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^{13}C NMR study of the acid-catalyzed carbonylation of methyl *tert*-butyl ether (MTBE)

Ned C. Haubein[a,*], Linda J. Broadbelt[a], Edmund J. Mozeleski[b], Richard H. Schlosberg[b], Raymond A. Cook[b], Christian P. Mehnert[c], and Dan Fărcaşiu[d]

[a] *Department of Chemical Engineering, Northwestern University, Evanston, IL 60208, USA*
[b] *ExxonMobil Chemical Company, Annandale, NJ 08801, USA*
[c] *ExxonMobil Research and Engineering Company, Annandale NJ 08801, USA*
[d] *Department of Chemical Engineering, University of Pittsburgh, Pittsburgh, PA 15261, USA*

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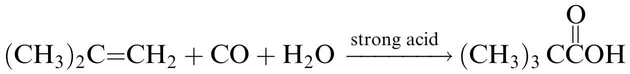
Methyl *tert*-butyl ether (MTBE) is a widely used additive in oxygenated gasoline that has recently been identified as a potential health threat to the drinking water supply due to leaking underground storage tanks. One alternate use for MTBE is the production of methyl 2,2-dimethylpropanoate (methyl pivalate) *via* Koch carbonylation chemistry. BF_3/H_2O catalysts are employed in industrial applications of Koch chemistry, but cannot be used for direct ester production because the presence of water in the system leads to the formation of carboxylic acids and lowers the selectivity to esters. Therefore, a BF_3/CH_3OH complex was investigated for the carbonylation of MTBE to avoid this loss in selectivity. This study used ^{13}C NMR spectroscopy and *ab initio* calculations to investigate this carbonylation reaction. NMR results and *ab initio* calculations suggest a structure for the BF_3/CH_3OH acid which is in agreement with previous studies, and a Hammett acidity value of −4.2 was calculated for BF_3–$2.19CH_3OH$ using the $\Delta\delta$ method. It is believed that these are the first reported *ab initio* calculations on the BF_3/CH_3OH system. NMR results also show that MTBE begins to react between 50 °C and 75 °C to produce oligomers of isobutene when no CO is present and carbonylated species when CO is present.

KEY WORDS: ^{13}C NMR; MTBE; methyl pivalate; BF_3–$2CH_3OH$; BF_3/H_2O; Koch carbonylation; *ab initio* NMR calculations.

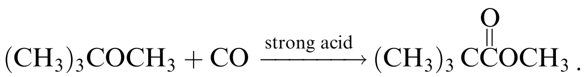
1. Introduction

Methyl *tert*-butyl ether (MTBE) has become a very large-volume product based on its widespread usage as an oxygenate in motor gasoline. MTBE is the oxygenate used in about 85% of reformulated gasoline, which, in turn, accounts for about one-third of all U.S. gasoline sales [1]. Recently, various agencies, most notably the California Environmental Protection Agency, have raised concerns regarding the detection of MTBE in surface and ground water [2]. Thus, removal of MTBE from gasoline in California by December 2002 was decreed by an executive order of the governor [3]. Consequently, current MTBE producers are looking for alternate outlets for their product or for the raw materials which go into its production.

One potential conversion route for MTBE is carbonylation using Koch chemistry. Generally, the process steps in Koch chemistry to make trialkyl acetic acids are complex formation in a strong acid system, degassing, hydrolysis and purification/fractionation, with the net reaction shown in equation (1a). Usual industrial reaction conditions for carbonylation of olefins using BF_3-based systems are *ca.* 40–70 °C and 1000–1500 psi (70–100 bar) carbon monoxide pressure [4]. An analogous conversion of MTBE via Koch chemistry entails the reaction of MTBE with carbon monoxide under acidic conditions to form methyl 2,2-dimethylpropanoate (methyl pivalate), with the stoichiometry as indicated in equation (1b).This chemistry was first reported in a Shell patent using 98% HF as the catalyst [5].



$$(CH_3)_2C{=}CH_2 + CO + H_2O \xrightarrow{\text{strong acid}} (CH_3)_3\,\overset{\overset{\displaystyle O}{\|}}{C}OH \tag{1a}$$



$$(CH_3)_3COCH_3 + CO \xrightarrow{\text{strong acid}} (CH_3)_3\,\overset{\overset{\displaystyle O}{\|}}{C}OCH_3\,. \tag{1b}$$

Methyl pivalate is a methyl ester, a class of compounds that find use as solvents (*e.g.* methyl acetate) and as agents for transesterification reactions where they serve as alternatives for corrosive carboxylic acids and thus afford ease of handling. Methyl pivalate has recently been shown to have environmental benefits as a fluid [6] in that it has a much lower ozone-forming potential than such common oxygenated solvents as *n*-butyl ethanoate (butyl acetate) and butanol, as measured by a maximum incremental reactivity scale [7]. Thus, replacement of a high ozone-forming fluid (*e.g.* butyl acetate) with a low ozone-forming fluid (*e.g.* methyl pivalate) at comparable levels results in a formulation which could significantly lower the environmental impact as measured by ground-level ozone formation.

