

Superacid-Catalyzed Carbonylation of Methane, Methyl Halides, Methyl Alcohol, and Dimethyl Ether to Methyl Acetate and Acetic Acid¹

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Superacid-catalyzed (BF_3 , $\text{BF}_3\text{-H}_2\text{O}$, HF-BF_3 , and $\text{CF}_3\text{SO}_3\text{H}$) carbonylation of methane and its substituted derivatives (particularly, methyl alcohol and dimethyl ether) gave acetic acid and methyl acetate. HF-BF_3 was found to be the most effective catalyst, giving nearly complete conversion of methyl alcohol or dimethyl ether. $\text{CF}_3\text{SO}_3\text{H}$ led to lower yields and also to the formation of methyl trifluoromethanesulfonate. Possible reaction pathways and mechanisms are discussed on the basis of experimental results. Contrasted with Rh-catalyzed carbonylation of methyl alcohol, the superacid-catalyzed reaction does not necessitate expensive catalyst and conditions necessary with sensitive organometallic catalyst systems.

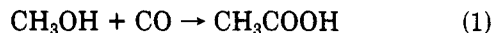
Introduction

Carbonylation reactions provide a convenient route for functionalizing organic starting materials and for their one-carbon homologation.^{2,3} In general, the low reactivity of carbon monoxide toward organic molecules makes it necessary to catalyze the reactions in order to achieve good yields under practical conditions. Consequently, these reactions are often classified according to the type of catalyst employed to accomplish this purpose. We may distinguish reactions catalyzed by transition metals (Repe reactions) and acid-catalyzed reactions (Koch reaction).³ It must be remarked that these broad classes encompass various pathways and mechanisms and that in some cases metal complexes in strongly acidic solutions have been employed.^{3,4}

Various combinations of substrate, catalyst, and reaction conditions have allowed a large variety of products to be obtained from olefins, alcohols, ethers, and halides: most often homologated products, aldehydes, carboxylic acids, esters, anhydrides and halides, but also amides or more complex products.^{2,3,5} Many of these reactions have achieved great industrial importance.

Acetic acid is one of the most important organic intermediates. For many years it was manufactured by the oxidation of acetaldehyde (obtained from ethanol or hydration of acetylene), and later by oxidation of $\text{C}_3\text{-C}_4$ alkanes. Subsequently, manufacturing processes were developed by oxidation of $\text{C}_4\text{-C}_8$ alkanes and alkenes, preferentially butane or crude oil distillates. Carbonylation of methyl alcohol gained significance after syn-gas based methyl alcohol became a large-scale industrial process.

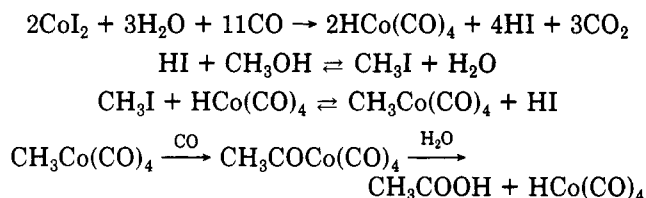
The reaction in eq 1 is exothermic by 33 kcal/mol. An effective catalyst is CoI_2 , which reacts with CO and H_2O to give tetracarbonylhydridocobalt. With the interme-



diately formed CH_3I it forms the key intermediate $\text{CH}_3\text{-Co}(\text{CO})_4$. This is converted by CO via hydrolysis into acetic acid and regenerates the catalyst (Scheme I). Despite considerable corrosion problems, this process was

commercially developed by BASF in Germany. Subsequently, Monsanto developed the Rh/ I_2 -catalyzed liquid-phase carbonylation of methyl alcohol using Wilkinson's catalyst.⁶ In addition to the capital cost of the rhodium catalyst tied up in the process, there are again significant corrosion problems and handling of a sensitive organometallic process. Thus there still is substantial interest in developing simplified and efficient ways for the preparation of acetic acid.

Scheme I



Both methyl alcohol (MeOH) and dimethyl ether (Me_2O) have been used as starting materials for the preparation of acetic acid,¹⁻³ and various methods have been employed. Among Reppe-type reactions are (a) reactions catalyzed by a transition-metal carbonyl or precursor (possibly supported) with an iodine source (I_2 , CH_3I) and an amine or phosphine as promoters⁷ and (b) vapor-phase reactions with active carbon-supported metals.⁸ These reactions yield methyl acetate (AcOMe) and acetic acid. Depending on the conditions, AcOMe may be further carbonylated to acetic anhydride (eq 2). Under conditions



a, Ac_2O is usually the major product from both Me_2O and AcOMe , with good yields (30-70%), so that in most processes AcOMe is the preferred starting material. In case b, high selectivities to AcOMe can be achieved, though with lower yields (15-30%).

