Selective isotopic oxygen incorporation into C_5 and C_6 ethers via solid acid-catalyzed reaction of methanol and ethanol with isobutanol

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Reaction of $CH_3{}^{18}OH$ with ^{16}O-containing isobutanol (2-methylpropan-1-ol) over strong acid Nafion-H and Amberlyst-H 35 resin catalysts gave the two distinctly labelled C_5 ethers 1-methoxy(^{16}O)-2-methylpropane (also designated as methyl isobutyl ether, ^{16}O-MIBE) and 2-methoxy(^{18}O)-2-methylpropane (also designated as methyl tertiary-butyl ether, ^{18}O-MTBE). Reaction of $CH_3CH_2{}^{18}OH$ with isobutanol gave the analogously labelled C_6 ethers, ^{16}O-EIBE and ^{18}O-ETBE. These results show that the isobutyl and tertiary-butyl ethers are formed from the alcohols by distinctly different mechanistic pathways, i.e. the former are produced by *surface*-catalyzed S_N2 reactions that follow Langmuir–Hinshelwood kinetics involving competitive adsorption while the latter arise via carbenium or olefinic intermediates. There is no pathway for isomerization of the two ethers, MIBE and MTBE, under the reaction conditions employed.

Keywords: alcohols; ethers; S_N2 mechanism; MTBE; ETBE

1. Introduction

The reaction of methanol and 2-methylpropan-1-ol (isobutanol) over Nafion-H perfluorinated sulfonic acid resin catalysts was earlier reported to produce predominately 1-methoxy-2-methylpropane (methyl isobutyl ether (MIBE)) [1,2], although the isomeric C_5 ether 2-methoxy-2-methylpropane (methyl tertiary-butyl ether (MTBE)) was also formed as a minor product [2], along with small quantities of dimethyl ether (DME), butenes, and C_8 ethers, primarily diisobutyl ether (DIBE). It was subsequently shown that the coupling reactions could also be carried out over other polymeric acid resin catalysts under moderate reaction conditions, e.g. 90°C, as well as over certain inorganic acid catalysts at higher temperatures, $\geqslant 125$°C [3,4]. The product selectivity was determined by the catalyst and the specific reaction conditions used. Nafion-H was highly selective for the formation of MIBE, even though MTBE is thermodynamically more stable by ~9.5

kJ/mol (ΔG°) at 400 K [1,2]. The alcohol coupling reaction to MIBE has been extensively studied by Nunan et al. [2], who found that MIBE was the kinetically favored reaction product and that Langmuir–Hinshelwood kinetics based on competitive sorption of the two reacting alcohols fully describe the MIBE, DME, and DIBE production. The dominant feature of that analysis was that isobutanol and methanol must both be adsorbed on adjacent surface acid sites. It was also determined that isobutanol was preferentially adsorbed on the acid sites in agreement with its stronger basicity compared with methanol.

It is generally believed that the syntheses of ethers from secondary and tertiary alcohols in the *liquid phase* with an acid catalyst such as H_2SO_4 follow the S_N1 mechanistic pathway pattern, while synthesis from primary alcohols follow the S_N2 pattern [5]. Dehydration of ethanol to diethyl ether over the sulfonated poly(-styrene-divinylbenzene) resin catalyst was proposed by Thornton and Gates to proceed via a hydrogen-bonded intermediate [6]. A series of studies on butanol dehydration over the H-ZSM-5 zeolite catalyst was performed by Makarova et al. [7,8], and ether formation was proposed to proceed via a surface-held $O–C_4H_9$ intermediate.

The two reactant alcohols, methanol and isobutanol, used in the current research can be produced from H_2/CO synthesis gas (a non-petroleum feedstock) over base-promoted Cu/ZnO catalysts [9–12]. Since MTBE is an oxygenated, high octane fuel additive and MIBE has a high cetane number of 53 (determined with a sample of MIBE provided to us by J. Erwin [13]), it is desirable to shift the selectivity of the alcohol coupling reaction to control MIBE or MTBE as required by fuel composition. Mechanistic insight will clarify the feasible approaches to achieve this goal. Herein, it is shown by isotopic labelling of the alcohols, e.g. $CH_3{}^{18}OH$, that the reaction pathways to MIBE and MTBE are distinctly separate and involve specific incorporation of the oxygen either from isobutanol or from methanol, respectively. Further, due to the fundamentally different mechanisms of the MIBE and MTBE formation, there is no pathway for isomerization of MIBE to the thermodynamically more stable MTBE.

