

with all the parts made of 316 stainless steel. The reactor was loaded with a finely ground mixture of  $\text{Cu}_2\text{O}$  and  $\text{SbF}_5/\text{graphite}$  (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 controller. 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 chromatog-

raphy using a Hewlett-Packard 5730A gas chromatograph equipped with a 3390A integrator, flame ionization detector, and a Poropak QS packed column (365 cm  $\times$  3.2 mm) operated at 170  $^\circ\text{C}$ .

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

**Registry No.**  $\text{Cu}_2\text{O}$ , 1317-39-1;  $\text{SbF}_5$ , 7783-70-2;  $\text{Me}_2\text{O}$ , 115-10-6;  $\text{CH}_3\text{Cl}$ , 74-87-3;  $\text{CH}_3\text{Br}$ , 74-83-9;  $\text{CH}_3\text{F}$ , 593-53-3;  $\text{CuO}$ , 1317-38-0;  $\text{Cu}$ , 7440-50-8;  $\text{O}_2$ , 7782-44-7;  $\text{CH}_4$ , 74-82-8;  $\text{AcOMe}$ , 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<sup>1</sup>

George A. Olah\* and Jozef Bukala

Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90089-1661

Received December 12, 1989

Superacidic antimony pentafluoride/graphite catalyzed oxidative carbonylation of methyl halides with carbon monoxide and copper oxides (or copper metal and oxygen) gives methyl acetate ( $\text{AcOMe}$ ). The reaction was investigated in a pressure reactor in the temperature range of 100 to 300  $^\circ\text{C}$  and pressures of 20 to 150 atm. The oxidative carbonylation of methyl bromide ( $\text{MeBr}$ ) with  $\text{CO}$  and  $\text{Cu}_2\text{O}$  at 270  $^\circ\text{C}$  under a pressure of 130 atm gave 48 mol %  $\text{Me}_2\text{O}$  and 33 mol %  $\text{AcOMe}$ . Replacing  $\text{Cu}_2\text{O}$  with  $\text{CuO}$  gave about 40–50%  $\text{AcOMe}$ , with 10–20%  $\text{Me}_2\text{O}$ . Using  $\text{Cu}$  and  $\text{O}_2$  gave ~50%  $\text{AcOMe}$ , with 5%  $\text{Me}_2\text{O}$ . In the reaction 5–10%  $\text{MeF}$  is also formed due to halogen exchange. The reactivity of the methyl halides shows the decreasing order of  $\text{MeBr} > \text{MeCl} > \text{MeF}$ .

### Introduction

The synthesis of a wide variety of oxygenated hydrocarbons can be achieved by using carbon monoxide or "synthesis gas" (i.e.,  $\text{CO} + \text{H}_2$  mixtures).<sup>2</sup> Most of these syntheses are carried out in homogeneous systems using soluble catalysts.<sup>3</sup> Some reactions are also carried out in heterogeneous system, over solid catalysts.<sup>2</sup> The insertion of  $\text{CO}$  into the  $\text{C-X}$  bonds in alkyl halides and polyhalides can be carried out in the presence of Friedel-Crafts catalysts such as  $\text{AlCl}_3$ ,  $\text{BF}_3$ ,  $\text{BF}_3\text{-HF}$ ,  $\text{FeCl}_3$ , or  $\text{BiCl}_3$ .<sup>4a</sup> 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.<sup>4b</sup> Trichloroacetyl chloride was prepared by the reaction of  $\text{CCl}_4$  with  $\text{CO}$  with  $\text{AlCl}_3$  catalyst or with iron, nickel, chromium, cobalt, or manganese carbonyls as catalysts.<sup>5</sup> Methyl chloride or methyl bromide was carbonylated with  $\text{CO}$  in the presence of rhodium or iridium tertiary phosphine catalysts.<sup>6</sup> The products of the reaction are acetyl chloride or bromide, respectively. The reactions

were carried out in toluene at 130  $^\circ\text{C}$  under 20 atm of  $\text{CO}$  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  $^\circ\text{C}$  and pressures of 600–1000 atm).<sup>2</sup> 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,<sup>7–9</sup> sodium or potassium methoxide,<sup>10</sup> or alkali carbonates.<sup>11–13</sup> When alcohol is added to the reaction mixture carboxylic acids or esters are the products. The reaction proceeds at temperature of 20–100  $^\circ\text{C}$  and pressures of 1–30 atm.<sup>10–12</sup>

Carbonylation of saturated hydrocarbons, olefins, or alcohols with  $\text{CO}$  was reported in the presence of cuprous compounds,<sup>14–21</sup> copper and cupric oxide,<sup>22,23</sup> or copper

(1) Heterogeneous Catalysis by Solid Superacids. 25. For part 24, see: Olah, G. A.; Bukala, J. *J. Org. Chem.*, preceding paper in this issue.

(2) Falbe, J. *Carbon Monoxide in Organic Synthesis*; Springer-Verlag: New York-Heidelberg, Berlin, 1970.

(3) Parrshall, G. W. *Homogeneous Catalysis*; J. Wiley-Interscience: New York, 1980, and references given therein.

(4) (a) Olah, G. A. *Friedel-Crafts and Related Reactions*; Wiley-Interscience: New York, 1963; Vol. 3, p 1298. (b) Olah, G. A.; Zadok, E.; Edler, R.; Adamson, D.; Kasha, W.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1989**, *111*, 9123.