Koch-type reactions proceed in strong acids or superacids and can be depicted as the reaction of the weak

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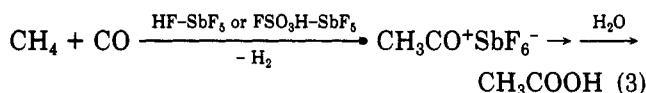
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nucleophile CO with a fully formed or incipient carbocation, yielding an acylium ion that is then hydrolyzed or solvolyzed to a carboxylic acid or ester.^{3,9} Koch carbonylation has been reported in various strong Brønsted acids such as H₂SO₄,⁶ HF,¹¹ H₃PO₄,¹² or CF₃SO₃H¹⁰ or in superacidic FSO₃H-SbF₅¹³ and HF-SbF₅.¹⁴ However, none of these systems is suited to catalyze the production of acetic acid or methyl acetate from methyl alcohol. MeOH and Me₂O were reported in the patent literature to react with CO in the presence of BF₃^{15,16} or BF₃-H₂O¹⁷ to give acetic acid or methyl acetate, but the reactions required pressures of 800–900 atm and temperatures of 150–325 °C.

In view of our continuing interest in the utilization of methane and its derivatives for the preparation of higher hydrocarbons and derivatives, we would now like to report our studies on the superacid-catalyzed preparation of acetic acid and methyl acetate from methane and substituted methanes. In particular, we report our studies on the HF-BF₃ and trifluoromethanesulfonic (triflic) acid catalyzed preparation of acetic acid and methyl acetate by carbonylation of MeOH and Me₂O.

Results and Discussion

Carbonylation of Methane. Our studies directed toward the superacid-catalyzed preparation of acetic acid started some years ago when we,^{18a} as well as Hogeveen,¹⁹ found that methane can be carbonylated to give the acetyl cation and acetic acid through its hydrolysis:



This reaction can be considered as a Koch-Haaf reaction by the incipient methyl cation, formed via protolytic oxidation of methane. In view of the higher proton affinity of CO than CH₄, however, the possibility can be raised that O-protonated CO, i.e., the isoformyl cation COH⁺, is the de facto carbonylating agent.^{18b} Although the reaction is of interest from a fundamental chemical point of view, reactions in which methane is oxidized at the expense of the superacid, it is not attractive from a practical point of view.

Carbonylation of Methyl Halides. In the course of our studies, we turned our interest to the possibility of achieving the acid-catalyzed carbonylation of monosubstituted methanes, such as methyl chloride and bromide, readily obtainable in high selectivity through electrophilic or metal-catalyzed halogenation of methane.²⁰

Table I. Carbonylation of Methyl Alcohol^a

catalyst	time (h)	yield (mol %)			
		Me ₂ O	AcOMe	AcOH	other
BF ₃	23	41.2	53.6	5.2	traces of C ₁ -C ₄
BF ₃ -H ₂ O	8	45.2	48.7	6.1	same
HF-BF ₃	8	12.8	75.7	11.5	same
HF-BF ₃	24	5.3	68.4	26.0	0.01–0.1% C ₁ -C ₄

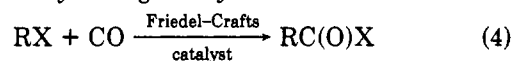
^a MeOH/BF₃ molar ratio = 2. Reaction temperature 190 °C; pressure 160 atm.

Table II. HF-BF₃-Catalyzed Carbonylation of Methyl Alcohol. Effect of Reaction Time^a

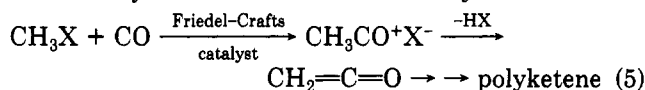
reactn time (h)	yield (mol %)			
	Me ₂ O	AcOMe	AcOH	other
0.5	14.1	76.5	8.9	0.3% C ₁ -C ₃ ; 0.2% C ₄
1.5	3.6	59.0	34.6	0.4% C ₁ -C ₃ ; 2% C ₄
3	0.8	39.4	56.7	0.3% C ₁ -C ₃ ; 3% C ₄
8	0.1	20.6	62.0	0.5% C ₁ -C ₃ ; 2% C ₄

^a MeOH/BF₃ molar ratio = 2. Reaction temperature 260 °C; pressure 150 atm.

Alkyl halides are known to react with CO under Friedel-Crafts catalysis to give acyl halides.²¹



This reaction, however, was not studied with methyl halides. We undertook such a study including CH₃X (X = F, Cl, Br) with BF₃, AlCl₃, and AlBr₃ as catalysts and found the reaction of little use in preparing acetyl halides, as it generally resulted in extensive polymerization of the acetyl halide formed in situ.²² This is due to the ease with which acetyl halides form ketene via acylium ion:



The Friedel-Crafts-catalyzed polymerization of acetyl halides to polyketenes can thus be applied to methyl halide/CO systems and consequently to the methane/Cl₂/CO system. This polymerization is pursued separately.²²

Carbonylation of Methyl Alcohol/Dimethyl Ether. Methyl alcohol is produced on a large scale from synthesis gas. We have reported the selective conversion of methane via its oxidative halogenation-hydrolysis under heterogeneous catalytic conditions. An accompanying paper describes the oxidative nonhydrolytic conversion of methyl halides into dimethyl ether.