2. Experimental

The solid acid catalysts employed in this study were Nafion-H Microsaddles (C.G. Processing, Inc.), which is a specially prepared porous form of duPont Nafion, with an ion exchange capacity of 0.9 meq H^+/g, and Amberlyst-H 35 cross-linked polystyrene sulfonic acid resin (Rohm and Haas) with 5.2 meq H^+/g. The alcohol coupling and dehydration reactions were carried out in a gas phase downflow stainless steel tubular reactor with on-line gas analysis using a model 5890 Hewlett-Packard gas chromatograph (GC) equipped with heated automatic Valco sampling valves and a CP-Sil 5 or CP-Sil 13 capillary WCOT column and interfaced with a PC data station with Chrom Perfect software and a Hewlett-Packard model 3396 series II recorder/integrator. The alcohols were fed into N_2

(with a flow rate of 405 ℓ/(kg catal h) (16.6 mol/(kg catal h)) over Nafion-H) or $N_2/He = 12/88$ vol% (with a flow rate of 12 000 ℓ/(kg catal h) over Amberlyst-H 35) carrier gas just prior to the preheater section of the reactor as a solution by means of a Gilson high pressure pump or individually by means of high pressure ISCO pumps. The ^{18}O-methanol and ^{18}O-ethanol employed in this study were obtained from MSD Isotopes and contained >97 at% ^{18}O, while the anhydrous isobutanol was obtained from Aldrich Chemical Co. and contained the natural abundance of ^{16}O, 99.8 at%. Conversions of the alcohols were kept below 5% to minimize any secondary reactions and to keep the reaction within the differential regime.

The butene product is generally given as the sum of isobutene and the linear trans-2-butene and cis-2-butene. The 2-butenes were minor products at the low reaction temperatures that were utilized, e.g. 88–91% of the total was isobutene except for Nafion-H where the linear butenes were generally not detectable. The 1-butene product was not determined by GC methods, but ^{1}H NMR analyses showed that this product was $\leqslant 3$ mol% of the olefin product even under all conditions where isobutene was the dominant product formed from the alcohols.

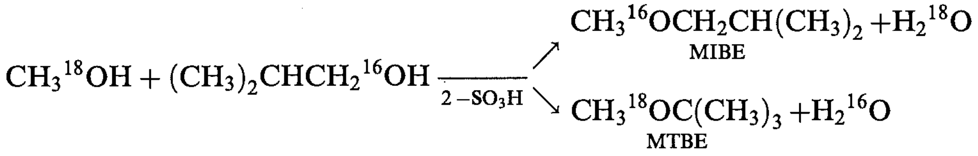
Isotopic composition analysis was accomplished off-line via GC/MS analysis (Hewlett-Packard GC/MS instrument equipped with a CP-Sil 13 capillary WCOT column), following the trapping and condensation of the reactor effluent in a dry ice or liquid nitrogen cooled cold-trap. Mass spectra were compared to those of reference compounds for identification of the catalytic products [14]. The molar abundances of each ^{16}O- or ^{18}O-containing product separated by GC were quantified via GC/MS analyses by comparing the most intense MS peak intensities to one another. It was observed that the most abundant fragment from both DME and MIBE was CH_3OCH_2 (with loss of the $CH(CH_3)_2$ part of the MIBE molecule, which was further fragmented), while from MTBE it was $(CH_3)_3CO$ (with loss of the CH_3 group). Specifically, for MIBE analysis the peak at a mass-to-charge ratio $(m/q) = 47$ was normalized to the most intense peak at $m/q = 45$, corresponding to the CH_3–^{16}O–CH_2 fragment [15], in order to calculate the fraction of ^{18}O-containing MIBE relative to ^{16}O-containing MIBE, respectively. Likewise for MTBE, the peaks at $m/q = 75$ and 73 [15], corresponding to the $(CH_3)_3$–C–^{18}O and $(CH_3)_3$–C–^{16}O fragments, respectively, were used, while the $m/q = 47$ peak intensity, corresponding to the CH_3–^{18}O–CH_2 fragment, was compared to that of the $m/q = 45$ peak (CH_3–^{16}O–CH_2) for DME quantification. Other less intense MS peaks were also analyzed for further verification of the analyses.

