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 × 3.2 mm) was used for most analyses; acetic acid and dimethyl ether were analyzed on an OV-101 (200 cm × 3.2 mm) column.

In CF_3SO_3H-catalyzed reactions, the reactor was cooled to room temperature, and the gas phase was vented into a cold trap, in which some $Ni(CO)_4$ could be found. A small aliquot of the crude liquid mixture was diluted with CF_3SO_3H and centrifugated (in order to eliminate Cu(II) and NI(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 × 0.25 mm).

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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; CF_3SO_3H, 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 Ether[1]

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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]

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

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 synthesis[5] 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.

$$CH_3X + MOCH_3 \rightarrow CH_3OCH_3 + MX$$
$$X = \text{halogen}$$

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.

$$CO + 2H_2 \rightarrow CH_3OH$$

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 catalysts[4]

$$CH_4 \xrightarrow[-HX]{X_2/\text{cat.}} CH_3X \xrightarrow[-HX]{H_2O/\text{cat.}} CH_3OH \xrightarrow[-H_2O]{CH_3OH} CH_3OCH_3$$
$$X = Cl, Br$$

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, Annaheim, CA, Spring 1986, Abst. Paper DR6N 328.

(2) Weissermel, 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.

0022-3263/90/1955-4289$02.50/0 © 1990 American Chemical Society

Table I. SbF_5/Graphite-Catalyzed Conversion of Methyl Halides to Dimethyl Ether with Cuprous Oxide at 220 °C

methyl fluoride		methyl chloride			methyl bromide		
reactn time (h)	yield, mol %	reactn time (h)	yield, mol %		reactn time (h)	yield, mol %	
	Me_2O		Me_2O	MeF		Me_2O	MeF
1.0	50	0.5	43	3	0.5	20	4
2.5	55	2.0	53	6	1.0	50	5
3	58	3.5	72	5	2.0	78	7
3.25	57	4.5	68	7	4	91	6
24	67	24	71	10	24	91	7

mol ratio $CH_3X/Cu_2O/SbF_5$ = 5:3:1

in case of oxybromination, but was found also feasible in case of oxychlorination.

$$CH_4 \xrightarrow[\text{Pt on } Al_2O_3]{HX/O_2} CH_3X + \tfrac{1}{2}H_2O$$

Dimethyl ether can be subsequently readily converted into ethylene and derived hydrocarbon products. With our continuing goal to utilize methane as the starting material for hydrocarbon synthesis and preparation of related chemical products[6] instead of first producing syn-gas, we were interested in an alternate way to convert readily available methyl halides into dimethyl ether under anhydrous conditions. Dimethyl ether can subsequently be carbonylated under superacid catalysis to methyl acetate or using bifunctional acid–base catalysis converted into ethylene.

Results and Discussion

It is known from the early work of Wurtz[7] that when silver oxide was reacted with methyl halides, dimethyl ether was formed.

$$2CH_3I + Ag_2O \rightarrow CH_3OCH_3 + 2AgX$$

This conversion of methyl halides into dimethyl ether is, however, impractical, since it uses a molar equivalent of expensive silver oxide. The possibility of replacing silver with a more feasible, cheaper metal and further to find a possible catalytic way for the oxidative conversion of methyl halides into dimethyl ether led us to investigate the reaction of methyl halides with copper oxides, as well as with copper metal and oxygen.

Dry copper(I) oxide was found not to react with methyl chloride or bromide in the temperature range of 140–250 °C. It was expected, however, that complexation with a strong Lewis acid should polarize the C–X bonds, enhancing the reactivity of the methyl halides with copper oxides.