(5) Korbanka, H. West German Patent 2,648,134, 1978; *Chem. Abstr.* **1978**, *89*, 42465y.

(6) Kuriyama, I. Japan Patent 78 46912, 1978; *Chem. Abstr.* **1978** *89*, 90070n.

(7) Japan Patent 81,61322, 1981; *Chem. Abstr.* **1981**, *95*, 150212w.

(8) Meck, R. F. U.S. Patent 3,988,358, 1974.

(9) Uchida, Y.; Ogata, I. *Organotransition-Met. Chem., Proc. Jpn.-Am. Semin.* **1st** **1974**, 265–71.

(10) Schneider, K.; Kummer, R.; Schwirten, K.; Schindler, M. D. West German Patent 2,521,610, 1976; *Chem. Abstr.* **1977**, *86*, 55177.

(11) Tustin, G. C.; Membre, R. T. *J. Org. Chem.* **1984**, *49*, 1761.

(12) Japan Patent 80 53241; *Chem. Abstr.* **1981**, *94*, 3757d.

(13) Japan Patent 82 183740; *Chem. Abstr.* **1983**, *98*, 106993.

(14) Japan Patent 83 201748; *Chem. Abstr.* **1983**, *100*, 138609v.

(15) Souma, Y.; Sano, H. Japan Patent 75123614, 1975; *Chem. Abstr.* **1975**, *84*, 43333n.

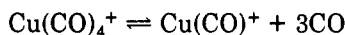
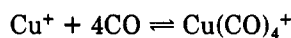
(16) Japan Patent 49 95916, 1974; *Chem. Abstr.* **1974**, *82*, 139363s.

(17) Sano, H.; Souma, Y. Japan Patent 74 03511; *Chem. Abstr.* **1974**, *81*, 151548h.

(18) Souma, Y.; Sano, H. Japan Patent 74 61113, 1974; *Chem. Abstr.* **1974**, *81*, 1 19986p.

(19) Pirozhkov, S. D.; Stepanyan, A. S.; Myshentrova, T. N.; Ordyan, M. B.; Lapidus, A. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1982**, *9*, 2100; *Chem. Abstr.* **1983**, *98*, 4262h.

carbonyls<sup>24-26</sup> in a strong acid (BF<sub>3</sub>·H<sub>2</sub>O, H<sub>2</sub>SO<sub>4</sub>, HSO<sub>3</sub>F, H<sub>3</sub>PO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>·BF<sub>3</sub>) solution at temperatures of -10 to +70 °C under atmospheric pressure. The cuprous compounds are assumed to react with carbon monoxide, forming copper carbonyl ions.<sup>24,26</sup>



Matsushima et al.<sup>27</sup> reported the formation of Cu(CO)<sub>4</sub><sup>+</sup> in BF<sub>3</sub>·H<sub>2</sub>O solution as the predominant carbonyl compound at temperatures below 20 °C. At higher temperatures under atmospheric pressure it decomposes to Cu(CO)<sup>+</sup> and carbon monoxide. Cu(CO)<sup>+</sup> is much more stable than Cu(CO)<sub>4</sub><sup>+</sup>. Even at temperatures above 80 °C it is formed in BF<sub>3</sub>·H<sub>2</sub>O solution.<sup>27</sup> It has been found that copper carbonyl complexes of strong acids such as Cu(C-O)AsF<sub>6</sub>,<sup>28</sup> Cu(CO)CF<sub>3</sub>SO<sub>3</sub>, Cu(CO)C<sub>2</sub>H<sub>5</sub>SO<sub>3</sub>, and Cu(C-O)CH<sub>3</sub>SO<sub>3</sub><sup>29</sup> can be isolated as stable crystalline solids. According to Souma and Sano<sup>26</sup> copper carbonyls play the role of "CO carrier" in the carbonylation reactions in solution. Cu(II) compounds did not show any complexing or catalytic activity,<sup>26</sup> but the mixture of equimolar amount of Cu<sup>2+</sup> compounds and metallic copper in concentrated H<sub>2</sub>SO<sub>4</sub> acts similarly to Cu<sup>+</sup> compounds.<sup>26</sup>

Carbonylation of hydrocarbons or alcohols in strong acid solution in the presence of cuprous compounds can be considered as an improved Koch reaction because the reaction proceeds at lower temperatures and under much reduced pressure. The main disadvantages of these carbonylation methods are the difficulty in separation of products from solutions of acid catalyst and their strongly corrosive nature.<sup>2</sup>

We have reported in the preceding paper the conversion of methyl halides to dimethyl ether with copper oxides (or with copper and oxygen) over supracidic SbF<sub>5</sub>/graphite catalyst.<sup>1</sup> In continuation of our work we report now a new method of the preparation of methyl acetate (AcOMe) by the heterogeneous oxidative carbonylation of methyl halides with copper oxide (or metallic copper and oxygen) using intercalated SbF<sub>5</sub>-graphite catalyst.

### Results and Discussion

The oxidative carbonylation of methyl halides with carbon monoxide and copper oxides (or copper powder and oxygen) was studied in a heterogeneous system over solid superacidic SbF<sub>5</sub> intercalated into graphite catalyst. The reactions were found to be dependent on the temperature, pressure, and amount of the catalyst.