3. Results

3.1. ISOTOPIC LABELLING STUDIES OF ETHER FORMATION OVER NAFION-H

^{18}O-methanol and ^{16}O-isobutanol were mixed in a molar ratio of 1/1 and injected at the rate of 3.4 mol alcohol/(kg catal h) into a N_2 carrier gas just above the preheater section of the reactor in a continuous fashion, which yielded a total gas hourly space velocity (GHSV) of 488 ℓ/(kg catal h). Over the Nafion-H Microsaddles resin, the methanol and isobutanol conversions were 1.4 and 1.1 mol%, respectively, under the reaction conditions given in table 1. Isotopic composition analyses in terms of ^{18}O and ^{16}O contents of the ether products were carried out and are also reported in this table, along with the product selectivities.

Over 90% selectivity of incorporation of the isotopically labelled oxygen atoms in the ether products was observed, as shown in table 1. The isotopic composition of DME, 91.8% ^{18}O, indicated that isotopic scrambling of methanol did not occur to a significant extent over the Nafion-H catalyst. It is clear that MIBE retained the oxygen of the isobutanol reactant, while the oxygen in MTBE was retained from methanol. These results are summarized as follows:



$$CH_3{}^{18}OH + (CH_3)_2CHCH_2{}^{16}OH \xrightarrow[2-SO_3H]{} \begin{cases} \underset{\text{MIBE}}{CH_3{}^{16}OCH_2CH(CH_3)_2} + H_2{}^{18}O \\ \underset{\text{MTBE}}{CH_3{}^{18}OC(CH_3)_3} + H_2{}^{16}O \end{cases}$$

3.2. ISOTOPIC LABELLING STUDIES OF ETHER FORMATION OVER AMBERLYST-H 35

To determine the mechanistic features of the coupling reactions over Amberlyst-H 35, analogous isotopic labelling studies utilizing ^{18}O-methanol and ^{18}O-ethanol were carried out over this catalyst that has a large concentration of acid sites. A similar procedure was used for the three experiments listed below, viz. over 0.5 g of Amberlyst-H 35 catalyst at 110°C and 1.0 MPa (10 atm) total pressure, the liquid alcohol mixture consisting of 0.5 ml $CH_3CH_2{}^{18}OH$ mixed with 4 ml isobutanol was injected into the N_2/He carrier gas at a rate of 60 μl liquid/min just above the reactor preheater/vaporization section filled with Pyrex beads. The

Table 1

Selectivities (C mol%) and oxygen isotopic composition (mol%) of the products formed from the ^{18}O-methanol/^{16}O-isobutanol = 1/1 reactant mixture over 2 g of Nafion-H Microsaddles at 90°C and 0.10 MPa. A nitrogen carrier gas was used with the reactant mixture consisting of 8.5 mol% of each of the alcohols, flowing with a total GHSV of 488 ℓ/(kg catal h) for the three-component gas mixture

Product	Selectivity (C mol%)	%^{18}O (mol%)	%^{16}O (mol%)
MIBE	70.7	5.9	94.1
DME	9.1	91.8	8.3
isobutene	15.2	–	–
MTBE	5.0	97.2	2.8
C_8 ethers	trace	–	–

experiment was run for 1.5 h, and the liquid products were trapped via a glass bubbler cooled with liquid nitrogen.

For comparison purposes, series of experiments were carried out over the Amberlyst-H 35 resin utilizing the following three sets of reactant alcohols:

(I) $CH_3{}^{18}OH + (CH_3)_2CHCH_2{}^{16}OH$

(II) $CH_3CH_2{}^{18}OH + (CH_3)_2CHCH_2{}^{16}OH$

(III) $CH_3{}^{18}OH + CH_3CH_2{}^{16}OH$.