We have found that methyl halides when reacted with Cu(I) and Cu(II) oxide or Cu + O_2 in the presence of intercalated SbF_5/graphite catalyst[8] give dimethyl ether in good yield. The reactions were studied batch-wise in

$$2CH_3X + Cu_2O \rightarrow CH_3OCH_3 + 2CuX$$
$$X = Br\ (Cl, F)$$

$$2CH_3Br + CuO \rightarrow CH_3OCH_3 + CuBr_2$$

$$2CH_3Br + Cu + 1/2O_2 \rightarrow CH_3OCH_3 + CuBr_2$$

a static pressure reactor at temperatures of 100–280 °C and pressure of 1.5 to 150 atm. Subsequently experiments were also carried out in a continuous flow system using a tubular reactor.

Methyl halides were reacted with Cu_2O in the presence of SbF_5/graphite under an argon pressure of ~120 atm at 220 °C. After loading the pressure reactor with the catalyst and reagents, it was pressurized with argon to 100 atm at ambient temperature. The yield of dimethyl ether (Me_2O) obtained is shown in Table I. Yields always related to conversion of methyl halides. Pressures are initial pressures at the given reaction temperatures; usually three independent experiments were carried out and data were generally within ±10%. The yield of dimethyl ether from methyl bromide was 90 mol % after 4 h of reaction time. Methyl chloride and methyl fluoride gave 57 and 68% yield, respectively, under similar conditions. In the reaction of methyl bromide and methyl chloride with Cu_2O in the presence of SbF_5/graphite, methyl fluoride was formed as a byproduct in 4 to 7%. In these reactions small amounts of ethane were also formed. In control experiments CH_3Cl and CH_3Br when reacted with SbF_5/graphite alone gave CH_3F.

As in the reaction of methyl halides with cuprous oxide, methyl bromide was found to be the most reactive; in our studies with cupric oxide and copper + oxygen we chose to study the reaction with methyl bromide. The SbF_5/graphite-catalyzed reactions of CH_3Br with CuO or with Cu + O_2 both gave dimethyl ether. Methyl fluoride was formed as a byproduct, indicating some fluorine exchange with the SbF_5–catalyst. All reactions were carried out at temperatures of 210–228 °C and under pressures of 2–5 atm.

The reaction of methyl bromide with CuO gave dimethyl ether but in lower yield than with cuprous oxide. Results of the reaction showing time dependence of conversion are shown in Table II.

Table II. SbF_5/Graphite-Catalyzed Reation of Methyl Bromide with CuO at 210 °C

reaction time (h)	yield, mol %	
	Me_2O	MeF
1	10	8
2.5	25	9
4	28	8
10	30	8
24	36	9

mol ratio $CH_3Br/CuO/SbF_5$ = 4.5:2.9:1

The reaction of MeBr with Cu + O_2 was also carried out and gave dimethyl ether with small amounts of methane, propane, methyl acetate, and acetone also formed, in addition to methyl fluoride. The results are shown in Table III.

Table III. SbF_5/Graphite-Catalyzed Reaction of Methyl Bromide with Copper Powder and Oxygen at 228 °C

reaction time (h)	yield, mol %				
	Me_2O	MeF	$CH_4C_3H_8$	AcOMe	CH_3COCH_3
1	15	10	1	0.3	0.3
2.5	24	10	1.5	0.6	0.2
4	27	10	1.5	0.8	0.2
10	41	10	2	1.0	0.2
24	60	6	1.5	1.7	0.2

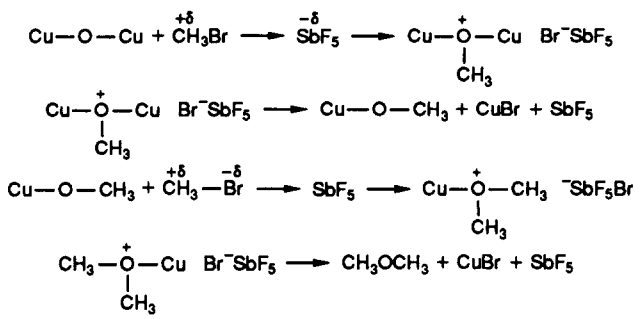
mol ratio $CH_3Br/Cu{:}O_2/SbF_5$ = 4.5:2.6:2.6:1

Comparing the reactions of CH_3Br with cuprous oxide, cupric oxide, and copper/oxygen, the best results were obtained with cuprous oxide. The reaction is fast and dimethyl ether is obtained in high yield.

