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$Cu(OAc)_2$-catalyzed partial oxidation of methane to methyl trifluoroacetate in the liquid phase

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Simple transition-metal salts were investigated as the catalysts for the partial oxidation of methane. In trifluoroacetic acid (TFA), methane could be efficiently converted to methyl trifluoroacetate by the $Cu(OAc)_2/K_2S_2O_8$ catalyst system. A quantitative yield (96.3%) based on methane has been obtained under the optimized conditions. A possible mechanism involving radical intermediates has been suggested for this reaction. Copyright © 2000 John Wiley & Sons, Ltd.

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INTRODUCTION

Partial oxidation of the lower alkanes, such as methane, to oxygenates is a challenging problem in chemistry, because they are the least reactive in the hydrocarbon family, and their expected products are more reactive than the alkanes in general, which causes selectivity problems. Methane is the least reactive of the alkanes [C–H bond energy: 105 kcal mol^{-1} (439 kJ mol^{-1})]. Furthermore, the expected products, methanol, formaldehyde and formic acid, are more reactive than methane, which results in difficulty in obtaining high yields of these expected products. However, methane is the most abundant of the hydrocarbons, and its utilization is of great practical interest. Various catalyst systems have also been investigated for the partial oxidation of methane to oxygenates in the liquid phase.[1–7] Recently we reported that the vanadium-containing heteropolyacid catalyst systems gave high yields of methyl trifluoroacetate.[8] In continuing studies on C–H bond activation, we report here our new results on the partial oxidation of methane to methyl trifluoroacetate using a $Cu(OAc)_2$ catalyst in trifluoroacetic acid (TFA).

RESULTS AND DISCUSSION

Some transition-metal compounds were investigated as the catalyst for the partial oxidation of methane to oxygenates. These results are summarized in Table 1. In TFA with a small amount of trifluoroacetic anhydride (TFAA), methane could be efficiently converted to methyl trifluoroacetate (**1**) and methyl acetate (**2**) by metal catalysts with potassium persulfate ($K_2S_2O_8$) as the oxidant, as shown in Eqn [1].

$$\mathrm{CH_4} \xrightarrow[\text{TFA/TFAA}]{\text{Cat./K}_2\text{S}_2\text{O}_8} \underset{\mathbf{1}}{\mathrm{CF_3CO_2CH_3}} + \underset{\mathbf{2}}{\mathrm{CH_3CO_2CH_3}} \qquad [1]$$

In the absence of catalyst, methyl trifluoroacetate (**1**) and methyl acetate (**2**) were obtained in the total yield of 4.6% based on methane (Table 1, entry 1). Although $TiO(acac)_2$ (acac = acetoacetate) has no catalyst activity (total yield 4.4%; entry 2), higher yields of 11%, 13.3% or 15.7% could be obtained when $Fe(OAc)_2$, $Cr_2(OAc)_4$ or $Mn(OAc)_2$ was used as the catalyst, respectively (entries 3, 4 and 5). In these cases, methyl acetate (**2**) comprised more than half of the product. However, methyl trifluoro-

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Table 1 Partial oxidation of methane to methyl trifluoroacetate (**1**) and methyl acetate (**2**) by various catalysts[a]

Entry	Catalyst	Yield (%)[b]	Ratio (**1**:**2**)
1	—	4.6	41:59
2	$TiO(acac)_2$	4.4	38:62
3	$Fe(OAc)_2$	11.0	34:66
4	$Cr_2(OAc)_4$	13.3	47:53
5	$Mn(OAc)_2$	15.7	18:82
6	$Cu(OAc)_2$	29.2	98:2
7	$Cu(PA)_2$	5.7	100:0
8	$Cu(bpy)_2(OAc)_2$	7.5	89:11

[a] Reaction conditions: 25-ml autoclave, catalyst 0.054 mmol, CH_4 20 atm, TFA 5 ml, TFAA 10 mmol, $K_2S_2O_8$ 5 mmol, 100 °C with stirring for 20 h.