BF₃ and Its Conjugate Superacid Catalyzed Carbonylations. The reaction of MeOH or Me₂O with CO catalyzed by BF₃ or its conjugate acids with water or HF gave methyl acetate (AcOMe) and acetic acid (AcOH); small amounts of C₁-C₄ hydrocarbons and CH₃F were generally also formed. Yields and product composition depend on the activity of the catalyst, reaction temperature, and reaction time.

The reaction of methyl alcohol with CO was carried out in the presence of BF₃, BF₃-H₂O, and HF-BF₃ (1:1 complexes). The results are shown in Table I. The most active catalyst for the formation of AcOMe is HF-BF₃, while BF₃ and BF₃-H₂O formed Me₂O in amounts comparable to AcOMe. In all experiments complete conversion was observed.

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Table III. HF-BF₃-Catalyzed Carbonylation of Methyl Alcohol. Effect of Temperature^a

temp (°C)	yield (mol %)			
	Me ₂ O	AcOMe	AcOH	other
191	12.8	75.7	11.5	
222	2.3	66.1	30.1	1% C ₁ -C ₃ ; 0.4% C ₄
260	0.3	25.7	71.0	0.5% C ₁ -C ₃ ; 2% C ₄
295		3.7	82.9	8% C ₁ -C ₃ ; 6% C ₄

^a MeOH/BF₃ molar ratio = 2. Reaction time 8 h; pressure 150 atm.

Table IV. Carbonylation of Dimethyl Ether^a

catalyst	time (h)	yield (mol %)		
		AcOMe	AcOH	other
BF ₃	19	6.8		
BF ₃ -H ₂ O	19	65.6	11.4	
HF-BF ₃ ^b	6	44.4	45.7	1% CH ₄ ; 3% CH ₃ F
HF-BF ₃	24	61.8	35.4	0.2% CH ₄ ; 2% CH ₃ F
HF-BF ₃ H ₂ O ^b	5.5	70.0	10.0	0.3% CH ₄ ; 3.5% CH ₃ F

^a Me₂O/BF₃ molar ratio = 1. Reaction temperature ca. 190 °C; pressure 160 atm, except where noted. ^b At 250 °C.

The effect of reaction time on the carbonylation of methyl alcohol is shown in Table II. The reaction was carried out at 260 °C and 150 atm of CO, using HF-BF₃ as catalyst, for 0.5, 1.5, 3, and 8 h, respectively. The progress of the reaction can be monitored by the pressure drop as CO is being consumed. After 6-7 h the pressure remained constant. Under these conditions, methyl alcohol was always completely converted, mainly to Me₂O, AcOMe, and AcOH. With a prolonged reaction time the yield of AcOH increases at the expense of AcOMe, and increasing amounts of C₁-C₄ alkanes, particularly butanes, are formed.

The effect of temperature was assessed by studying the reaction in the temperature range of 180 to 300 °C, again using HF-BF₃ as catalyst (see Table III).

As before, increasing the temperature brings an increase of AcOH at the expense of Me₂O and AcOMe. At 295 °C, AcOH is obtained nearly exclusively, with 14% lower alkanes. While the reaction mixtures at lower temperatures were usually green colored, at 250 °C black viscous mixtures resulted. Vacuum distillation of this mixture gave BF₃-AcOMe and BF₃-AcOH complexes (85%) and a black solid residue, soluble in acetone.

These data indicate that initially MeOH is dehydrated to Me₂O, which is carbonylated to AcOMe. The latter is eventually hydrolyzed (or further carbonylated and hydrolyzed) to AcOH (see subsequent discussion of mechanism).

We next turned our attention to the study of the carbonylation of Me₂O. In this case, the order of the activity of the catalysts is BF₃ < BF₃-H₂O < HF-BF₃ (see Table IV). BF₃ itself leads to low yields of AcOMe (7%) after 19 h at 190 °C and 170 atm of CO pressure. Fair yields are obtained with BF₃-H₂O, while with HF-BF₃ the yield of AcOH is improved by a factor of 3 compared to BF₃-H₂O. Water decreases the activity of HF-BF₃; using HF-BF₃-H₂O (1:1:1) causes a 4.5-fold decrease in AcOH yield and a decrease in Me₂O conversion.

In Tables V and VI we show the effects of the catalyst/substrate ratio and temperature, respectively, on the carbonylation of Me₂O.