**Oxidative Carbonylation of Methyl Bromide (Chloride, Fluoride) with CO and Cu<sub>2</sub>O over SbF<sub>5</sub>/Graphite Catalyst.** Cuprous compounds have been widely studied concerning their adsorption properties of CO and catalytic activity<sup>30-33</sup> in heterogeneous carbony-

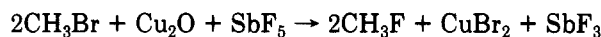
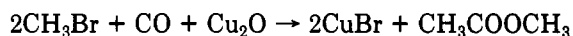
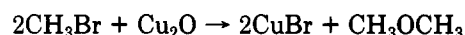
lation reactions. Herman et al.<sup>30</sup> reported that Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> or Cu/ZnO/Cr<sub>2</sub>O<sub>3</sub> are useful catalysts for methyl alcohol synthesis. Cu<sup>+</sup> ions are the active sites on which CO is adsorbed and subsequently transformed to methyl alcohol. In the catalyst prepared from CuO and Cr<sub>2</sub>O<sub>3</sub>, Cu<sup>+</sup> exists as a crystalline CuCrO<sub>2</sub> phase.<sup>31</sup> CuCrO<sub>2</sub> was formed in the reduction of the calcined catalyst with H<sub>2</sub>/CO at 270 °C.<sup>31</sup> Huang found that carbon monoxide is selectively adsorbed in Cu<sup>+</sup>Y zeolites, forming a Cu(CO)<sup>+</sup> complex with a strong Cu<sup>+</sup>-CO interaction.<sup>32</sup>

In our studies we investigated the oxidative carbonylation of MeBr over a catalyst composed of SbF<sub>5</sub> intercalated into graphite with carbon monoxide and cuprous oxide at temperature of 100-300 °C and pressures of 24-150 atm. The molar ratio of CH<sub>3</sub>Br/CO was generally about 1:32. The reaction was studied at temperatures of 100, 156, 226, 270, and 306 °C under CO pressure. In each experiment the same amounts of reagents and catalyst were used.

The reaction is very slow at a temperature of 100 °C and initial pressure of 140 atm. After a 24-h reaction time only about 7% AcOMe and 8% Me<sub>2</sub>O were formed, together with about 2% MeF (due to halogen exchange with SbF<sub>5</sub>). By raising the temperature to 160 °C the formation of Me<sub>2</sub>O increased to 80% in about 2 h but the amount of AcOMe remained at around 5%. At 270 °C and initial CO pressure of 140 atm the formation of AcOMe is increased to about 35% in 2 h with about 48% Me<sub>2</sub>O and 10% MeF also formed. More prolonged reaction time has little effect, the yield of AcOMe increasing only to 37% after 24 h (molar ratio of MeBr/CO/Cu<sub>2</sub>O in all experiments was about 1.7:50:1 and the MeBr/SbF<sub>5</sub> catalyst ratio 4.5:1).

Increasing the temperature further to 306 °C caused a decrease of yield of AcOMe and an increase in the formation of MeF (the halogen exchange byproduct with the catalyst).

Considering that the study of the reaction over prolonged periods of time indicates that Me<sub>2</sub>O, AcOMe, and MeF were formed in parallel reactions, the yield of any of the products is not dependent on the concentration of the others. The product forming reactions are



In the preceding paper<sup>1</sup> we described the conversion of MeBr with Cu<sub>2</sub>O over SbF<sub>5</sub>-graphite to Me<sub>2</sub>O. It is further known<sup>2,3,34,35</sup> that carbonylation of Me<sub>2</sub>O gives, depending on the catalyst and reaction condition, AcOMe, or acetic anhydride. Thus it could be also that in the present study Me<sub>2</sub>O is first formed and is subsequently carbonylated, forming AcOMe. In order to study the feasibility of this possible path of formation of AcOMe, carbonylation of Me<sub>2</sub>O was attempted under the reaction conditions. The carbonylation reaction of Me<sub>2</sub>O was carried out in the presence of Cu<sub>2</sub>O and SbF<sub>5</sub>-graphite at 280 °C under 75 atm of CO pressure. Even after 42 h of reaction time only 0.5% of AcOMe was formed (together with 2.9% MeF). Similarly the attempted carbonylation of Me<sub>2</sub>O with Cu and SbF<sub>5</sub>-graphite gave only 3% of AcOMe (with 5%

(20) Sano, H.; Souma, Y. Japan Patent 74 48616, 1974; *Chem. Abstr.* 1975, 82, 16329t.

(21) Souma, Y.; Sano, H. *Kogyo Kagaku Zasshi* 1970, 73 (12), 2723; *Chem. Abstr.* 1971, 74, 11151u.

(22) Souma, Y.; Sano, H. Japan Patent 74 61092, 1974; *Chem. Abstr.* 1975, 83, 137525h.

(23) Koyano, T.; Tachikawa, M.; Kumagai, K. Eur. Pat. Appl. EP 78162 A1, 1983; *Chem. Abstr.* 1984, 99, 70235y.

(24) Souma, Y.; Sano, H. *Bull. Chem. Soc. Jpn.* 1976, 49, 3296.

(25) Yoneda, N.; Fukuhara, T.; Takahashi, Y.; Suzuki, A. *Chem. Lett.* 1974, 607.

(26) Souma, Y.; Sano, H.; Jyodo, J. *J. Org. Chem.* 1973, 38, 2016.

(27) Matsushima, Y.; Koyano, T.; Kitamura, T.; Wada, S. *Chem. Lett.* 1973, 433.

(28) Desjardins, C. D.; Edwards, D. B.; Passmore, J. *Can. J. Chem.* 1979, 57, 2714.