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[*] To whom correspondence should be addressed.

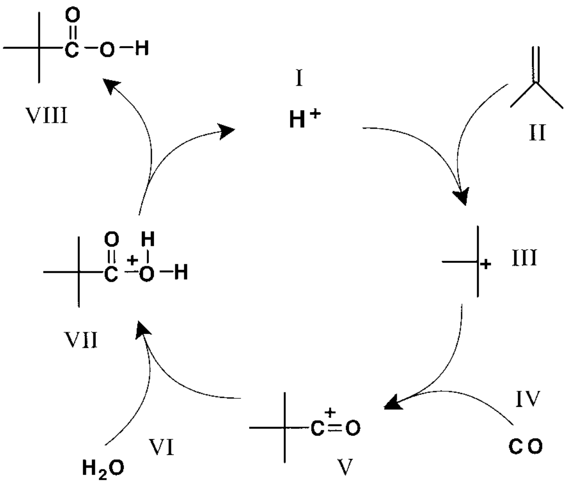
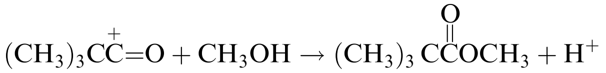


Figure 1. Pivalic acid is produced *via* the Koch carbonylation of isobutene [4]. The steps involved are protonation, carbonylation, solvent addition, and deprotonation.

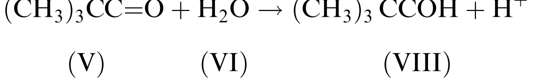
Currently, methyl pivalate can be produced via esterification of 2,2-dimethylpropanoic acid (pivalic acid) with methanol. Pivalic acid is produced *via* Koch carbonylation during a catalytic cycle involving isobutene and high-pressure carbon monoxide in an aqueous strong acid as illustrated in figure 1. The role of the strong acid (I), represented here as a proton, is to protonate the alkene (II) and form a carbocation (III) to which carbon monoxide (IV) can be added to form an acylium cation (V). The solvent (VI) can then add to the acylium cation to form the protonated acid (VII) which can release a proton (I) to form the carboxylic acid product (VIII) and complete the catalytic cycle.

A number of acids are able to catalyze Koch carbonylation chemistry including sulfuric acid, phosphoric acid, hydrofluoric acid, and combinations of these materials with Lewis acids such as BF_3, $AlCl_3$, or SbF_5 [4]. Koch chemistry is flexible in that any acid with sufficient strength to generate an alkyl carbenium ion can, in theory, catalyze Koch reactions. Industrially, catalysts based on combinations of BF_3 and H_2O are common because of issues related to catalyst recycle [4].

Koch chemistry is also flexible in the nature of the hydrocarbon reactant and solvent that can be employed. For example, replacing the water (VI) in figure 1 with methanol affords methyl esters in place of carboxylic acids, as shown in equations (2a) and (2b), respectively.

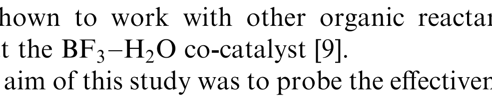


$$(CH_3)_3\overset{+}{C}C{=}O + CH_3OH \rightarrow (CH_3)_3\,C\overset{\overset{O}{\|}}{C}OCH_3 + H^+ \tag{2a}$$



$$\underset{(V)}{(CH_3)_3\overset{+}{C}C{=}O} + \underset{(VI)}{H_2O} \rightarrow \underset{(VIII)}{(CH_3)_3\,C\overset{\overset{O}{\|}}{C}OH} + H^+ \tag{2b}$$

Ethers or alcohols can also be used as starting materials in this type of chemistry in place of isobutene (II). These species can be protonated, as shown in equation (3), and can then participate in the reactions outlined in figure 1. If MTBE is used as the starting material, the products of the reaction are a *tert*-butyl carbenium ion and a molecule of methanol. This means that the methanol molecule required to generate the methyl ester in equation (2a) is generated *in situ.*



$$H^+ + (CH_3)_3COR \rightarrow (CH_3)_3C\underset{+}{\overset{H}{O}}R \rightarrow (CH_3)_3C^+ + ROH \tag{3}$$