Decreasing the catalyst concentration causes a decrease in conversion and in the yield of both AcOMe and AcOH. At a 1:1:4 molar ratio the products were AcOMe (no AcOH) and a small amount of methyl formate (0.4%), with an overall Me₂O conversion of only 23%. The temperature

Table V. HF-BF₃-Catalyzed Carbonylation of Dimethyl Ether. Effect of BF₃/HF/Me₂O Molar Ratio^a

BF ₃ /HF/Me ₂ O molar ratio	yield (mol %)		
	AcOMe	AcOH	other
1:1:4	17.1		0.2% CH ₄ ; 5% CH ₃ F; 0.4% HCOOMe
1:1:2	76.1	20.1	0.1% CH ₄ ; 3% CH ₃ F
1:1:1	61.8	35.4	0.2% CH ₄ ; 2% CH ₃ F

^a Reaction temperature 190 °C; time 20-24 h; pressure 160 atm.

Table VI. HF-BF₃-Catalyzed Carbonylation of Dimethyl Ether. Effect of Temperature^a

temp (°C)	yield (mol %)		
	AcOMe	AcOH	other
186	60.4	2.2	6% CH ₃ F
226	66.2	13.0	0.2% C ₁ -C ₃ ; 2% C ₄ ; 3% CH ₃ F
240	59.3	37.3	0.2% C ₁ -C ₃ ; 1% C ₄ ; 1% CH ₃ F
250	55.1	35.4	1% C ₁ -C ₃ ; 4% C ₄ ; 3% CH ₃ F
261	44.4	45.7	3% C ₁ -C ₄ ; 4% C ₄ ; CH ₃ F
300	9.5	80.7	5% C ₁ -C ₃ ; 4% C ₄ ; 1% CH ₃ F

^a Me₂O/BF₃ molar ratio = 1. Reaction time 6 h; pressure 150 atm.

Table VII. Conversion of AcOMe^a

pressure (atm)	catalyst/reag.	yield (mol %)		
		Me ₂ O	AcOH	other
7	HF	2.1	4.1	0.1% CH ₃ F
27	BF ₃ -HF	7.4	11.6	0.2% CH ₄
151	BF ₃ -HF + CO	1.9	37.4	0.2% CH ₄ ; 0.3% CH ₃ F

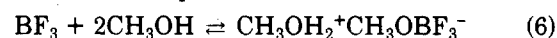
^a Reaction time 4 h; temperature 220 °C.

dependence of the carbonylation of Me₂O gives results similar to those of methyl alcohol. At temperatures higher than 230 °C the conversion was about 99% after 6 h, AcOH being the major product.

The question of how acetic acid is formed, especially in carbonylations of Me₂O reactions catalyzed by HF-BF₃, where no water is present, is answered by the study of the reaction of AcOMe with CO catalyzed by BF₃ or HF-BF₃ (see Table VII). AcOMe reacts readily with CO, giving AcOH in good yield. When the reaction was carried out in the presence of BF₃ itself, AcOH was again obtained, and the reaction mixture contained some black-brown polymeric residue, which is the product of ketene polymerization. Likewise, acetyl fluoride reacted at 220 °C with BF₃-HF to give polyketene.²² Acetic acid is not the product of acid-catalyzed hydrolysis of methyl acetate. When water was added to the reaction mixture of Me₂O, CO, and HF-BF₃ it in fact decreased the yield of acetic acid.

The above experiments show that a strong protic acid greatly enhances the carbonylation reactions, especially of Me₂O, and that catalyst activity depends on its acidity. HF-BF₃ is the strongest acid of those employed: a 7% molar solution of BF₃ in HF has *H*₀ = -16.6.²³ Adding water decreases the acidity and also the activity of the catalyst.

Methyl alcohol is sufficiently reactive even with BF₃ itself because of the equilibrium

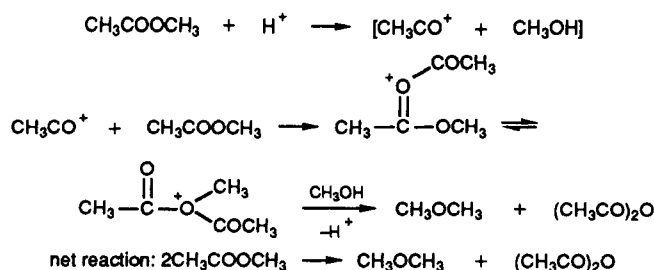


which gives the strong conjugate Brønsted acid.²⁴ In fact,

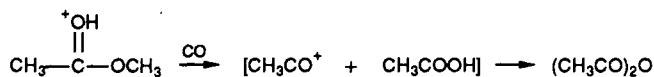
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Scheme II

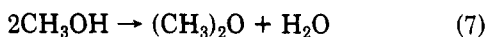


Scheme III

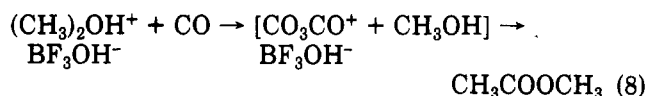


the $\text{BF}_3\text{-CH}_3\text{OH}$ complex is an efficient superacid catalyst. Since water is formed by dehydration of methyl alcohol, BF_3 and $\text{BF}_3\text{-H}_2\text{O}$ have about the same activity, because similar acids ($\text{BF}_3\text{-CH}_3\text{OH}$ and $\text{BF}_3\text{-H}_2\text{O}$) are formed in the reaction mixture. In the case of the carbonylation of Me_2O , no protic acid is formed and accordingly BF_3 leads to very low yields.