(29) Doyle, G.; Eriksen, K. A.; Van Eugen, D. *Inorg. Chem.* 1983, 22, 2892.

(30) Herman, R. G.; Klier, K.; Simmons, W. G.; Finn, B. P.; Bulko, J. B.; Kobylnski, T. P. *J. Catal.* 1979, 56, 407.

(31) Monnier, J. R.; Hanrahan, M. J.; Apai, G. *J. Catal.* 1985, 92, 119.

(32) Huang, Y. *J. Catal.* 1973, 30, 187.

(33) Naccache, C. M.; Taarit, Y. B. *J. Catal.* 1971, 22, 171.

(34) Pugach, J. U.S. Patent 4251458, 1981.

(35) Isshiki, T.; Kijima, Y.; Miyauchi, Y. West German Offen 2,842,267, 1979; *Chem. Abstr.* 1979, 91, 56336s.

**Table I. Effect of Pressure on  $\text{SbF}_5$ -Graphite-Catalyzed Oxidative Carbonylation of  $\text{CH}_3\text{Br}$  with CO and  $\text{Cu}_2\text{O}$  (270 °C,  $\text{CH}_3\text{Br}/\text{CO}/\text{Cu}_2\text{O}$  Molar Ratio 1.7:53:1;  $\text{CH}_3\text{Br}/\text{Catalyst}$  Ratio 4:1)**

25 atm					48 atm					95 atm					140 atm				
time (h)	yield, mol %				time (h)	yield, mol %				time (h)	yield, mol %				time (h)	yield, mol %			
	$\text{CH}_4$	MeF	$\text{Me}_2\text{O}$	AcOMe		$\text{CH}_4$	MeF	$\text{Me}_2\text{O}$	AcOMe		MeF	$\text{Me}_2\text{O}$	AcOMe	MeF		$\text{Me}_2\text{O}$	AcOMe		
1	0.4	12.0	59.6	1.4	1		7.2	60.9	2.0	1	10.4	64.8	14.6	1	3.4	47.5	5.2		
3	0.4	13.2	63.3	2.1	2		11.0	70.9	4.8	3	11.0	68.2	15.6	2	7.7	43.5	28.4		
5	0.6	14.6	70.0	2.4	4		10.9	74.0	5.9	4	10.3	66.7	18.1	4	9.2	45.7	32.8		
6	0.6	15.1	71.1	2.6	6		11.9	74.8	5.3	5	10.2	68.6	17.0	8	9.9	46.0	36.0		
24	0.7	15.5	74.0	4.0	24	0.3	10.4	77.0	5.4	8	9.1	66.2	21.5	24	8.9	47.3	41.3		
					27	0.2	9.7	79.2	7.3	24	11.2	68.6	17.8						
										27	19.7	67.7	19.9						

**Table II. Effect of Ratio of  $\text{CH}_3\text{Br}$  to  $\text{SbF}_5$ -Graphite on the Oxidative Carbonylation of  $\text{CH}_3\text{Br}$  with CO- $\text{Cu}_2\text{O}$  (270 °C; 140 atm; Molar Ratio of  $\text{CH}_3\text{Br}/\text{CO}/\text{Cu}_2\text{O}$  = 1.7:53:1)**

$\text{CH}_3\text{Br}/\text{SbF}_5 = 2.2$				$\text{CH}_3\text{Br}/\text{SbF}_5 = 4.5$				$\text{CH}_3\text{Br}/\text{SbF}_5 = 6.1$				$\text{CH}_3\text{Br}/\text{SbF}_5 = 9.0$				$\text{CH}_3\text{Br}/\text{SbF}_5 = 50.3$			
time (h)	yield, mol %			time (h)	yield, mol %			time (h)	yield, mol %			time (h)	yield, mol %			time (h)	yield, mol %		
	MeF	$\text{Me}_2\text{O}$	Ac-OMe		MeF	$\text{Me}_2\text{O}$	Ac-OMe		MeF	$\text{Me}_2\text{O}$	Ac-OMe		MeF	$\text{Me}_2\text{O}$	Ac-OMe		MeF	$\text{Me}_2\text{O}$	Ac-OMe
1.0	5.1	42.7	7.5	1.0	3.4	47.5	5.2	1.0	4.6	61.6	6.6	1.0	3.7	69.6	3.5	1	2.8	27.0	0.7
1.25	6.5	45.7	12.8	2.0	7.7	43.5	28.4	4.0	7.8	73.1	73.1	3.0	4.1	85.3	5.1	3.0	5.0	31.0	1.0
3.0	11.4	40.5	40.1	4.0	9.2	45.7	32.8	17.0	8.0	69.9	20.5	6.0	4.4	89.6	4.4	6.0	5.7	34.7	2.0
4.5	11.8	40.7	40.6	4.5	11.2	47.5	29.4	24.0	7.8	70.8	19.7	24.0	4.1	89.4	5.8	10.0	6.3	36.9	2.8
6.0	10.9	38.7	46.4	8.0	9.9	46.0	36.0					71.5	3.8	87.9	7.9	24.0	7.8	43.3	6.0
6.5	10.3	36.3	49.0	20.0	10.4	50.0	36.1												
7.0	13.4	38.4	43.5																
22.0	12.1	32.4	53.2																
24.0	14.8	35.5	49.1																

MeF). As small amounts of AcOMe could also be formed from byproduct MeF (vide infra),  $\text{Me}_2\text{O}$  is not considered to be involved in the formation of AcOMe in the oxidative carbonylation of methyl halides.