The reaction of cuprous oxide with CH_3Br is suggested to proceed through the following steps (for simplicity SbF_5

(6) Olah, G. A. *Acc. Chem. Res.* **1987**, *20*, 422 and references therein.
(7) Wurtz, A. *Ann. Chem.* **1856**, [3]46, 222.
(8) For the nature and applications of this catalyst, see: (a) Olah, G. A.; Messina, G.; Bukala, J.; Olah, J. A.; Mateescu, G. D. First North American Chemical Congress, Mexico City, 1974, Abstr. PHSC 153. (b) Olah, G. A.; Kaspi, J.; Bukala, J. *J. Org. Chem.* **1977**, *42*, 4187.

is shown only in its monomeric form).



When CH_3Br is contacted with the SbF_5/graphite catalyst, a polarized donor–acceptor complex is formed at the surface exposed areas of the catalyst. The surface complexed methyl halide should have sufficient activity and diffusion ability to lead to O-methylation of co-dispersed cuprous oxide. The intermediate copper methoxide would then be further methylated to give dimethyl ether with cuprous bromide as the byproduct. When no SbF_5 catalyst is present, the reaction does not take place under the reaction conditions. Thus electrophilic methylation is indicated.

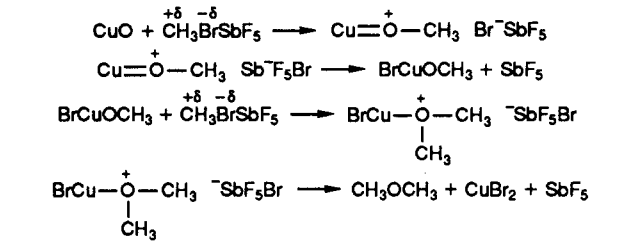
Thermal radical reactions with $CH_3^{\bullet}$, although also possible, are not considered to be of major significance, although isolated copper(I) methoxide is known to be very reactive and decomposes even at room temperature,[9] giving metallic copper, methyl alcohol, and formaldehyde. The decomposition of copper methoxide according to Costa et al. is a radical process.[9] In our experiments neither

$$CuOCH_3 \rightarrow Cu + CH_3O^{\bullet}$$

$$2\ CH_3O^{\bullet} \rightarrow HCHO + CH_3OH$$

formaldehyde or methyl alcohol has been observed, nor was water formed. This further supports the suggestion that dimethyl ether is formed by two-step O-methylation of cuprous oxide and not by a radical decomposition mechanism. The intermediate surface-bound copper methoxide may be only short lived and stabilized by complexation with antimony pentafluoride leading to rapid conversion to dimethyl ether.

In case of the SbF_5/graphite-catalyzed reaction of MeBr with cupric oxide the mechanism of ether formation is considered to be similar to that of the reaction with cuprous oxide.



Study of the reaction of methyl bromide with metallic Cu + O_2 showed a time-dependent increase of the yield of dimethyl ether, indicating initial formation of copper oxide followed by reaction with the $CH_3Br \rightarrow SbF_5$ complex. It seems improbable that oxygen physically adsorbed on copper metal itself plays a role in formation of dimethyl ether. Oxygen adsorbed on copper metal, however, seems to be responsible for the reactions in which small amounts of methyl acetate, acetone, propane, and methane are formed, probably by radical reactions.

(9) Costa, G.; Camus, A.; Morsich, N. *J. Inorg. Nucl. Chem.* **1965**, *27*, 281.