The choice of a catalyst for the conversion of MTBE to methyl pivalate is important. A catalyst based on the combination of BF_3 and H_2O would lead to a product mixture containing both methyl esters and carboxylic acids. This situation is shown in equations (2a) and (2b) and arises because the acylium ion (V) can be captured by both methanol, produced *in situ* when MTBE is protonated and decomposes to the *t*-butyl carbenium ion and methanol, and water, which is present as a component of the catalyst. Because methanol has a slightly higher affinity for BF_3 than does water (65 kJ/mol for methanol, 46 kJ/mol for water) [8], a fraction of the free methanol complexes with the BF_3 and displaces water which can form carboxylic acids *via* reaction (2b). This displacement can result in stoichiometric quantities of water because the catalyst to feed ratio is generally in excess of 1 : 1 [9]. Because the desired product is the methyl ester, it is best to operate the system under anhydrous conditions. To achieve the level of acidity required to catalyze the system while avoiding the loss of selectivity to carboxylic acid associated with the BF_3–H_2O system, a catalyst based on the combination of BF_3 and CH_3OH was used for this reaction. BF_3–$2CH_3OH$ has previously been shown to be effective in catalyzing the carbonylation of isobutene to methyl pivalate when combined with BF_3–H_2O, but it has not been shown to work with other organic reactants or without the BF_3–H_2O co-catalyst [9].

The aim of this study was to probe the effectiveness of BF_3–$2CH_3OH$ in carrying out the Koch carbonylation of MTBE. This reaction differs from the industrially practiced Koch carbonylation of olefins in two distinct ways. First, the catalyst used in this study is water-free as methanol replaces water as the oxygenated component of the acid system. Second, the feed for this study is MTBE, and hydrolysis is neither desired nor practiced in this direct route to manufacturing methyl esters. From a stoichiometric perspective, the desired product, methyl pivalate, is composed of MTBE and carbon monoxide moieties. This too is a departure from the olefin carbonylation wherein the water of the acid must be a reagent. Finally, the BF_3/CH_3OH catalyst system is more compatible with methyl pivalate than the BF_3/H_2O system is with pivalic acid. Thus, product analysis is more complex in the methanol system discussed below.

To monitor reaction products and the influence of temperature on the system, an *in situ* ^{13}C NMR investigation was carried out. In addition, *ab initio* NMR calculations were used to help identify peaks in the experimental spectra and to gain insight into the structure of BF_3–$2CH_3OH$.

2. Materials and methods

While the ultimate goal of the experiments was to analyze a system consisting of MTBE, CO, and BF_3–$2CH_3OH$, a number of additional experiments were performed to establish peak identities. All chemicals were purchased from Aldrich except for BF_3 gas (99.5%, AGA Specialty Gases) and ^{13}CO (Isotec, Inc.). Neat samples of BF_3–$2CH_3OH$, MTBE (99.8%), methyl pivalate (MP), and BF_3–CH_3OCH_3 were examined by ^{13}C NMR spectroscopy. Mixtures of BF_3–$2CH_3OH$ with MTBE, 2,4,4-trimethyl-1-pentene (diisobutylene (DIB), 99%), dimethyl ether (DME), MTBE and ^{13}CO, and methyl pivalate were also studied. It was important to monitor dimethyl ether because of the potential dehydration of methanol under acidic conditions [10] and diisobutylene because of potential oligomerization reactions resulting from the decomposition of MTBE to methanol and *t*-butyl carbenium ion [11,12]. A summary of the temperatures or temperature ranges that were examined for each system is shown in table 1.

The ^{13}C NMR experiments carried out in this study were performed on a Varian Unity 400 MHz spectrometer, and all shifts are reported relative to tetramethylsilane (TMS). BF_3–$2CH_3OH$ solutions were prepared by bubbling the appropriate amount of BF_3 gas through methanol (99.99%) in a 150 ml Hastelloy C EZE-Seal autoclave. Standard 10 mm NMR tubes were used for experiments performed at atmospheric pressure, and 10 mm sapphire NMR tubes were used for experiments performed at high pressure. In a typical experiment, BF_3–$2CH_3OH$ was introduced to the NMR tube at −78 °C, followed by MTBE at −78 °C and 1260 psi of ^{13}CO. The tube was briefly agitated by hand after the ^{13}CO was added to provide mixing, and the spectrum was collected. Binary mixtures of BF_3/CH_3OH and either DIB or DME were prepared using a 50 : 50 weight percent mixture of BF_3/CH_3OH (1 : 2.19 mol : mol) supplied by Aldrich.