Experiment I was carried out with a methanol/isobutanol = 1.0/3.2 reactant mixture (total GHSV = 14200 ℓ/(kg catal h)), and 2.9 mol% of the methanol was converted to products with a selectivity of 81.7% to MIBE, 13.1% to MTBE, and 5.2% to DME. At the same time, 4.6 mol% of the isobutanol was converted to MIBE (19.3%), MTBE (3.1%), higher ethers (32.8%), and isobutene (44.8%). With respect to the ethers formed fully or in part from methanol, the ^{16}O and ^{18}O isotopic distributions shown in table 2 were obtained. The oxygen isotopic incorporation pattern was very similar to that observed (table 1) for the coupling of $CH_3{}^{18}OH$ with $(CH_3)_2CHCH_2{}^{16}OH$ (1/1) over the Nafion-H catalyst at 90°C and 0.1 MPa.

Experiment II was carried out under the same reaction conditions but using ^{18}O-ethanol instead of ^{18}O-methanol. In this case, the reactant molar ratio was $CH_3CH_2{}^{18}OH/(CH_3)_2CHCH_2{}^{16}OH = 1/5$, and nearly equal conversion levels for the two alcohols were observed (1.7 mol% ethanol and 1.8 mol% isobutanol). Ethanol was converted into ethyl isobutyl ether (EIBE) (78.2%), ethyl tertiary-butyl ether (ETBE) (5.2%), and diethyl ether (DEE) (16.6%), while isobutanol was converted into isobutene (42.1%), EIBE (17.7%), ETBE (1.2%), and higher ethers (49.0%). The oxygen isotopic compositions of the principal ether products are shown in table 3. It is clear that these distributions are very similar to those shown in tables 1 and 2, where methanol rather than ethanol was reacted with isobutanol.

Experiment III was carried out with a reactant mixture consisting of $CH_3{}^{18}OH/CH_3CH_2{}^{16}OH = 1.0/4.4$, where 3.0 mol% of the methanol and 2.6 mol% of the ethanol were converted to products. Methanol was converted into methyl ethyl ether (MEE) (85%) and DME (15%), while ethanol was converted into MEE (18.5%) and DEE (81.5%). The oxygen isotopic distributions are shown

Table 2
Percent isotopic composition (±2 mol%) of oxygen-containing products from the reaction of a ^{18}O-methanol/^{16}O-isobutanol = 1.0/3.2 reactant mixture over 0.5 g Amberlyst-H 35 catalyst at 110°C, 1 MPa, and total GHSV = 14200 ℓ/(kg catal h)

Isotope	MIBE	MTBE	DME
^{18}O	2	93	94
^{16}O	98	7	6

Table 3
Percent isotopic composition (±2 mol%) of oxygen-containing products from the reaction of a ^{18}O-ethanol/^{16}O-isobutanol = 1.0/5.0 reactant mixture over 0.5 g Amberlyst-H 35 catalyst at 110°C, 1 MPa, and total GHSV = 14 200 ℓ/(kg catal h)

Isotope	EIBE	ETBE	DEE
^{18}O	<5	96	>93
^{16}O	>95	4	<7

in table 4, where it can be seen that ^{16}O and ^{18}O were found with equal abundance in MEE. This result shows, contrary to reactions of isobutanol with methanol and ethanol, that there was no steric preference in the mechanistic pathway of the coupling reactions involving methanol and ethanol only. Again, the isotopic distributions in the DME and DEE products show that no significant isotopic scrambling occurred during this reaction, and no formation of ethene was observed.

4. Discussion

Considering first the methanol/isobutanol reactants, there are four main reactions leading to the four principal products of primary interest. These consist of

(1) direct coupling of methanol and isobutanol to form MIBE,
(2) dehydration of isobutanol to form isobutene,
(3) dehydrative coupling of methanol to form DME, and
(4) coupling of methanol with isobutene to form MTBE.

In addition to these reactions, another reaction that should be considered is

(5) the isomerization of MIBE to MTBE.

Not considered in this reaction scheme are linear butenes (observed as minor products), C_8 ethers, and secondary products such as octenes. In addition to the products indicated, reactions (1), (2), and (3) also form water. Except for reaction (2), these reactions are mildly exothermic. An analogous reaction scheme could be constructed for the reaction of ethanol and isobutanol to form DEE, EIBE, and ETBE.