Table IV. Thermodynamic Data of the Reaction of Methyl Bromide with Copper Oxides or with Copper and O_2

reaction	ΔH, kcal/mol 298 K	ΔS, kcal/mol 298 K	ΔG, kcal/mol 300 K	400 K	500 K
$2CH_3Br + Cu_2O \rightarrow CH_3OCH_3 + 2CuBr$	−36.9	−30.6	−27.7	−24.7	−21.6
$2CH_3Br + CuO \rightarrow CH_3OCH_3 + CuBr_2$	−23.5	−41.5	−11.1	−6.9	−2.8
$2CH_3Br + Cu + {}^1/_2O_2 \rightarrow CH_3OCH_3 + CuBr_2$	−61.1	−63.7	−42.0	−35.6	−29.3

All the studied reactions of methyl bromide with copper oxides or with copper and oxygen are thermodynamically favorable (Table IV).[10]

The thermodynamic data indicated that the reaction of methyl bromide with cuprous oxide is expected to be more efficient at relatively lower temperatures. Studies were carried out at 100 °C, 160 °C, 206 °C, 215 °C, and 265 °C, respectively. At 100 °C the reaction is too slow to be studied. At 160 °C the reaction is still relatively slow but 95% conversion to dimethyl ether takes place after 24 h. Optimum conversion conditions were observed between 200 and 220 °C. Above this temperature methyl fluoride formation, due to halogen exchange with the catalyst, is becoming more predominant and reaches 10% at 265 °C.

We also studied the effect of pressure and the catalyst to methyl bromide ratio on the reaction of methyl bromide with cuprous oxide. Varying the reaction in the pressure range from 2 to 140 atm (pressurized with argon) and the temperature range of 200 to 225 °C had no significant effect on the yield of dimethyl ether. However, higher pressures decreased the amount of methyl fluoride and methane formed as byproduct. These results suggested that the reaction should be also feasible at modest or atmospheric pressure, allowing use of a flow system (vide infra).

In all experiments described in this paper commercially available SbF_5 intercalated in graphite catalyst was used (see Experimental Section). The catalyst had a nominal composition of 50 wt % of SbF_5, which corresponds to an averaged chemical formula of $C_{18.1}SbF_5$. The stoichiometry of the intercalate was found to be $C_{6.5n}SbF_5$, where n = stage. "Stage" is defined as the number of contiguous carbon layers between successive intercalant layers. The calculated stage value from the composition of SbF_5/graphite catalyst is thus 2.8.

It was found from X-ray diffraction studies that the commercially available SbF_5/graphite is a mixture of graphite and graphite/SbF_5 in stages from 1 to 4, with the stage 3 compound being the main component.

Experiments were carried out at ratios of 4.5, 9.0, 12.6, 19.6, and 50.3 to establish turnover numbers and to probe the effect of the CH_3Br to SbF_5 mol ratio. The results are given in Table V. As can be seen the yield of dimethyl ether decreased with increase of the CH_3Br to SbF_5 mol ratio, but even when the mol ratio of CH_3Br/SbF_5 was as high as 50.3, the yield of dimethyl ether still approached 40 mol %. These results show that SbF_5 is a real catalyst in the reaction of CH_3Br with Cu_2O since turnover numbers clearly are substantially higher than 1. To determine real turnover numbers, however, is difficult. It must be pointed out that the overall amount of SbF_5 of the in-

(10) Data for calculation of thermodynamic functions were taken from the NBS Tables of Chemical Thermodynamic Properties, *J. Phys. Chem. Ref. Data*, **1982**, Vol. II, Suppl. 2.