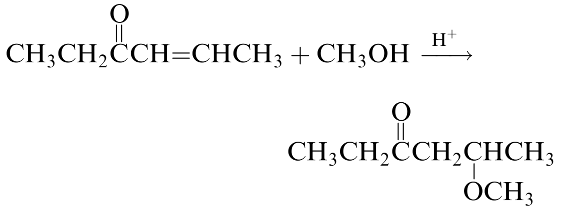
Table 1
Summary of environment and temperatures (°C) studied in ^{13}C NMR experiments

Species	Neat	With BF_3–$2CH_3OH$	With BF_3–$2CH_3OH$ and CO
BF_3–$2CH_3OH$	−80 to 25	–	–
BF_3–DME	25	–	–
DME [a]	–	25 [e]	–
DIB [b]	–	25 [e]	–
MTBE [c]	25	−80 to 125	−80 to 125
MP [d]	25	25	–

[a] Dimethyl ether.
[b] Diisobutylene.
[c] Methyl *t*-butyl ether.
[d] Methyl pivalate.
[e] BF_3–$2.19CH_3OH$.

Acidity measurements of BF_3–$2.19CH_3OH$ were made using the $\Delta\delta$ method at −10 °C using 4-hexen-3-one as an indicator [13]. These experiments were carried out on a Bruker DMX300 NMR instrument, operating at 75.468 MHz for ^{13}C. A spectral width of 15 kHz, a number of 16384 (16K) points in the time domain and 16K points for the Fourier transform, an excitation pulse of 5.0 μs (90° pulse, 9.0 μs), a receiver blanking delay of 30 ms, and a relaxation delay of 3 s were used. Proton decoupling was achieved by a Waltz sequence [14], the 90° pulse for decoupling being 100 μs. A pulse sequence with presaturation of the methanol signal was employed for all spectra, because the very large methanol peak obscured the signals needed to calculate the $\Delta\delta$ parameter for the highest dilution of indicator.

In the range of acidity of the solution, a slow nucleophilic addition of methanol to the unsaturated ketone occurred, as shown in equation (4). It was established by running the spectra at varying intervals after mixing of the reactants that this reaction had very little effect on the determined value for $\Delta\delta°$; that is, the adduct and the indicator have about the same basic strength. Nevertheless, the spectra used for the determination of the $\Delta\delta°$ parameter were recorded at −10 °C where the rate of methanol addition was too slow to measure.



$$CH_3CH_2\overset{O}{\overset{\|}{C}}CH{=}CHCH_3 + CH_3OH \xrightarrow{H^+} CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2\underset{OCH_3}{\underset{|}{C}}HCH_3 \quad (4)$$

The methanol to boron trifluoride ratio was measured by the two-step titration of the latter, as reported previously [15]. The absence of water in the mixture was determined by integration of the proton spectrum (methyl peak : OH peak = 3.0).

Ab initio chemical shifts were calculated using the gauge independent atomic orbital (GIAO) method at the MP2 level of theory using the 6-31G** Gaussian basis set. Optimized geometries were found for all species using density functional theory (DFT) with the B3LYP exchange-correlation functional and the 6-31G** Gaussian basis set [16].

3. Results and discussion

The results for the starting materials and reference systems are presented first to provide baseline information about the system, and this information is then used to understand the more complex spectra collected during experiments generating multiple species.

3.1. BF_3–$2CH_3OH$

^{13}C analysis of neat BF_3–$2CH_3OH$ revealed a very clean spectrum. At 25 °C, a single peak was present with a chemical shift of 52.4 ppm. Upon cooling the sample to −50 °C, two peaks of approximately equal size were observed at 51.4 and 52.9 ppm. A reported infrared analysis [17] indicates that BF_3–$2CH_3OH$ complexes consist of a BF_3–CH_3OH species hydrogen bonded to the second CH_3OH molecule. The splitting observed in the NMR spectrum is consistent with this structure which contains non-equivalent methanol molecules. At higher temperatures, the carbon atoms of both methanol molecules become equivalent due to rapid chemical exchange.