[b] GC yield based on methane.

acetate (**1**) was obtained as a major product when $Cu(OAc)_2$ was chosen as the catalyst, and the total yield was as high as 29.2% (entry 6). No methyl acetate (**2**) was detected in the products if $Cu(PA)_2$ (PA = pyridine-2-carboxylate) was used as the catalyst (entry 7). A small amount of methyl acetate (**2**) was formed in the reaction with $Cu(bpy)_2(OAc)_2$ (bpy = bipyridyl) as the catalyst (entry 8). These results suggested that, if copper salts were used as the catalysts, high selectivity of methyl trifluoroacetate (**1**) could be obtained.

Thus, the partial oxidation of methane was investigated in detail with a $Cu(OAc)_2$ catalyst. The time course of methane oxidation is shown in Fig. 1. The initial yield of the products, methyl trifluoroactate (**1**) and methyl acetate (**2**), increased with increasing reaction time. If the reaction was carried out at 80 °C, the highest yield (21.1%) was obtained at a reaction time of 40 h, and the yield then decreased to 13.2% at 50 h due to over-oxidation of the products. The best yield (40.2%) could be obtained if the reaction was carried out at 100 °C for 30 h, and the yield went down to 33% at 40 h.

Then the effect of temperature on the reaction was investigated (Fig. 2). If the reaction was run at 60 °C for 20 h, the yield of **1** and **2** was only 2.3%. With increasing temperature, the yield increased continuously. A yield of 29.2% could be obtained at 100 °C and 38.4% at 120 °C. With increasing temperature, the oxidant ($K_2S_2O_8$) would probably decompose more rapidly, catalyzed by the copper(II) cation in TFA to form the $HSO_4^{\cdot}$ radical, which abstracts a hydrogen atom from methane.

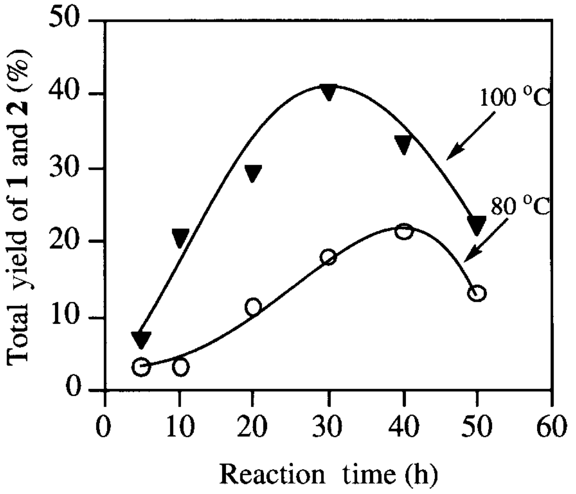

Figure 1 Time course of the partial oxidation of methane to esters **1** and **2** by $Cu(OAc)_2$ catalyst. Reaction conditions: 25-ml autoclave, $Cu(OAc)_2$ 0.054 mmol, CH_4 20 atm, TFA 5 ml, TFAA 10 mmol, $K_2S_2O_8$ 5 mmol, heated at 100 °C or 80 °C with stirring.

In the next step, the effect of the amount of the oxidant, $K_2S_2O_8$, was investigated (Fig. 3). In 5 ml TFA and 10 mmol TFAA solvents, the yield of the products **1** and **2** increased with increasing amount of $K_2S_2O_8$. A yield of 7.7% was obtained when 1 mmol of $K_2S_2O_8$ was added, and the highest yield