Table V. Effect of CH_3Br/SbF_5 Molar Ratio on the Reaction of CH_3Br with Cu_2O (CH_3Br/Cu_2O = 1.7)

CH_3Br/SbF_5 molar ratio = 4.5 (264 °C, 139–119 atm)			CH_3Br/SbF_5 molar ratio = 9.0 (288 °C, 129–122 atm)			CH_3Br/SbF_5 molar ratio = 12.6 (265 °C, 133–123 atm)			CH_3Br/SbF_5 molar ratio = 19.6 (266 °C, 139–119 atm)			CH_3Br/SbF_5 molar ratio = 50.3 (275 °C, 119–112 atm)		
	yield, mol %			yield, mol %			yield, mol %			yield, mol %			yield, mol %	
time (h)	Me_2O	MeF	time (h)	Me_2O	MeF	time (h)	Me_2O	MeF	time (h)	Me_2O	MeF	time (h)	Me_2O	MeF
1	53	5	1	41	3	2	52	5	2	31	2	1	20	1
2	71	8	6	75	8	4	58	6	4	47	2	4	28	3
4	77	10	12	77	9	6	64	6	16	75	5	6	29	3
20	86	11	22	85	9	24	79	9	23	81	5	23	39	6
28	88	9	46	88	9				30	84	6			

tercalated graphite catalyst does not reflect the de facto active catalyst concentration. It was shown previously based on comparing the analytically determined SbF_5 content of spent catalysts with ESCA measurement of SbF_5 in the surface layer (of some 50-Å depth) that SbF_5 intercalated into the graphite layers plays little or no role in catalytic reactions.[8] It is the surface exposed SbF_5 that is responsible for the catalytic reactivity. Consequently turnover numbers must be much higher than calculated based on overall SbF_5 content of the bulk graphite–SbF_5 catalysts. Observed formation of methyl fluoride due to halogen exchange by SbF_5 even further decreases the de facto amount of catalytically active SbF_5.

Whereas so far discussed experiments were carried out in a static closed pressure autoclave, it was also of interest to carry out studies in a flow system.

A gaseous mixture of 10 mol % methyl chloride in argon was continuously fed through a tubular reactor packed with a mixture of Cu_2O and SbF_5/graphite catalyst with a mol ratio of Cu_2O to SbF_5 of 2.7 and 21. Reactions were carried out at temperatures of 161 °C and 221 °C, under pressures of 5 and 12 atm. Gaseous hourly space velocities, $mL^{-1}\ h^{-1}$ (GHSV), varied from 50 to 500. The product of the reaction is dimethyl ether with some methyl fluoride byproduct. There is an initial period of the reaction where methyl chloride is absorbed on the catalyst and product formation is observed only after its saturation, which takes about 15–20 min.

Conversion to dimethyl ether reaches 85% at 161 °C with GHSV 50, whereas 40% is obtained at 221 °C with GHSV 500. The reaction proceeds at this level till the amount of Cu_2O in the reactor is significantly depleted and then conversion declines.

Methyl chloride and bromide needed for oxidative conversion to dimethyl ether can be selectively prepared by electrophilic halogenation of methane, as reported in our preceding studies.[4] Subsequent oxidative conversion to dimethyl ether under nonaqueous conditions is of substantial interest, because it improves the hydrolytic pathway used so far. Dimethyl ether in turn can be

$$CH_4 \xrightarrow[\text{cat.}]{X_2} CH_3X + HX$$
$$X = Cl, Br$$

$$2CH_3X + Cu_2O \xrightarrow{\text{cat.}} CH_3OCH_3 + (CuX)_2$$

$$2CH_3X + Cu_2O \xrightarrow{\text{cat.}} CH_3OCH_3 + CuX_2$$

readily condensed to ethylene[11] or acetic acid (methyl acetate),[12] key building blocks in hydrocarbon chemistry.

As in these reactions the halogen ends up as copper halide, it must be regenerated for use in rehalogenating methane. This can be achieved by oxidation of copper halides in an oxygen atmosphere at elevated temperature.

$$(CuX)_2 + \tfrac{1}{2}O_2 \rightarrow CuO{\cdot}CuX_2 \rightarrow Cu_2O + X_2$$

As the oxidative regeneration of halogen, as in the case of the hydrogen halides, is much easier for the bromide, it is preferential to run the methane to dimethyl ether conversion cycle via bromination–oxybromination.