The results of the study of the time and temperature dependence of the reactions indicate that methyl alcohol is first dehydrated to Me_2O , which reacts with CO giving AcOMe, which in turn gives AcOH. The fastest reaction is the dehydration of methyl alcohol to dimethyl ether



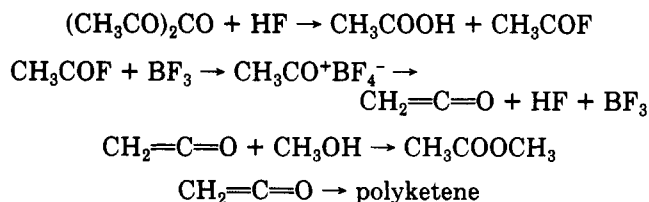
which in the strongly acidic reaction medium is largely present in its protonated form (vide infra). The carbonylation can be viewed as the methylation of CO by the incipient methyl cation thus formed to yield the acetyl cation, which then gives methyl acetate.



Two pathways can be suggested for the formation of AcOH from AcOMe, both of which involve the intermediate formation of Ac_2O . In the first case (Scheme II) Ac_2O is formed through acid-catalyzed ester cleavage and acylation with no intervention of CO, which explains the formation of Me_2O . Alternatively, further carbonylation of protonated AcOMe can take place (Scheme III).

Acetic anhydride subsequently reacts quantitatively with HF, giving AcOH and acetyl fluoride. The latter forms acetylum tetrafluoroborate with BF_3 , which can undergo HF elimination to ketene. This explains the observed formation of polymeric product (Scheme IV).

Scheme IV



An additional although less probable pathway under acidic conditions could involve initial carbonylation of methyl alcohol to methyl formate. Methyl formate was reported in the patent literature to rearrange to acetic acid under Rh catalysis:²⁵

Table VIII. Conversion of Methyl Formate^a

catalyst/reagent	pressure (atm)		yield (mol %)		
	initial	final	Me_2O	AcOMe	AcOH
BF_3	119	132	69.9	29.8	
$\text{BF}_3\text{-H}_2\text{O}$	31	31	82.0	17.3	0.5
$\text{BF}_3 + \text{CO}$	163	190	46.8	35.8	5.3
$\text{BF}_3\text{-H}_2\text{O} + \text{CO}$	146	167	32.7	54.2	11.2

^a $\text{HCOOCH}_3/\text{CO}/\text{BF}_3/\text{H}_2\text{O}$ molar ratio = 1:6:1:1. Reaction temperature 180 °C; time 18 h.

Table IX. Carbonylation of Dimethyl Ether and Methyl Alcohol in Triflic Acid^a

substrate	acid/ substrate molar ratio	T (°C)	yield (mol %)	
			AcOMe	AcOH
Me_2O	5:1	22		
Me_2O	1:1	100	1	3
Me_2O^b	5:1	100	4	9
Me_2O	5:1	100	18	19
MeOH	5:1	100	25	7

^a Reaction pressure 80 atm CO; time 18 h, except as otherwise noted. ^b Reaction time 6 h.

This rearrangement, however, was never more closely studied. It was not even established whether it is truly a rearrangement process or if acetic acid is formed via prior dissociation into CH_3OH and CO.

In our studies we found that methyl formate quantitatively gives Me_2O and AcOMe as the final products in 70% and 30% yields, respectively, at 180 °C under 120 atm of CO in the presence of BF_3 . The pressure increased during the course of the reaction, as CO was formed. When the autoclave was pressurized with CO (150 atm) the yield of AcOMe increased at the expense of Me_2O , and 5% AcOH was found, but Me_2O remained the major product. When water was added in excess of the amount that could be formed by the decomposition of methyl formate, it increased the yields of both AcOMe and AcOH.

When the reaction was carried out with $\text{BF}_3\text{-H}_2\text{O}$ as catalyst, at 180 °C, with no CO added, the pressure reached 31 atm, but the yield of AcOMe was lower (see Table VIII).

These results indicate that methyl formate, in the presence of BF_3 or $\text{BF}_3\text{-H}_2\text{O}$, decarbonylates according to eq 10. Methyl alcohol is then dehydrated to Me_2O and



in the strongly acid medium protonated Me_2O is carbonylated to give AcOMe as before. Acetic acid (AcOH) is formed either by acid-catalyzed hydrolysis of AcOMe or by further carbonylation to Ac_2O , which is then hydrolyzed. It is clear that even if methyl formate would be intermediately formed, it would convert to methyl acetate and acetic acid under the reaction conditions.