Experiments were carried out at initial pressures of 26, 48, 93, and 240 atm, respectively, to study the effect of pressure on the oxidative carbonylation of MeBr with CO- $\text{Cu}_2\text{O}$  at 270 °C. In each experiment the molar ratio of  $\text{CH}_3\text{Br}/\text{CO}$  was about 1:30.

During the reactions the pressure generally drops about 15% due to the progress of the reaction and taking of gas samples for GC analysis from the reactor. The results of the experiments are summarized in Table I. Yields always relate to conversion of methyl bromide. Pressures are initial pressure at the given reaction temperatures. Usually three independent experiments were carried out and data were generally within  $\pm 10\%$ . The studies showed that the formation of AcOMe increased significantly with increasing pressure of CO. At higher CO pressures, the formation of the cuprous carbonyl complex (vide infra) is enhanced and this increases the yield of AcOMe.

Having established that the optimum condition for the oxidative carbonylation of MeBr to AcOMe is about at 270 °C temperature and a pressure of 140 atm, we subsequently studied the effect of the ratio of  $\text{CH}_3\text{Br}$  to  $\text{SbF}_5$  (contained in the  $\text{SbF}_5$ -graphite catalyst). It should be pointed out, however, that only the surface-exposed  $\text{SbF}_5$  is considered to be active.<sup>36</sup>  $\text{SbF}_5$  intercalated within the layers cannot contact the reagents, although during the reaction it can, in part, slowly diffuse to the surface. Consequently any discussion of the molar ratio of MeBr to  $\text{SbF}_5$  is arbitrary, and the "effective"  $\text{SbF}_5$  concentration is probably only  $1/10$  of the overall  $\text{SbF}_5$  in the system. Although the methylation reaction of CO by polarized MeBr is catalytic, with a turnover estimated to be at least 50–100, halogen exchange giving MeF tends to consume  $\text{SbF}_5$ -catalyst. The results of reactions with different

amount of catalyst are given in Table II. The yield of AcOMe decreases rapidly as the apparent molar ratio of  $\text{CH}_3\text{Br}/\text{SbF}_5$  increases from 2 to 9. At a molar ratio of about 50 the yield increase of  $\text{AcOCH}_3$  is less than 8 mol % even after prolonged reaction time. These results, irrespective of the de facto  $\text{CH}_3\text{Br}/\text{active catalyst}$  ratio, suggest that the amount of catalyst and thus the number of active sites has an important influence on the formation of AcOMe. It is most likely that the strongly polarized  $\text{CH}_3^{\delta+}\text{Br} \rightarrow \text{SbF}_5^{\delta-}$  complex is formed at the active sites.

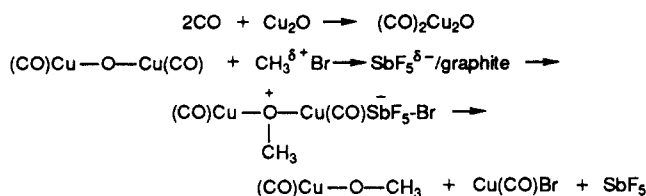
We also carried out the oxidative carbonylation of MeCl or MeF with CO and  $\text{Cu}_2\text{O}$  over  $\text{SbF}_5/\text{graphite}$  under conditions similar to those of the reaction of MeBr (270 °C, 140 atm; mol ratio of  $\text{Cu}_2\text{O}/\text{SbF}_5$  3:1;  $\text{CH}_3\text{Cl}(\text{F})/\text{CO}/\text{Cu}_2\text{O}$  = 1:35:0.6). In the reaction of MeCl with CO and  $\text{Cu}_2\text{O}$ ,  $\text{Me}_2\text{O}$  is the main product that is formed in more than 60 mol % yield after 2 h of reaction time. MeF and AcOMe were formed as byproducts in about 12 mol % yield for each. Methyl fluoride was found to be the least reactive methyl halide in the studied oxycarbonylation reaction. AcOMe and  $\text{Me}_2\text{O}$  are formed in its reaction in about 15 mol % yield for each after 6 h of reaction time. The yield of the products does not increase further even after 46 h of reaction time. There was also some methane (2%) formed in the beginning of the reaction, which slowly increases to 6 mol % during 46 h of reaction time. These results again suggest that  $\text{Me}_2\text{O}$  is not an intermediate in the formation of AcOMe.

Mechanistically the oxidative carbonylation of MeBr (as well as of other methyl halides) is considered to be initiated by formation of a strongly polarized donor-acceptor complex of MeBr and  $\text{SbF}_5/\text{graphite}$  (involving surface exposed active sites). Without  $\text{SbF}_5$  catalyst the reaction does

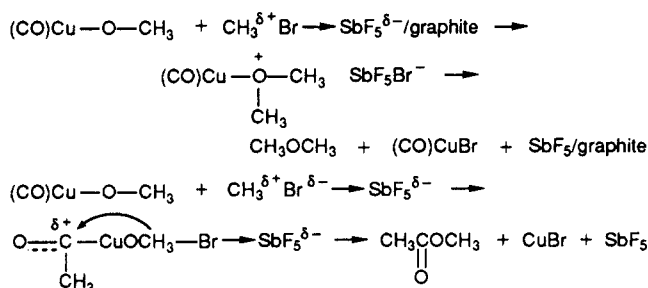
$\text{CH}_3\text{Br} + \text{SbF}_5/\text{graphite} \rightarrow \text{CH}_3^{\delta+}\text{Br} \rightarrow \text{SbF}_5^{\delta-}/\text{graphite}$

not take place under the reaction conditions. Thermal radical reactions involving  $\text{CH}_3^{\cdot}$  consequently cannot be significant.  $\text{Cu}_2\text{O}$  adsorbs CO, forming a cuprous carbonyl complex. The formed methoxy copper complex ( $\text{CO}$ )- $\text{CuOCH}_3$  is considered the key intermediate in the formation of  $\text{Me}_2\text{O}$  or AcOMe, respectively. If a second methylation occurs on the methoxy oxygen of the complex,