Ab initio quantum chemistry was used to identify a minimum energy structure for BF_3–$2CH_3OH$, as shown in figure 2. As revealed by the calculated distances between the atoms in figure 2, one methanol molecule is closely associated with the BF_3 (B–O distance of 1.64 Å), while the second methanol is farther from the boron center and interacts through hydrogen bonding with the first methanol (H···O distance of 1.63 Å). The O–O distance in this hydrogen-bonded complex is 2.60 Å and is comparable to a reported O–O distance of 2.68 Å measured for solid methanol [18]. The methanol farther from the boron center also interacts with one of the fluorine atoms on the BF_3. This is indicated by the longer B–F distance (1.39 Å) compared to the other B–F distances (1.37 Å and 1.36 Å) and the deviation of the O–H···O angle from 180° (159.7°).

Although a small number of *ab initio* calculations have been carried out on the related BF_3/H_2O system [19,20], it is believed that this study represents the first such investigation of the BF_3/CH_3OH system. *Ab initio* NMR calculations based on the DFT optimized structure in figure 2 predict chemical shifts, relative to TMS, of 50.0 ppm for both carbon atoms in the complex, as indicated in table 2. GIAO-MP2 calculations generally predict chemical shifts to within 2 ppm for ^{13}C [21]. The calculated value for neat methanol is 50.1 ppm, compared to an experimentally measured value of 49.0 ppm [22], and does not differ significantly from the shifts found in BF_3–$2CH_3OH$. *Ab initio* NMR calculations are very sensitive to the geometry of the molecule being studied, and subtle changes induced upon interaction with other BF_3–$2CH_3OH$ complexes could account for the discrepancy between the calculated and measured chemical shifts. A calculation involving multiple BF_3–$2CH_3OH$ complexes has not been carried out due to the difficulties in finding an optimized geometry for a system containing six or more distinct species [23]. Given the state of the art of both the calculated and experimentally measured chemical shifts, the structure in figure 2 is the best possible assessment of the actual structure of the BF_3–$2CH_3OH$ system.

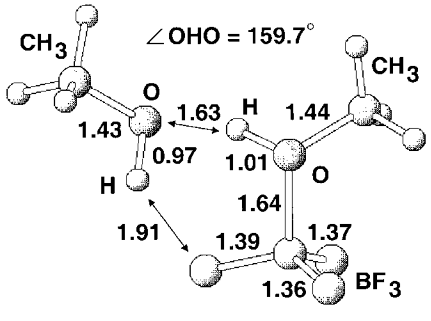


Figure 2. B3LYP/6-31G** optimized geometry of BF_3–$2CH_3OH$ indicates strong interaction of one methanol molecule with BF_3 and hydrogen bonding with the second methanol molecule as indicated by the 1.63 Å bond length (distances in Å).

Table 2
Calculated and experimental ^{13}C chemical shifts

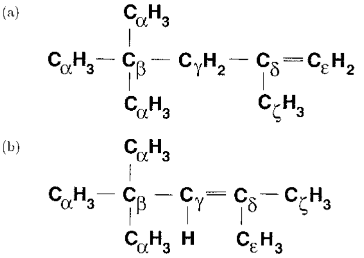
Species	Experimental	*Ab initio*
BF_3–$2CH_3OH$	52.4[a]	50.0
BF_3–$2CH_3OH$	51.4, 52.9[b]	50.0
DME	59.7	58.0
BF_3–DME	63.8	58.6
BF_3–$2.19CH_3OH$/DME	60.7	–
Protonated DME	–	72.0, 71.3

[a] 25 °C.
[b] −80 °C.

Additional NMR experiments, described in section 2, were performed on BF_3–$2.19CH_3OH$ to determine its Hammett acidity value (H_0) using the $\Delta\delta$ method. The H_0 value was found to be −4.2 for this system compared to −7.0 for BF_3–$2H_2O$ [24]. This indicates that while the methanol-based system is a strong acid, it is a much weaker acid than the water-based system.