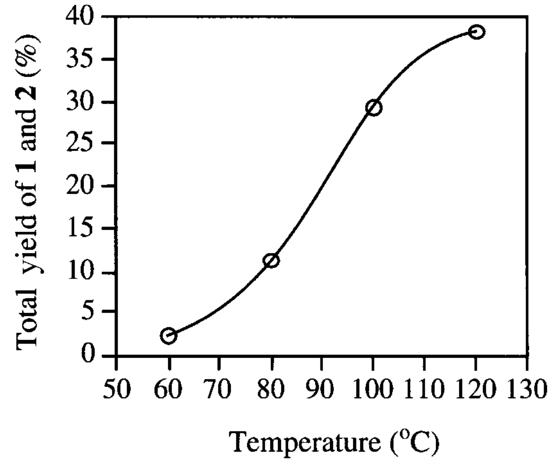

Figure 2 Effect of temperature on the partial oxidation of methane to esters **1** and **2** by $Cu(OAc)_2$ catalyst. Reaction conditions: 25-ml autoclave, $Cu(OAc)_2$ 0.054 mmol, CH_4 20 atm, TFA 5 ml, TFAA 10 mmol, $K_2S_2O_8$ 5 mmol, heated at various temperatures with stirring for 20 h.

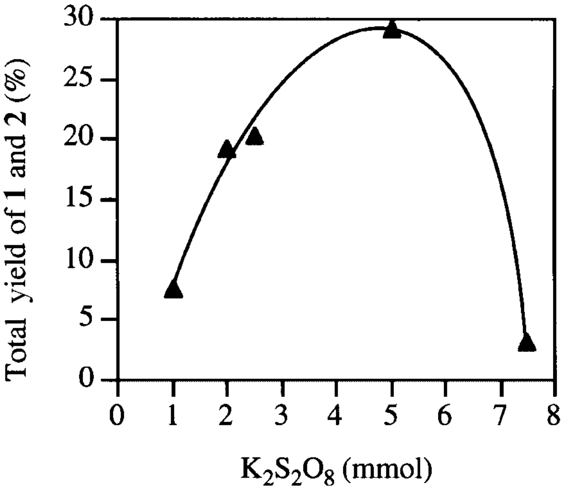

Figure 3 Influence of the amount of $K_2S_2O_8$ on the partial oxidation of methane to esters **1** and **2** by $Cu(OAc)_2$ catalyst. Reaction conditions: 25-ml autoclave, $Cu(OAc)_2$ 0.054 mmol, CH_4 20 atm, TFA 5 ml, TFAA 10 mmol, heated at 100 °C with stirring for 20 h.

Table 2 Quantitative oxidation of methane to esters **1** and **2** by $Cu(OAc)_2$ catalyst[a]

Entry	TFA (ml)	Product (**1** + **2**) (mmol)	Yield (%)[b]	Ratio (**1**:**2**)
1	5[c]	1.15	11.4	93:7
2	5	2.93	29.2	98:2
3	5[d]	4.04	40.2	97:3
4	5[e]	2.05	40.8	98:2
5	9[f]	1.26	73.9	100:0
6	9[g]	1.32	77.7	98:2
7	9[h]	1.53	90	100:0
8	9[i]	1.64	96.3	94:6

[a] Reaction conditions: 25-ml autoclave, $Cu(OAc)_2$ 0.054 mmol, $K_2S_2O_8$ 5 mmol, CH_4 20 atm, TFAA 10 mmol, heated at 100 °C with stirring for 20 h unless otherwise indicated.
[b] GC yield based on CH_4.
[c] 80 °C.
[d] 30 h.
[e] CH_4 10 atm.
[f] CH_4 5 atm.
[g] CH_4 5 atm and N_2 5 atm.
[h] CH_4 5 atm and N_2 15 atm.
[i] CH_4 5 atm and N_2 25 atm.

(29.2%) could be obtained when 5 mmol of $K_2S_2O_8$ was added. However, only a 3.1% yield was obtained when 7.5 mmol of $K_2S_2O_8$ was added to the reaction mixture, due to the large amount of solid $K_2S_2O_8$ remaining undissolved in the solvent which caused less efficient stirring for the reaction.