Conclusions

The antimony pentafluoride/graphite catalyzed reaction of methyl halides with copper oxides or metallic copper and oxygen has been found to give dimethyl ether in good yield. This provides a nonaqueous alternative to the hydrolytic preparation of methyl alcohol and dimethyl ether. The optimum temperature of the reaction was found to be 200–220 °C with yields in excess of 90%. Mechanistically the formation of dimethyl ether is considered to involve initial formation of a polarized complex of methyl halides with SbF_5, which then O-methylates copper oxides.

Experimental Section

Materials. Cuprous oxide (MCB reagent), cupric oxide (General Chemical Company), and copper metal (Atlas Scientific Co.) were dried at 120 °C under 0.3 Torr pressure for 24 h before use. Dry copper was further reduced under H_2 at 270–320 °C for 24 h in a flow system. Methyl bromide (Matheson), methyl chloride (Matheson), and methyl fluoride (Columbia Organic Chemicals) were 99% pure. Oxygen extra dry grade (MG Scientific Gases) and argon purified grade (MG Scientific Gases) were used without further purification.

Catalyst. Antimony pentafluoride (50 wt %) intercalated into graphite (Alfa Products) showed the composition (analyzed by Galbraith Laboratories) 50.59 wt % C, 0.10 wt % H, 28.28 wt % Sb, and 22.13 wt % F. Oxygen content could not be accurately determined in the presence of high fluorine content.

Reactors and Experimental Procedure. A T316 stainless steel pressure reactor (Parr Instrument Co.) of 128 cm^3 capacity with an inside diameter of 3.81 cm was used in the static experiments as the batch reactor. It was fitted with a gage block assembly including a needle valve, pressure gage, a safety rupture disc, and a sample port. The vessel was electrically heated in a sand bath. Temperature was measured with a platinum resistance thermometer and digital monitor type 199B (Omega Engineering, Inc.).

In a typical experiment the gage block of the autoclave was connected to a vacuum pump and the bomb was evacuated to 0.5 Torr at 200 °C for 1 h. After cooling, it was purged with argon and transferred under argon to a drybox, where it was opened in an argon atmosphere and charged with the given amounts of finely ground Cu, Cu_2O, or CuO and SbF_5/graphite. The components were thoroughly mixed and the vessel was sealed under an argon atmosphere. The corresponding methyl halide (20 mmol) was then charged and the vessel pressurized with argon to the required pressure. The reactor was heated to the reaction temperature in an electrically heated sand bath. During the course of the reaction samples were periodically taken for the GC analysis.

Flow experiments were carried out in a tubular reactor of 3.6-mm inside, 6.0-mm outside diameter, and 65-mm length. Swagelok-type fittings and Whitey-type needle valves were used

(11) (a) Chang, C. D. *Cat. Rev. Sci. Eng.* **1983**, *25*, 1 and references therein. (b) Olah, G. A.; Gupta, B.; Farnia, M.; Felberg, J. D.; Ip, W. M.; Husain, A.; Karpeles, R.; Lammertsma, K.; Melhotra, A. K.; Trivedi, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 7097.

(12) Olah, G. A.; Bukala, J. *J. Org. Chem.*, following paper in this issue.

with all the parts made of 316 stainless steel. The reactor was loaded with a finely ground mixture of Cu_2O and SbF_5/graphite (usually 1.4 g) under an argon atmosphere in a drybox. The inlet of the reactor was connected to a tubular preheater (length 250 mm) and the outlet to a sample port (Swegelok T fitting). The reactor and the preheater were electrically heated. Temperature was measured by two platinum resistance thermometers (Omega Engineering Inc.) and controlled by a Parr temperature controler. The reactor was flushed with argon and heated to the reaction temperature. A mixture of 10% by volume methyl chloride with argon was continuously fed through the reactor. Periodically samples of the reaction mixture were taken for GC analysis.