3.2. BF_3–$2.19CH_3OH$/diisobutylene

BF_3–$2.19CH_3OH$ was mixed with DIB (7.4:1 mol:mol) to obtain a reference spectrum for the olefin in the acidic media. The mixture separated into two phases upon mixing, and the lower, acid phase was examined in the NMR experiment. In addition to the peak at 52.2 ppm corresponding to the methanol in the acid, peaks were found at 26.2, 31.1, and 31.7 ppm and minor peaks at 14.6, 22.8, and 33.0 ppm. Experimental chemical shifts for neat DIB [25] are shown in figure 3. The BF_3–$2.19CH_3OH$/DIB reference spectrum was



Isomer	α	β	γ	δ	ϵ	ζ
a	30.0	31.3	51.6	144.0	113.6	25.2
b	31.1	32.0	130.1	135.0	28.0	18.8

Figure 3. Experimental chemical shift assignments for neat diisobutylene isomers (ppm) [25]. Peaks for olefinic carbons are not present in the BF_3–2.19CH_3OH/DIB spectrum as this system is strongly acidic.

obtained using the isomer shown in (a), while isomer (b) is included for comparison to spectra in which DIB was formed as a product. The peaks missing from the BF_3–2.19CH_3OH/DIB spectrum correspond to olefinic carbons which would not be present as such under acidic conditions. Minor peaks in this spectrum have not been definitively assigned, but those peaks which have been observed serve as a fingerprint for DIB in BF_3–2.19CH_3OH.

3.3. BF_3–DME and BF_3–2.19CH_3OH/DME

Spectra were obtained for both BF_3–DME (1 : 1 mol : mol) and BF_3–2.19CH_3OH/DME (1.15 : 1 mol : mol) at 25 °C. A single peak was present for the BF_3–DME system at 63.8 ppm. The BF_3–2.19CH_3OH/DME system resulted in two peaks: a dimethyl ether peak at 60.7 ppm and a peak from the methanol in the acid at 51.6 ppm. The peak from the methanol split into two peaks below 0 °C, as for neat BF_3–2CH_3OH below −50 °C. Neat dimethyl ether produces one peak at 59.7 ppm [22]. The chemical shift difference between neat DME and BF_3–2.19CH_3OH/DME may be due to competition between DME and methanol for BF_3. This is supported by the fact that the chemical shift for BF_3–2.19CH_3OH/DME moves in the direction of the BF_3–DME chemical shift, as well as *ab initio* calculations which indicate that DME interacts more strongly (71 kJ/mol) with BF_3 than does methanol (65 kJ/mol) [8]. In addition, partial protonation of DME may result in an increase in its chemical shift. *Ab initio* calculations shown in table 2 predict chemical shifts of 58.0 ppm for DME, 72.0 ppm and 71.3 ppm for protonated DME, and 58.6 ppm for BF_3–DME. Two signals are calculated for protonated DME because the C–O–H angles are slightly different for the two methyl groups due to their staggered rotational configuration.

Table 3
Chemical shifts (ppm) of neat and complexed MTBE and methyl pivalate at 25 °C

Identity of carbon	Neat	In BF_3–2CH_3OH
$(\mathbf{C}H_3)_3COCH_3$	27.5	27.6
$(CH_3)_3\mathbf{C}OCH_3$	72.6	80.3
$(CH_3)_3CO\mathbf{C}H_3$	49.5	51.1
$(\mathbf{C}H_3)_3C\overset{\overset{O}{\|}}{C}OCH_3$	27.7	24.3
$(CH_3)_3\mathbf{C}\overset{\overset{O}{\|}}{C}OCH_3$	39.1	37.0
$(CH_3)_3C\overset{\overset{O}{\|}}{\mathbf{C}}OCH_3$	178.2	180.9
$(CH_3)_3C\overset{\overset{O}{\|}}{C}O\mathbf{C}H_3$	51.7	58.1

3.4. MTBE and methyl pivalate

Neat samples of MTBE and MP both yielded very clean spectra. Chemical shifts and assignments are shown in table 3 along with the chemical shifts for MTBE and MP in BF_3–2CH_3OH. The chemical shifts in the acid differ from the neat samples due to complexation and solvent effects. Most notably, the tertiary carbon in MTBE and the methyl ester carbon in methyl pivalate were shifted by 7.7 ppm and 6.4 ppm, respectively, in the presence of the acid. MTBE has been studied previously under acidic conditions, and the results suggest that it is protonated in the current system and not complexed with BF_3 [26]. Esters are stronger Lewis bases than ethers [27], and therefore, methyl pivalate could be both complexed and protonated.

3.5. BF_3–2CH_3OH/MTBE temperature study

Spectra were obtained for a mixture of BF_3–2CH_3OH and MTBE (2.68 : 1 mol : mol) at selected temperatures between −80 °C and 125 °C. At −80 °C, the MTBE peaks shown in table 3 and two peaks (52.2 and 52.9 ppm) from the methanol constituting the acid were present. The methanol peaks merged to form a single peak at 52.8 ppm between 0 °C and 25 °C due to rapid exchange. Between −80 °C and 50 °C, there were only minor (<1 ppm) shifts from those reported in table 3 for MTBE in BF_3–2CH_3OH at 25 °C.