To improve the yield of the products, the reaction conditions were optimized; the results are summarized in Table 2. The selectivity of methyl trifluoroacetate (**1**) is always above 90%; sometimes, no methyl acetate (**2**) is detected (entries 5 and 7). The largest amount (4.04 mmol) of the products was obtained with a yield of 40.2% (entry 3). At the lower pressure of methane (5 atm), the yield could reach 73.9% (entry 5). In particular, if an inert gas (nitrogen) was present, almost quantitative partial oxidation of methane could be attained (yield 90% or 96.3%; entries 7 and 8).

Recently, we reported that the vanadium-containing heteropolyacid-catalyzed partial oxidation of methane could give quantitative yields (95%) of methyl esters **1** and **2** and, in some case, the turnover numbers based on $PV_2Mo_{10}O_{40}$ could reach up to 161. Here, the turnover numbers of copper(II) could also be improved up to 151 under similar reaction conditions to those for a $PV_2Mo_{10}O_{40}$ catalyst. This result shows that the simple copper salt, $Cu(OAc)_2$, is as active as the complicated heteropolyacids for the partial oxidation of methane.

Radical intermediates usually exist in reactions with $K_2S_2O_8$ as the oxidant.[1,9–11] Some radical characteristics were also observed in our reaction system. The effect of a radical scavenger on the reaction is also shown in Fig. 4. Compared with the reaction using no radical scavenger in the reaction mixture, smaller amounts of the products were formed in the reaction with the radical scavenger 2,6-di-*t*-butyl-*p*-methylphenol (DBMP). After reaction for 20 h, only a 4.5% yield was obtained with added DBMP, whereas a 29.2% yield could be obtained without DBMP. This result suggests that a radical intermediate occurs in the reaction process, and could be trapped by the radical scavenger, resulting in the lower yield. A possible mechanism is shown in Scheme 1. In TFA as solvent, $K_2S_2O_8$ would first be converted to peroxodisulfuric acid ($H_2S_2O_8$). Then $H_2S_2O_8$ would be decomposed by the copper(II) catalyst to form the HSO_4^- anion and the $HSO_4^\cdot$ radical, which abstracts a hydrogen atom from methane to form the methyl radical, which is then oxidized by the copper(II) cation (a good oxidant for the alkyl radical)[1,12,13] to form the methyl cation. Finally, the methyl cation would react with TFA to give methyl trifluoroacetate (**1**). The catalytic reaction is thought to be initiated by the thermal decomposition of $H_2S_2O_8$ to form the $HSO_4^\cdot$ radical. The key step for the high selectivity of methyl trifluoroacetate (**1**) must be the oxidation of the methyl radical to the methyl cation by Cu(II).

Other metal ions could also decompose $H_2S_2O_8$, but would not efficiently oxidize the methyl radical to the methyl cation, resulting in the low selectivity of methyl trifluoroacetate (**1**). The by-product methyl acetate (**2**) would be derived from acetic acid which would be formed from the reaction of CH_4 and CO, derived from the decomposition of TFA and/or TFAA.[8]

EXPERIMENTAL

General

Methane (Sumitomo Pure Chemical) and nitrogen (BOC Gases) gases were commercial grade. TFA, TFAA, $Cu(OAc)_2$ and $K_2S_2O_8$ were purchased from Wako Pure Chemicals. Product analyses were performed on a Shimadzu GC-8A with an internal standard.

