1s line showed that there were both Lewis and Brönsted acid sites on the catalyst, and to-date no difference has been found between dry (calcined to 620°C) and wet (H_2O exposed) samples of this catalyst. In contrast, analogous XPS analyses showed that the Nafion-H catalyst had only Brönsted acid sites, while γ-alumina had only Lewis acid sites.

Using samples of MIBE prepared by us, it was found that MIBE has low blending research and motor octane numbers in unleaded regular gasoline. It was shown that a 1/1 mixture of MIBE/MTBE could be added to gasoline to enhance the oxygenate content while not changing the research and motor octane numbers of the gasoline. With respect to cetane numbers, it was found that MIBE has an elevated cetane number of $\approx$53, which is significantly above the 40-45 cetane level of diesel fuel used in the U.S.

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