The isotopic results presented here show that MIBE and EIBE (tables 1–3) derive

Table 4
Percent isotopic composition (±2 mol%) of the ethers formed from the ^{18}O-methanol/^{16}O-ethanol = 1.0/4.4 reactant mixture over Amberlyst-H 35 catalyst at 110°C, 1 MPa, and total GHSV = 15 250 ℓ/(kg catal h)

Isotope	DME	DEE	MEE
^{18}O	>98	<2	50
^{16}O	<2	>98	50

their ether oxygens from isobutanol, while the oxygen in MTBE and ETBE is obtained from methanol and ethanol, respectively. This result demonstrates that MIBE (EIBE) and MTBE (ETBE) are not formed from a common intermediate and that MTBE (ETBE) is not the product of isomerization of MIBE (EIBE). Moreover, MIBE and EIBE are produced by a kinetically controlled pathway that is mechanistically more efficient than that leading to the thermodynamically more stable MTBE and ETBE products. For ^{18}O-methanol/^{16}O-isobutanol, the results of the isotope discriminating reactions, taken in conjunction with those of the prior kinetic analyses of ether synthesis over Nafion-H [2], support the reaction scheme shown in fig. 1. The path leading to MIBE has mechanistic features of an S_N2 solution-phase reaction, but exhibits distinctly different kinetics unique to *surface-catalyzed* reactions in which both alcohols are activated by being adsorbed on the acid sites of the Nafion-H catalysts. This results in kinetics that show self-poisoning of the reaction by either alcohol when present in high concentration, at variance with the kinetics of S_N2 reactions in solutions in which the rate is proportional to the concentrations of both reactants [16]. In fact, the surface-catalyzed four-center reaction (involving two $-SO_3H$ surface groups and the two alcohols) exhibits a maximum rate at optimum concentrations of the reactant alcohols, which falls off when either alcohol is in excess as a negative power of the partial pressure of the excess reactant [2].

The specific mode of bonding of the alcohols to the sulfonic acid sites is not resolved in full detail but the current ^{18}O label flow rules out the formation of the isobutyl ester of the sulfonic acid or isobutyl carbenium ion put forward as a possibility earlier [1], as in this case isobutanol would lose its oxygen and MIBE would gain ^{18}O from methanol, contrary to the experiment. A likely type of bonding is via oxonium of the alcohols, with methanol oxonium suffering a rear attack by isobutanol that is just leaving its bonded state on the neighboring sulfonic group by proton elimination; the $^{18}OH_2$ is then the leaving group from methanol and the MIBE produced retains ^{16}O from isobutanol (fig. 1). The reverse attack of isobutyl oxonium by methanol is sterically hindered, in analogy with steric hindrance of

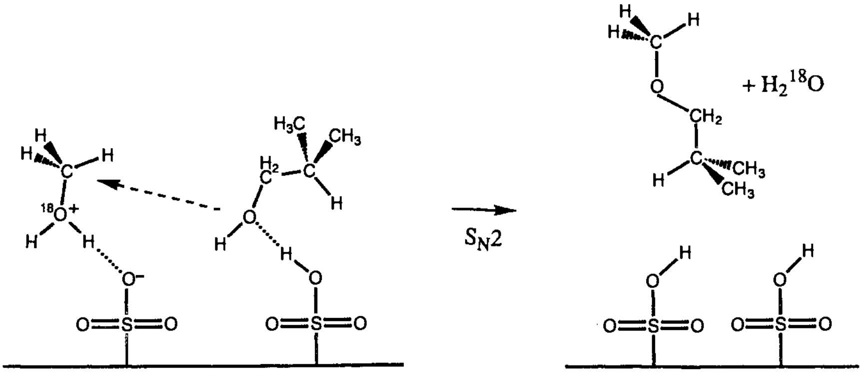


Fig. 1. The S_N2 reaction pathway for ^{18}O-methanol and ^{16}O-isobutanol to form ^{16}O-MIBE.

the attack of isobutyl group by ethoxide in the related S_N2 reactions of alkyl halides [15].