Between 50 °C and 75 °C the system began to react, as measured by the reduction in the MTBE peak area. The spectra for 50 °C and 75 °C are shown in figures 4 and 5, respectively. In both figures, the tertiary carbon appears at 80.1 ppm, the methoxy carbon appears at 51.0 ppm, the *t*-butyl methyl carbons appear at 27.6 ppm and the methanol from the acid appears at 53.2 ppm. Two important differences in the spectra should be noted. First, the methanol peak at 53.2 ppm begins to dominate the spectrum as temperature increases and becomes the

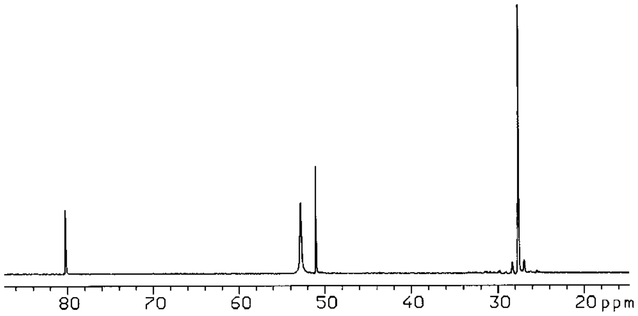


Figure 4. The ^{13}C spectrum of MTBE in BF_3–$2CH_3OH$ at 50 °C is shown where the peak at 80.1 ppm is the tertiary carbon, 51.0 ppm is the methoxy carbon, 27.6 ppm is the *t*-butyl methyl carbons, and 53.2 ppm is the methanol from the catalyst.

only major peak remaining in the spectrum by 125 °C (not shown). This indicates that the carbon atoms from MTBE are no longer visible in the spectrum, which is consistent with the experimental observation that, under these conditions, an organic phase forms above the position at which the spectrum is taken, thus removing the MTBE carbons from the NMR experiment. The second change is the appearance of a number of small peaks between 30 and 34 ppm. These peaks, along with the formation of an organic phase above the acid phase, match the NMR results of the binary mixture of BF_3–$2.19CH_3OH$/DIB discussed above and suggest that oligomerization reactions to form diisobutylene, triisobutylene, etc. have occurred. These come about when MTBE decomposes to methanol and a *t*-butyl cation, the *t*-butyl cation loses a proton to form isobutylene, and the isobutylene is alkylated by a second *t*-butyl cation.

Finally, at 125 °C, a small peak appeared at 61 ppm in the spectrum. This peak falls at approximately the same shift as that found in the BF_3–$2.19CH_3OH$/DME mixture, and the peak at 61 ppm is therefore assigned to DME.

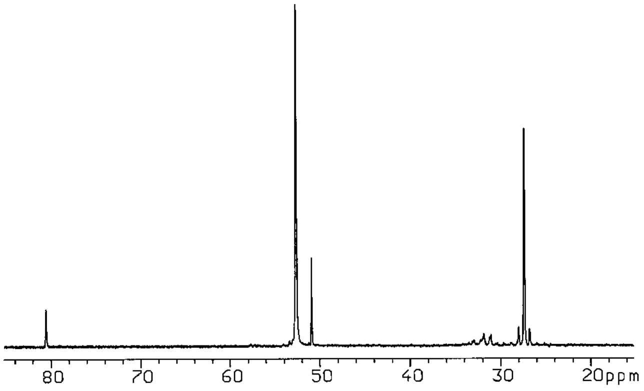


Figure 5. The ^{13}C spectrum of MTBE in BF_3–$2CH_3OH$ at 75 °C shows significant differences when compared to the same system at 50 °C. Many of the carbon atoms from MTBE are not visible in the spectrum because they have moved to an organic phase above the position at which the spectrum is taken. The peak at 53.2 ppm is the only major peak remaining if the system is heated to 125 °C.