$\text{CF}_3\text{SO}_3\text{H}$ -Catalyzed Carbonylation. Triflic acid is a superacidic Brønsted acid ($H_0 = -14.1$)²³ and, unlike other acids (e.g., CF_3COOH and H_2SO_4), it is a fair solvent for CO,¹⁰ possibly because of partial protonation of CO (cf. 0.19 mol L⁻¹ atm⁻¹ in 1:1 HF-SbF_5).²⁶ These properties make triflic acid a good candidate as a catalyst for carbonylation reactions. We have studied the carbonylation of methyl alcohol and Me_2O in triflic acid under CO pressure in the range of 40 to 120 atm, assuring that a large excess of CO was always used. For control purposes, re-

(25) (a) Hoeg, H. U.; Bub, G. Ger. Pat. 3,236,351, 1984. (b) Drent, E. Eur. Pat. 118,151, 1984.

(26) Hogeveen, H.; Baardman, F.; Roobeek, C. F. *Recl. Trav. Chim. Pays-Bas* 1970, 89, 227.

actions were also carried out with AcOMe. The results are summarized in Table IX.

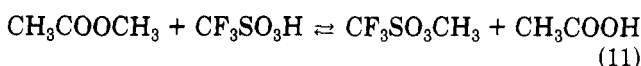
Carbonylation of Me₂O yielded MeOH, AcOMe, AcOH, and methyl triflate. A ratio of AcO⁻/CH₃OH < 1 was always found (some Me₂O is also hydrolyzed by KOH during workup). The optimal conditions were 100 °C under ca. 80 atm CO for 18 h with a 5:1 triflic acid/Me₂O molar ratio. No reaction took place at room temperature; higher temperatures (150 °C) caused severe corrosion of the autoclave (with metal carbonyl formation), appreciable decomposition of the acid catalyst (vide infra), and decrease of yield. There was no improvement of yield when pressures above 80 atm were used. On the other hand, the reaction is dependent on the acid/ether ratio. Changing from a 1:1 to 5:1 molar ratio brought a tenfold increase in the yield of AcOMe; further increase caused only minor changes.

The reaction of AcOMe itself with triflic acid under CO or Ar pressure gave acetic acid and methyl triflate in >90% yield.

Under the discussed reaction conditions, the CF₃SO₃H-catalyzed carbonylation of Me₂O gave 37% yield with ca. 18% AcOMe and 19% AcOH. We obtained the same results both in a Monel 400 (66% Ni, 31.5% Cu, 1.2% Fe) and a stainless steel reactor. In the first case, however, the crude mixture contained a yellow, water-soluble solid, which was found to be a mixture of Ni(II) and Cu(II) triflates (which are sparingly soluble in triflic acid), and the vapor phase contained some Ni(CO)₄.

Methyl alcohol was also carbonylated under the above conditions, with 32% conversion. The major products were methyl triflate, Me₂O, and AcOMe, with AcOH only as a minor product.

These data indicate that, like in the case of BF₃ catalysis, protonated dimethyl ether reacts with CO. Dialkyl ethers are ca. 95% protonated in 100% H₂SO₄^{27,28} (*H*₀ = -11.9),²³ thus in much stronger CF₃SO₃H (*H*₀ = -14.1) Me₂O is close to complete protonation. The formation of AcOMe follows a path similar to eqs 7 and 8, but in this case the formed AcOMe also reacts with CF₃SO₃H to give the acidolysis products: acetic acid and methyl triflate (eq 11). In the

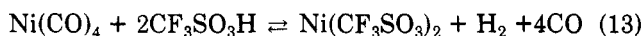


case of the carbonylation of methyl alcohol, the expected hydrolysis of the two product esters (methyl acetate and triflate) takes place only to a small extent; this is probably due to the fact that the limited amount of water present is largely protonated by triflic acid, resulting in retardation of ester hydrolysis.²⁹

The carbonylation step is irreversible, as shown by the reaction of AcOMe, giving no Me₂O. Contrary to what happens in most metal- (and possibly BF₃-) catalyzed carbonylations, AcOMe is not converted to Ac₂O in this system. The formation of Ac₂O cannot proceed through acylation of the ester (Scheme II), as Me₂O is not observed as a byproduct in the reaction of AcOMe. That no further carbonylation of AcOMe (Scheme II) is involved is also shown by the AcO⁻/CH₃OH ratio (Ac₂O formation would give a ratio >1).