Analysis. Products were analyzed by gas–liquid chromatography using a Hewlett-Packard 5730A gas chromatograph equipped with a 3390A integrator, flame ionization detector, and a Poropak QS packed column (365 cm × 3.2 mm) operated at 170 °C.

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

Registry No. Cu_2O, 1317-39-1; SbF_5, 7783-70-2; Me_2O, 115-10-6; CH_3Cl, 74-87-3; CH_3Br, 74-83-9; CH_3F, 593-53-3; CuO, 1317-38-0; Cu, 7440-50-8; O_2, 7782-44-7; CH_4, 74-82-8; AcOMe, 79-20-9; graphite, 7782-42-5; propane, 74-98-6.

Antimony Pentafluoride/Graphite Catalyzed Oxidative Carbonylation of Methyl Halides with Carbon Monoxide and Copper Oxides (or Copper/Oxygen) to Methyl Acetate[1]

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Superacidic antimony pentafluoride/graphite catalyzed oxidative carbonylation of methyl halides with carbon monoxide and copper oxides (or copper metal and oxygen) gives methyl acetate (AcOMe). The reaction was investigated in a pressure reactor in the temperature range of 100 to 300 °C and pressures of 20 to 150 atm. The oxidative carbonylation of methyl bromide (MeBr) with CO and Cu_2O at 270 °C under a pressure of 130 atm gave 48 mol % Me_2O and 33 mol % AcOMe. Replacing Cu_2O with CuO gave about 40–50% AcOMe, with 10–20% Me_2O. Using Cu and O_2 gave ~50% AcOMe, with 5% Me_2O. In the reaction 5–10% MeF is also formed due to halogen exchange. The reactivity of the methyl halides shows the decreasing order of MeBr > MeCl > MeF.

Introduction

The synthesis of a wide variety of oxygenated hydrocarbons can be achieved by using carbon monoxide or "synthesis gas" (i.e., CO + H_2 mixtures).[2] Most of these syntheses are carried out in homogeneous systems using soluble catalysts.[3] Some reactions are also carried out in heterogeneous system, over solid catalysts.[2] The insertion of CO into the C–X bonds in alkyl halides and polyhalides can be carried out in the presence of Friedel–Crafts catalysts such as $AlCl_3$, BF_3, BF_3–HF, $FeCl_3$, or $BiCl_3$.[4a] Acetyl chloride or chloroacetyl chlorides were reported to be formed from methyl chloride or polychloromethanes, respectively, with carbon monoxide with aluminum chloride as catalyst, but no details were given and in case of methyl chloride the reaction was found to give polyketene.[4b] Trichloroacetyl chloride was prepared by the reaction of CCl_4 with CO with $AlCl_3$ catalyst or with iron, nickel, chromium, cobalt, or manganese carbonyls as catalysts.[5] Methyl chloride or methyl bromide was carbonylated with CO in the presence of rhodium or iridium tertiary phosphine catalysts.[6] The products of the reaction are acetyl chloride or bromide, respectively. The reactions were carried out in toluene at 130 °C under 20 atm of CO pressure. Carbonylation of alkyl and aryl halides with carbon monoxide also proceeds over nickel, cobalt, iron, palladium, or rhodium catalysts but generally requires severe reaction conditions (200–300 °C and pressures of 600–1000 atm).[2] More moderate reaction conditions are sufficient when carbonylations of alkyl or aryl halides with carbon monoxide or with transition-metal carbonyls are carried out in the presence of strong bases such as tertiary amines,[7–9] sodium or potassium methoxide,[10] or alkali carbonates.[11–13] When alcohol is added to the reaction mixture carboxylic acids or esters are the products. The reaction proceeds at temperature of 20–100 °C and pressures of 1–30 atm.[10–12]

Carbonylation of saturated hydrocarbons, olefins, or alcohols with CO was reported in the presence of cuprous compounds,[14–21] copper and cupric oxide,[22,23] or copper

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