3.6. BF_3–$2CH_3OH$/MTBE/^{13}CO temperature study

The system containing all of the reactants needed to perform the Koch chemistry, BF_3–$2CH_3OH$, MTBE, and ^{13}CO, was examined at temperatures between −80 °C and 125 °C. This system appears identical to the BF_3–$2CH_3OH$/MTBE system between −80 °C and 50 °C except for the presence of ^{13}CO at 186 ppm. The reaction initiates, as in the BF_3–$2CH_3OH$/MTBE system, between 50 °C and 75 °C. This is consistent with the postulated mechanism, shown in equation (3) with $R = CH_3$, which indicates that the protonation of MTBE and subsequent release of methanol are the first steps in the carbonylation of an ether because the BF_3–$2CH_3OH$/MTBE system also began to react in this temperature range. Above 75 °C, peaks corresponding to the carbons in MTBE steadily decrease or vanish, and peaks assigned to carbonylated species appear in the region of 180–186 ppm, as shown in figure 6. The methyl

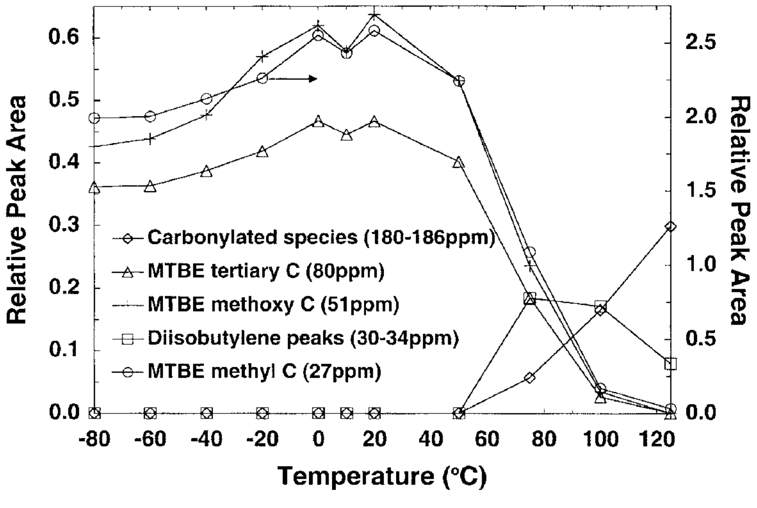


Figure 6. The areas of major peaks relative to the area of the peak for the carbons in BF_3–$2CH_3OH$ in the BF_3–$2CH_3OH$/MTBE/^{13}CO system are shown. Peaks assigned to MTBE decrease or vanish above 75 °C, and those assigned to DIB and carbonylated species appear.

pivalate peaks at 58 and 37 ppm are not included in this figure because they were very weak signals. Poor selectivity to carbonylated products in this experiment is attributed to CO starvation resulting from an inability to provide adequate mixing in the instrument. The limited CO availability favors oligomerization reactions, a result which is supported by the observation of diisobutylene peaks near 32 ppm and the formation of an organic phase. Dimethyl ether is also present in this system above 50 °C as indicated by a peak at 62 ppm.

3.7. BF_3–$2CH_3OH$ stability

While the temperature study indicates that BF_3–$2CH_3OH$ is capable of carbonylating MTBE, initial activity is only one of the criteria which needs to be examined when considering the utility of a catalyst system. There are two modes by which BF_3–$2CH_3OH$ could be chemically deactivated in a batch system: irreversible decomposition of the BF_3 moiety [28] and strong binding of a product to the BF_3–$2CH_3OH$, which drives the turnover number towards one. Liquid and gas analyses showed no detectable fluorinated products in the system, which indicates that no measurable decomposition of the BF_3 occurred under the experimental conditions studied. Binding of the BF_3–$2CH_3OH$ to the methyl pivalate product does occur; however, this is an issue which can be dealt with through engineering solutions. These kinds of reactions are almost always carried out with a stoichiometric excess of acid catalyst so that the catalyst to feed ratio is greater than one [9,29]. One possible separation route is the addition of methanol, which reduces the acidity of the system and releases the ester product. The excess methanol can then be removed via distillation to re-form the stable BF_3–$2CH_3OH$ complex [28].

4. Conclusions

Production of methyl pivalate from MTBE via Koch chemistry converts a compound facing environmental pressures to one with potential environmental benefits. BF_3–$2CH_3OH$ is an attractive acid for this conversion because it is strong enough to catalyze the reaction without the loss in selectivity due to carboxylic acid production seen in the BF_3–H_2O catalyst system. A ^{13}C NMR study has shown that MTBE is carbonylated in the presence of BF_3–$2CH_3OH$ with the reaction commencing between 50 °C and 75 °C. *Ab initio* NMR calculations were used to support the postulated structure of the acid system required for the desired chemistry. Undesired side products in the system include dimethyl ether and diisobutylene. The proposed mechanism points to those features (acid strength, CO availability *via* adequate CO pressure and mixing, temperature, etc.) which control the reaction selectivity to methyl pivalate.

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