A catalytic effect of Ni(CO)₄ formed by corrosion of the autoclave (which is a well-known carbonylation catalyst)¹ on the reaction seems to be ruled out by a comparison of

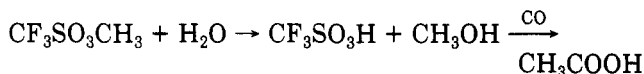
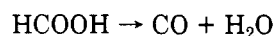
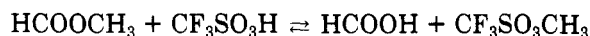
the results of Monel and steel reactors. In fact, Ni(CO)₄ is known to react with acids to give Ni(II) salts:¹



Even if the salt can be again reduced to Ni⁰ by CO or H₂, the amount of Ni(CO)₄ observed in the acid phase is quite small.

We also studied the possibility of a CF₃SO₃H-catalyzed conversion of methyl formate to acetic acid. When methyl formate was reacted with triflic acid (molar ratio ester/acid 6:1, 100 °C for 18 h under 80 atm of N₂), an NMR spectrum of the reaction mixture showed a nearly complete conversion, mainly to methyl triflate. Me₂O, MeOH, and AcOH were present only as minor products; no formic acid was found. These findings are consistent with initial acidolysis of methyl formate to methyl triflate and formic acid and subsequent decomposition of the latter to CO and H₂O (Scheme V). Under these conditions methyl triflate is again not hydrolyzed to any significant extent, so that the carbonylation of MeOH cannot become a significant reaction. Based on these results, initial carbonylation of methyl alcohol to methyl formate followed by "rearrangement" to acetic acid cannot be involved as a pathway in the formation of AcOMe and AcOH in the triflic acid catalyzed reactions.

Scheme V



Conclusions

Superacid-catalyzed carbonylation of methyl alcohol or dimethyl ether gives methyl acetate and acetic acid. With HF-BF₃ catalyst conversion is nearly quantitative. CF₃SO₃H catalysis gives lower yields.

Experimental Section

Materials. Carbon monoxide, methyl alcohol, dimethyl ether, methyl acetate, methyl formate, acetyl fluoride, boron trifluoride, and boron trifluoride-dimethyl ether complex were commercial products used without further purification. BF₃-HF (Air Products and Chemicals Inc.) and trifluoromethanesulfonic acid (3M) were purified by distillation before using.

Reactor and Experimental Procedure. A T316 stainless steel, 128-mL autoclave was used for BF₃-catalyzed reactions, while a Monel 400, 300-mL autoclave (Parr Instruments Co.) was used for CF₃SO₃H-catalyzed reactions. Both reactors were fitted with a pressure gauge, safety rupture disc, and sample port. The reactor was kept at the desired temperature by using an electrical heater or an oil bath. The temperature was measured on the outside wall of the vessel with a Pt resistance or a thermocouple. Magnetic stirring (Teflon bar) was used. Pressures given in the tables, if not otherwise stated, are initial pressures at the reaction temperatures. All experiments were usually repeated three times. Reproducibility was generally within 10%. Yields refer to conversion of starting methyl compounds.

In a typical run, the reactor was dried and flushed with nitrogen and loaded with the liquid reagents. Dimethyl ether was condensed in an acetone/dry ice bath (*d* = 0.80 at -80 °C) and poured rapidly. The reactor was sealed and pressurized with BF₃ if required and finally with carbon monoxide.

In BF₃-catalyzed reactions, the reactor was cooled in acetone/dry ice and samples of the gas phase were withdrawn for GC analysis. The autoclave was depressurized and opened while cold, and the liquid contents were neutralized with urea. The neutral mixture was then analyzed by GC; product yields were

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(28) Bagno, A.; Scorrano, G. *J. Am. Chem. Soc.* 1988, 110, 4577.

(29) Patai, S., Ed. *The Chemistry of Carboxylic Acids and Esters*; Wiley Interscience: New York, 1969.

calculated from the combined gas-phase and solution data. GC analyses were performed on a Hewlett-Packard 5730A gas chromatograph with an FID. A Porapak QS packed column (365 cm \times 3.2 mm) was used for most analyses; acetic acid and dimethyl ether were analyzed on an OV-101 (200 cm \times 3.2 mm) column.

In $\text{CF}_3\text{SO}_3\text{H}$ -catalyzed reactions, the reactor was cooled to room temperature, and the gas phase was vented into a cold trap, in which some $\text{Ni}(\text{CO})_4$ could be found. A small aliquot of the crude liquid mixture was diluted with $\text{CF}_3\text{SO}_3\text{H}$ and centrifuged (in order to eliminate $\text{Cu}(\text{II})$ and $\text{Ni}(\text{II})$ salts) for NMR analysis. The remainder was usually split into two equal aliquots. One was quenched with cold aqueous KOH (which precipitates Cu and Ni and hydrolyzes all esters), centrifuged, and analyzed by NMR for methyl alcohol and acetate ion, which gives the conversion. Tetramethylammonium triflate was used as the integration and chemical shift standard. The other was quenched with a slight

excess of pyridine in toluene at 0 °C (which eliminates the acid and methyl triflate), filtered, and analyzed for dimethyl ether and methyl acetate by GC. ^1H , ^{19}F , and ^{13}C NMR spectra were taken on a Varian XL 200 instrument operating at 200 MHz for proton. GC analyses were performed on Varian 3300 and 3400 instruments with FID or TCD and a DB-5 or DB-WAX capillary column (30 m \times 0.25 mm).