(36) (a) Olah, G. A.; Messina, G.; Bukala, J.; Olah, J. A.; Mateescu, G. D. 1st North American Chem. Conf., Mexico City, Dec. 1975, Abstr. Paper PHSC 153. (b) Olah, G. A.; Kaspi, J.; Bukala, J. *J. Org. Chem.* 1977, 42, 4187.



$\text{Me}_2\text{O}$  will be readily formed. If, however, the carbonyl group is methylated upon rearrangement, methyl acetate is formed.



The highest yield of  $\text{Me}_2\text{O}$  was obtained at  $\sim 156^\circ\text{C}$ , whereas that of  $\text{AcOMe}$  was at  $270^\circ\text{C}$ . The significant effect of temperature can be explained by the difference in activation energies. The reaction in which  $\text{Me}_2\text{O}$  is formed has a lower activation energy than that in which  $\text{AcOMe}$  is formed. Raising the temperature increases more rapidly the rate of the reaction with the higher activation energy. Comparing the yields of  $\text{Me}_2\text{O}$  in the reaction of  $\text{MeBr}$  with  $\text{CO}$  and  $\text{Cu}_2\text{O}$  over  $\text{SbF}_5$ -graphite, much higher yields of  $\text{Me}_2\text{O}$  are obtained at lower temperatures ( $100$ – $160^\circ\text{C}$ ). These results suggest that carbon monoxide plays the role of cocatalyst in formation of  $\text{Me}_2\text{O}$ . Probably the cuprous oxide-carbonyl complex is more reactive with  $\text{MeBr}$  than cuprous oxide itself.

Methyl fluoride formed in the reactions of  $\text{MeBr}$  and  $\text{MeCl}$  comes from fluorine exchange with the  $\text{SbF}_5$ /graphite catalyst. The use of  $\text{MeF}$  would eliminate halogen exchange, but the reactivity of  $\text{MeF}$  is relatively low in the oxidative carbonylation reaction.

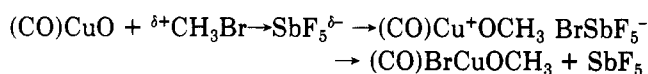
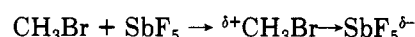
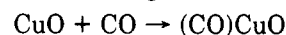
**Oxidative Carbonylation of  $\text{MeBr}$  with  $\text{CO}$ -Cupric Oxide over  $\text{SbF}_5$ -Graphite Catalyst.** Cupric oxide was shown to be a good oxidizing agent and can be used as a catalyst for oxidation of olefins. It can be easily reduced to cuprous oxide or copper with  $\text{CO}$  or  $\text{H}_2$  at temperatures of  $300$ – $400^\circ\text{C}$ .<sup>33</sup> Cupric oxide is used for the preparation of  $\text{Cu}/\text{ZnO}$  or  $\text{Cu}/\text{Cr}_2\text{O}_3$  catalysts and for synthesis of methyl alcohol from syn-gas. It has been found that during the synthesis cupric oxide is reduced to  $\text{Cu}^+$  compounds and in this form exists at the active sites in the catalysts.<sup>32</sup> We consequently extended our studies to the oxidative carbonylation of  $\text{MeBr}$  with  $\text{CO}$ -cupric oxide over  $\text{SbF}_5$ -graphite catalyst and carried out the reactions at the optimum conditions found for the preceding reactions with carbon monoxide and cuprous oxide, i.e. reaction temperature of  $270^\circ\text{C}$ ,  $150$  atm pressure, molar ratio of  $\text{CH}_3\text{Br}/\text{CO}/\text{CuO} = 1.7:50:1$  and molar ratio of  $\text{CuO}/\text{SbF}_5 = 2.9:1$ . The results of the reactions are given in Table III.

The results of the reactions are different from those obtained in the carbonylation of  $\text{MeBr}$  with  $\text{CO}$  and  $\text{Cu}_2\text{O}$  over  $\text{SbF}_5$ -graphite catalyst. The reaction with  $\text{CuO}$  caused the main product to be  $\text{AcOMe}$  with  $\text{Me}_2\text{O}$  only a relatively minor product. After 6 h of reaction time, the yield of  $\text{AcOMe}$  was twice that of  $\text{Me}_2\text{O}$ . The results suggest that the reaction with  $\text{CO}$  and  $\text{CuO}$  over  $\text{SbF}_5$ -graphite catalyst proceeds via an intermediate different from that of the reaction with  $\text{CO}$  and  $\text{Cu}_2\text{O}$ .