Oxidation reaction

To a 25-ml stainless steel autoclave, $Cu(OAc)_2$ (0.0105 g; 0.054 mmol), $K_2S_2O_8$ (1.35 g; 5 mmol), TFA (5 ml) and TFAA (1 ml; 10 mmol) were added successively. The autoclave was flushed with methane three times, then pressurized to 20 atm. The reaction mixture was heated at 100 °C with stirring for 20 h. Finally, the products was analyzed by GC with an internal standard. The formation of the esters **1** and **2** was confirmed by ^{1}H and ^{13}C NMR spectra of the reaction mixture. Methyl trifluoroacetate (**1**): ^{1}H NMR (CF_3COOH): $\delta = 4.04$ (s, CF_3COOCH_3); ^{13}C NMR (CF_3COOH): $\delta = 54.8$ (s, CH_3), 115.1 (q, CF_3, $J_{C-F} = 282$ Hz), 162.6 (q, C=O, $J_{C-F} = 43.5$ Hz). Methyl acetate (**2**): ^{1}H NMR (CF_3COOH): $\delta = 2.17$ (s, CH_3CO, $3H$), 3.81 (s, CH_3O, $3H$); ^{13}C NMR (CF_3COOH): $\delta = 19.5$ (s, CH_3), 53.2 (s, CH_3O), 178.8 (s, C=O).

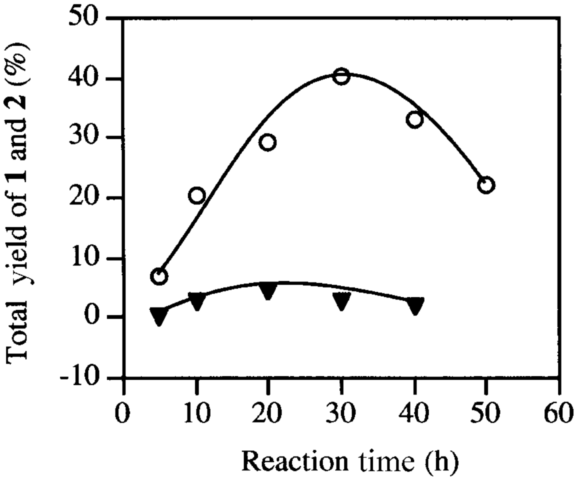

Figure 4 Influence of a radical scavenger on the partial oxidation of methane to esters **1** and **2** by $Cu(OAc)_2$ catalyst. Reaction conditions: ○, 25-ml autoclave, $Cu(OAc)_2$ 0.054 mmol, CH_4 20 atm, TFA 5 ml, TFAA 10 mmol, $K_2S_2O_8$ 5 mmol, 100 °C with stirring; ▼, as above, plus DBMP 0.54 mmol.

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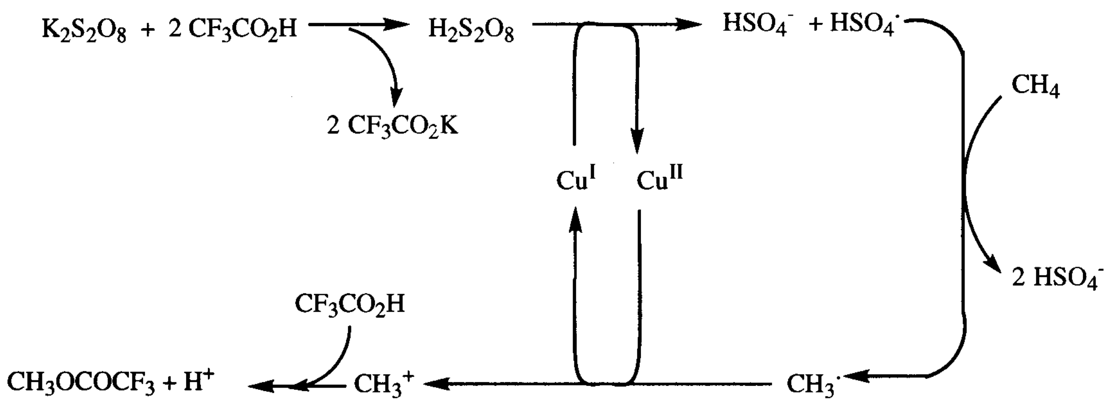

Scheme 1 A possible mechanism for the partial oxidation of methane catalyzed by the Cu(II) cation.