Acknowledgment. Our work was supported by the National Science Foundation and the Loker Hydrocarbon Research Institute.

Registry No. MeOH , 67-56-1; Me_2O , 115-10-6; CH_3COOH , 64-19-7; CH_3F , 593-53-3; CH_3Cl , 74-87-3; CH_3Br , 74-83-9; BF_3 , 7637-07-2; HF , 7664-39-3; AcOMe , 79-20-9; HCOOCH_3 , 107-31-3; $\text{CF}_3\text{SO}_3\text{H}$, 1493-13-6; CH_4 , 107-31-3.

Antimony Pentafluoride/Graphite Catalyzed Oxidative Conversion of Methyl Halides with Copper Oxides (or Copper/Oxygen) to Dimethyl Ether¹

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Nonaqueous conversion of methyl halides into dimethyl ether in good to excellent yield was achieved by their superacidic, antimony pentafluoride/graphite catalyzed reaction with copper oxides or with copper metal and oxygen. The reaction was studied in static batch-wise experiments at pressures of 2 to 150 atm and temperatures of 100 to 265 °C, as well as in a flow system. The reaction of methyl bromide (MeBr) with Cu_2O at 220 °C and 140 atm gives a >90% yield of dimethyl ether. Methyl fluoride (MeF) and methyl chloride (MeCl) being less reactive gave yields of 50–60 mol %. The reaction involves initial formation of a polarized methyl halide– SbF_5 complex, which then O-methylates copper oxide and subsequently yields dimethyl ether. Copper bromides formed as byproducts can be oxidatively recycled for oxybromination of methane and regeneration of copper oxide, thus allowing a selective, catalytic oxidation of methane into dimethyl ether.

Introduction

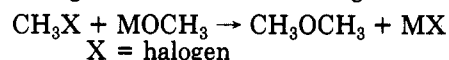
Dimethyl ether is the dehydration product of methyl alcohol and is readily obtained under either acid- or base-catalyzed conditions.²



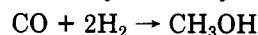
In our studies on solid superacid catalyzed reactions we have found that Nafion-H perfluorinated resin sulfonic acid at 170–180 °C effectively catalyzes the dehydration of methyl alcohol to dimethyl ether in a continuous flow system.³

The hydrolysis of methyl halides yields methyl alcohol, which in turn can be dehydrated to dimethyl ether.⁴ As hydrogen halides are byproducts of the hydrolysis reaction, corrosion problems exist for practical application and oxidative recycling of aqueous hydrogen halides can be difficult.

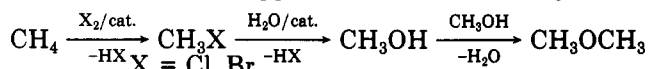
Williamson ether synthesis⁵ from methyl halides gives dimethyl ether in excellent yield and is applicable under mild conditions but necessitates equimolar alkali methoxides, making it uneconomical for large scale use.



Regardless what variation is used, methyl alcohol is needed in the preparation of dimethyl ether. Methyl alcohol is presently exclusively manufactured from synthesis gas.² The operation is highly efficient, but for economic reasons is carried out only on a very large scale.



We have recently reported our studies on preparing methyl alcohol and dimethyl ether by the catalytic gas-phase hydrolysis of methyl chloride or bromide, obtained by the selective catalytic monohalogenation of methane over solid acidic or supported noble metal catalysts⁴



The hydrogen halide byproduct of the reactions can be recycled via oxyhalogenation, which is particularly effective

(1) (a) Heterogeneous Catalysis by Solid Superacids. 24. For part 23, see: Olah, G. A.; Ip, W. M. *New J. Chem.* 1988, 12, 299. (b) Presented in part at the 192nd National Meeting of the American Chemical Society, Anaheim, CA, Spring 1986, Abst. Paper DR6N 328.

(2) Weissner, K.; Arpe, H. *J. Industrial Chemistry*; Verlag Chemie: Weinheim-New York, 1978, and references therein.

(3) Olah, G. A.; Iyer, P. S.; Prakash, G. K. S. *Synthesis* 1986, 513.

(4) Olah, G. A.; Gupta, B.; Farnia, M.; Fellberg, J. D.; Ip, W. M.; Husain, A.; Karpeles, R.; Lammertsma, K.; Melhotra, A. K.; Trivedi, N. *J. J. Am. Chem. Soc.* 1985, 107, 7097.

(5) For a review, see: Feuer, H.; Hooz, J. *The Chemistry of the Ether Linkage*; Patai, S., Ed.; Wiley-Interscience: New York, 1967; p 445.