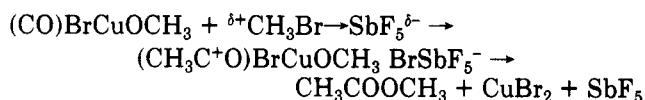
**Table III. Oxidative Carbonylation of  $\text{MeBr}$  with  $\text{CO}$  and  $\text{CuO}$  over  $\text{SbF}_5$ -Graphite at  $270^\circ\text{C}$  and  $150$  atm (Molar Ratio  $\text{CH}_3\text{Br}/\text{CO}/\text{CuO} = 1.7:50:1$ ,  $\text{CuO}/\text{SbF}_5 = 2.9:1$ )**

time (h)	yield, mol %		
	$\text{MeF}$	$\text{Me}_2\text{O}$	$\text{AcOMe}$
1	7	7	19
2	10	12	37
4	11	18	38
6	11	19	41
22	12	22	40
26	11	21	45

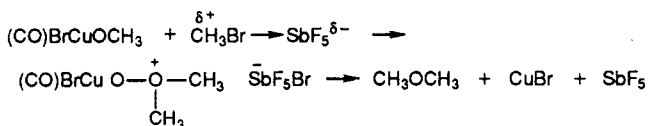
Although it is possible that during the reaction  $\text{CuO}$  could be reduced to  $\text{Cu}_2\text{O}$  by  $\text{CO}$ , this can only happen to a very limited degree. The presence of a significant amount of  $\text{Cu}_2\text{O}$  would accelerate the formation of  $\text{Me}_2\text{O}$ , which was not observed. Thus  $\text{CuO}$  itself plays a significant role in the formation of  $\text{AcOMe}$  via carbonylation of  $\text{MeBr}$ . It was<sup>32</sup> reported that on cupric oxide surfaces a large amount of carbon monoxide was absorbed. Consequently, formation of a carbonyl complex with cupric oxide must be considered. The formation of  $\text{AcOMe}$  and  $\text{Me}_2\text{O}$  can proceed according to



Subsequent methylation of the carbonyl group leads to  $\text{AcOMe}$



Methylation of the methoxy oxygen bonded to copper leads to formation of  $\text{Me}_2\text{O}$



In addition to  $\text{AcOMe}$  and  $\text{Me}_2\text{O}$ ,  $\text{MeF}$  was again formed in the reaction by halogen exchange. Trace amounts of methane were also detected. The amount of  $\text{MeF}$  was similar to that observed in the oxidative carbonylation reaction of  $\text{MeBr}$  with  $\text{CO}$ - $\text{Cu}_2\text{O}$ . By necessity the suggested reaction mechanism is tentative, as we have no direct evidence or observation of copper carbonyl intermediates, or their methylated onium ions. The proposed scheme, however, at this time best accounts for the observed results.

**Oxidative Carbonylation of  $\text{MeBr}$  with  $\text{CO}/\text{Cu}/\text{O}_2$  with  $\text{SbF}_5$ -Graphite Catalyst.** Carbonylation of  $\text{MeBr}$  with  $\text{CO}/\text{O}_2$  and copper powder over  $\text{SbF}_5$ -graphite catalyst was also carried out using varying ratios of oxygen. Typical results of the reaction are given in Table IV. The reactions were again carried out at the optimum condition for oxidative carbonylation of  $\text{MeBr}$  found previously, i.e. at  $270^\circ\text{C}$  and  $140$  atm. The results obtained show high selectivity in forming  $\text{AcOMe}$ , with the amount of  $\text{Me}_2\text{O}$  only about 5%. Smaller amounts of methane and ethane are also formed.

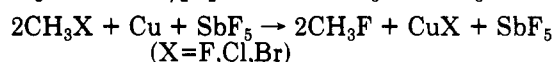
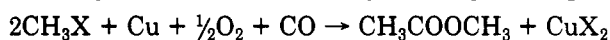
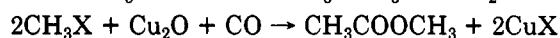
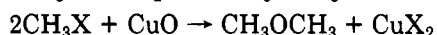
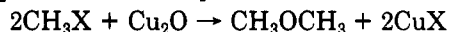
### Conclusions

A new oxidative carbonylation reaction of methyl halides giving methyl acetate has been found. Methyl bromide (and with decreasing reactivity methyl chloride and

**Table IV. Oxidative Carbonylation of MeBr with CO/Cu/O<sub>2</sub> over SbF<sub>5</sub>-Graphite Catalyst (270 °C, 140 atm, CH<sub>3</sub>Br/CO/O<sub>2</sub> = 1.5:44:1, Cu/SbF<sub>5</sub> = 2.4:1)**

time (h)	yield, mol %		
	MeF	Me <sub>2</sub> O	AcOMe
1	13	5	23
2	10	6	36
4	12	6	34
6	10	7	38
22	6	5	51
25	5	4	48

fluoride) reacts with carbon monoxide and copper oxides or copper and oxygen over SbF<sub>5</sub>-graphite catalyst to give methyl acetate. The reaction is an oxidative carbonylation because it proceeds only when a copper oxide or copper and oxygen is present. The major byproduct of the reaction is dimethyl ether (as well as methyl fluoride formed by halogen exchange with the catalyst). When Cu<sub>2</sub>O is used, AcOMe and Me<sub>2</sub>O are formed in comparable amounts in competing reactions. With Cu and Cu/O<sub>2</sub>, AcOMe becomes the major product. AcOMe was found not to be produced via prior formation of Me<sub>2</sub>O. AcOMe and Me<sub>2</sub>O are formed in parallel reactions.