Contrary to MIBE, the MTBE product contained nearly exclusively oxygen originating from methanol and not isobutanol. Since dehydration of isobutanol to isobutene proceeds by a reaction parallel to that of MIBE synthesis, the origin of MTBE can be traced to a coupling of isobutene with methyl oxonium (represented in fig. 2) or isobutyl carbenium with methanol [17,18]. The former path is thought to occur in the industrial acid resin-catalyzed liquid phase MTBE synthesis from methanol and isobutene [19].

The same reaction schemes shown in figs. 1 and 2 are applicable to the reaction of ^{18}O-ethanol/^{16}O-isobutanol. In this case, EIBE retained the ^{16}O label of isobutanol (table 3) via S_N2 axial attack of activated isobutanol onto acid-activated ethanol, where attack in the opposite direction is evidently sterically hindered. Similar to MTBE, ETBE contained ^{18}O from the ethanol reactant, indicating reaction between ethanol and isobutene and not isomerization of EIBE.

In contrast to the above results with isobutanol as a reactant, the $CH_3{}^{18}OH/CH_3CH_2{}^{16}OH$ experiment showed that there was no steric preference in the coupling reaction over Amberlyst-H 35 between these reactants (table 4).

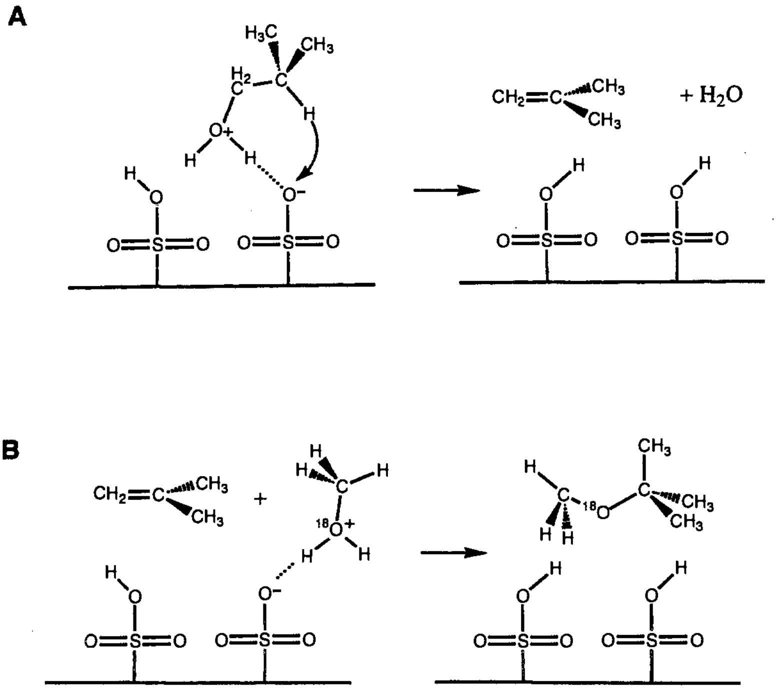


Fig. 2. The mechanistic scheme for synthesis of ^{18}O-MTBE via (A) dehydration of ^{16}O-isobutanol to form isobutene, with (B) subsequent reaction with surface activated ^{18}O-methanol.

Thus, there was nearly the same probability of surface-activated methanol and ethanol attacking one another to form MEE.

5. Conclusions

The present isotopic labelling experiments demonstrate that MIBE and MTBE, and similarly EIBE and ETBE, are synthesized from alcohols over strong acid resin catalysts by distinctly different mechanistic pathways, wherein the tertiary butyl ethers are formed via an "isobutene-like" intermediary species. In contrast, MIBE and EIBE are formed via a four-center, dual sorption site surface-catalyzed S_N2 reaction. These two pathways are very selective as shown by the oxygen isotope distributions in the ether products, which were not sensitive to the range of reaction conditions explored, e.g. temperature, pressure and relative concentration of the reactant alcohols, nor to the particular resin catalyst employed. Alcohol coupling to ethers appears to follow the general patterns observed here even when inorganic acid catalysts and secondary alcohols are involved. The S_N2 reaction is confirmed by a very high degree of enantiomeric inversion in the reaction of chiral secondary alcohols, e.g. of 2-pentanol with ethanol over a HZSM-5 zeolite catalyst to form inverted 2-ethoxypentane [20].

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