REFERENCES

1. (a) Nishiguchi T, Nakata K, Takaki K, Fujiwara Y. *Chem. Lett.* 1992; 1141; (b) Nakata K, Yamaoka Y, Miyata T, Taniguchi Y, Takaki K, Fujiwara Y. *J. Organomet. Chem.* 1994; **473**: 329; (c) Fujiwara Y, Takaki K, Taniguchi Y. *Chem. Lett.* 1992; 1141; (d) Nakata K, Yamaoka Y, Miyata T, Taniguchi Y, Takaki K, Fujiwara Y. *J. Organomet. Chem.* 1994; **473**: 329; (e) Fujiwara Y, Takaki K, Taniguchi Y. *Synlett* 1996; **7**: 591.
2. (a) Kao L, Huston AC, Sen A. *J. Am. Chem. Soc.* 1991; **113**: 700; (b) Lin M, Sen A. *J. Chem. Soc., Chem. Commun.* 1992; 892; (c) Lin M, Sen A. *J. Am. Chem. Soc.* 1991; **113**: 700; (d) Lin M, Sen A. *J. Chem. Soc., Chem. Commun.* 1992; 892; (e) Lin M, Sen A. *Nature (London)* 1994; **368**: 613.
3. (a) Periana RA, Taube DT, Evitt ER, Löffler DG, Wentrcek PR, Voss G, Masuda T. *Science* 1993; **259**: 340; (b) Periana RA, Taube DJ, Gramble S, Taube H, Satoh T, Fujii H. *Science* 1993; **259**: 340; (c) Periana RA, Taube DJ, Gramble S, Taube H, Satoh T, Fujii H. *Science* 1998; **280**: 560.
4. (a) Seki Y, Mizuno N, Misono M. *Appl. Catal. A* 1997; **158**: 47; (b) Mizuno N, Seki Y, Nishiyama Y, Kiyoto I, Misono M. *Appl. Catal. A* 1997; **158**: 47; (c) Mizuno N, Seki Y, Nishiyama Y, Kiyoto I, Misono M. *J. Catal.* 1999; **184**: 550.
5. (a) Yamanaka I, Soma M, Otsuka K. *J. Chem. Soc., Chem. Commun.* 1995; 2235; (b) Yamanaka I, Soma M, Otsuka K. *J. Chem. Soc., Chem. Commun.* 1995; 2235; (c) Yamanaka I, Soma M, Otsuka K. *Chem. Lett.* 1996; 565.
6. Vargaftik MN, Stolarov IP, Moiseev II. *J. Chem. Soc., Chem. Commun.* 1990; 1049.
7. (a) Nizova GV, Süss-Fink G, Shul'pin GB. *J. Chem. Soc.* 1997; 397; (b) Nizova GV, Süss-Fink G, Stanislas S, Shul'pin GB. *J. Chem. Soc.* 1997; 397; (c) Nizova GV, Süss-Fink G, Stanislas S, Shul'pin GB. *Chem. Commun.* 1998; 1855.
8. Piao D, Inoue K, Shibasaki H, Taniguchi Y, Kitamura T, Fujiwara Y. *J. Organomet. Chem.* 1999; **574**: 116.
9. Eberhardt MK. *J. Org. Chem.* 1977; **42**: 832.
10. Andreeva LK, Birger EA, Kheifits LA. *J. Org. Chem. (USSR)* 1975; **11**: 1263.
11. Fukagawa T, Fujiwara Y, Taniguchi H. *J. Org. Chem.* 1982; **47**: 2491.
12. (a) Kochi JK, Subramanian RV. *J. Am. Chem. Soc.* 1965; **87**: 4855; (b) Jenkins CL, Kochi JK. *J. Am. Chem. Soc.* 1972; **94**: 856.
13. Okada T, Kamiya Y. *Bull. Chem. Soc. Jpn.* 1979; **52**: 3321.