The results of the studied reactions showed that the preferred system for oxidative carbonylation of methyl halides to AcOMe uses CO and CuO or Cu powder and molecular oxygen in conjunction with SbF<sub>5</sub>-graphite catalyst. The optimum conditions of the reaction are at 270 °C and 140 atm pressure.

### Experimental Section

**Materials and Catalyst.** Carbon monoxide of 99.5% minimum purity (Matheson) was used in all experiments without further purification. According to GC analysis carbon monoxide contained small impurities of methane (≈0.1% and ethane (≈0.05 mol%). Cuprous oxide, cupric oxide, and copper powder were as used previously.<sup>1</sup> Purified argon was used for flushing and blanketing the reactors. Oxygen used was extra dry (Matheson). Methyl halides (Matheson) were used as received. Intercalated SbF<sub>5</sub>-graphite catalyst was obtained from Alfa Products.

**General Experimental Procedure and Analysis.** The pressure reactor, general procedures used, and analytical methods were described previously.<sup>1</sup>

In typical runs 17.6 mmol of CH<sub>3</sub>Br (1 mL) or 20 mmol of CH<sub>3</sub>F or CH<sub>3</sub>Cl was used together with 10 mmol of Cu<sub>2</sub>O and 1.7 g of SbF<sub>5</sub>-graphite catalyst. The molar ratio of MeBr/CO/Cu<sub>2</sub>O in typical experiments was about 1.7:50:1 and the MeBr/SbF<sub>5</sub> catalyst ratio was 4.5. The results are summarized in the tables.

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

**Registry No.** MeBr, 74-83-9; MeCl, 74-87-3; MeF, 593-53-3; CO, 630-08-0; Cu<sub>2</sub>O, 1317-39-1; SbF<sub>5</sub>, 7783-70-2; Me<sub>2</sub>O, 115-10-6; AcOMe, 79-20-9; Cu, 7440-50-8.

## Electrochemical Reduction of *p*-Nitrophenyl Azide: Evidence Consistent with the Formation of *p*-Nitrophenylnitrene Anion Radical as a Short-Lived Intermediate

Dale E. Herbranson and M. Dale Hawley\*

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506-3701

Received December 28, 1989

The electrochemical reduction of *p*-nitrophenyl azide in DMF, acetonitrile, and butyronitrile is initially a one-electron process that affords the corresponding anion radical as a transient intermediate. Although *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>N<sub>3</sub><sup>-</sup> is too short-lived to be observed by our methods, product studies are consistent with a reaction pathway in which *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>N<sub>3</sub><sup>-</sup> decomposes by loss of dinitrogen to give the corresponding nitrene anion radical, *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>N<sup>-</sup>, as a short-lived intermediate. In the absence of added reagents, 4,4'-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>N=NC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub><sup>2-</sup> is formed as the principal product via dimerization of anion radicals. In DMF, hydrogen atom abstraction and carbonyl addition/radical β-fragmentation are observed also as reaction pathways and become increasingly important processes with decreasing current density and increasing temperature. The products of the two latter reaction pathways are *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NH<sup>-</sup> and *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>N<sup>-</sup>CON(CH<sub>3</sub>)<sub>2</sub>, respectively. In the presence of the weak oxygen acid (CF<sub>3</sub>)<sub>2</sub>CHOH, reduction of *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>N<sub>3</sub> is a two-electron process that yields dinitrogen and *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> as products. In the presence of weak methylene carbon acids such diethyl malonate, a chain reaction involving diazo transfer ensues, producing the corresponding diazoalkane and *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> in high yields.

### Introduction

Dissociative electron attachment to diazoalkanes (R<sub>2</sub>C=N<sub>2</sub>) has been shown to be a convenient and ready method for the preparation of certain carbene anion radicals (R<sub>2</sub>C<sup>-</sup>) in the gas<sup>1</sup> and condensed phases.<sup>2</sup> In the

condensed phase, R<sub>2</sub>C<sup>-</sup> formation has only been observed from those R<sub>2</sub>C=N<sub>2</sub><sup>-</sup> where the negative charge has been stabilized by electron-withdrawing substituents (e.g., (EtO<sub>2</sub>C)<sub>2</sub>C<sup>-</sup>)<sup>2a</sup> or where the carbene carbon center has been incorporated into a cyclopentadienyl ring.<sup>2d</sup> In the few

(1) (a) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 6491. (b) Zittle, P. F.; Ellison, G. B.; O'Neil, S. V.; Lineberger, W. C.; Reinhardt, W. R. *J. Am. Chem. Soc.* **1976**, *98*, 3731. (c) McDonald, R. N.; Chowdhury, A. K.; McGhee, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 4112. (d) McDonald, R. N.; Gung, W. Y. *J. Am. Chem. Soc.* **1987**, *109*, 7328.

(2) (a) Van Galen, D. A.; Young, M. P.; Hawley, M. D.; McDonald, R. N. *J. Am. Chem. Soc.* **1985**, *107*, 1465. (b) Van Galen, D. A.; Hawley, M. D. *J. Electroanal. Chem.* **1987**, *218*, 227. (c) Bethell, D.; Parker, V. D. *J. Am. Chem. Soc.* **1986**, *108*, 7194. (d) Bethell, D.; Parker, V. D. *J. Chem. Res.* **1987**, 116. (e) McDonald, R. N. *Tetrahedron* **1989**, *45*, 3993. (f) Bethell, D.; Parker, V. D. *Acc. Chem. Res.* **1988**, *21*, 400.