Highly Selective Partial Oxidation of Methane to Methyl Trifluoroacetate

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Methane has been oxidized stoicheiometrically by cobalt(III) trifluoroacetate in CF_3CO_2H solution at 150—180 °C and 10—40 atm to give methyl trifluoroacetate in 90 ± 10% yield based on Co^{III}, which is reduced to Co^{II}; in the presence of O_2 (1—5 atm) the reaction becomes catalytic with respect to the cobalt(III) salt, giving methyl trifluoroacetate as the sole product of the oxidation of methane by dioxygen.

The reaction of alkanes with transition metal complexes is an effective method for the oxidative functionalization of methane and its homologues under mild conditions.[1,2] Recently, methane was found to be oxidized by Pd^{II} acetate in trifluoroacetic acid solution at 80 °C and 56—70 atm to give methyl trifluoroacetate in 60% yield after several hours[3] or 4 days.[4] Our attempts to reproduce this result were unsuccessful; only traces of CF_3CO_2Me were found, even after 10 days under the above conditions. Unknown admixtures in the reagents are presumed to be responsible for the difference between our results and those cited.[3,4]

In our search for transition metal reagents capable of partial methane oxidation under mild conditions, we have studied the interaction of Mn^{III}, Fe^{III}, Co^{III}, Cu^{II}, and Pb^{IV} trifluoroacetates with CH_4 in CF_3CO_2H solution. Some of these transition metal ions have been used previously as effective initiators of radical-chain oxidation of higher alkanes by dioxygen.[5] Cobalt(III) and manganese(III) salts are known to oxidize C_4–C_{10} alkanes in CF_3CO_2H solution.[6] Trifluoroacetic acid functions both as a non-oxidizable solvent and as a trapping reagent for fixation of the products of partial methane oxidation.

The reaction between methane and 0.1—0.3 M solutions of the metal trifluoroacetates in CF_3CO_2H was carried out in sealed glass tubes at 100—200 °C and 10—40 atm of initial CH_4 pressure followed by GLC analysis of the gaseous and liquid products. These experiments showed that methane was oxidized at 150—180 °C by all the metal salts studied, with the exception of $Fe(OCOCF_3)_3$, to give methyl trifluoroacetate (Table 1). CF_3CO_2Me was identified by GLC and ^1H NMR spectroscopy both directly in the reaction solutions and as methanol in the hydrolysis products. Carbon dioxide was detected in the oxidation products, but this could be also formed by decarboxylation of CF_3CO_2H or the $CF_3CO_2^-$ anion in the presence of the metal ions studied.

The proportion of CO_2 formed by methane oxidation could not be determined directly by comparing the quantity of CH_4 consumed with that of CF_3CO_2Me formed, because of the 10- to 50-fold molar excess of CH_4 over metal ion taken. Nevertheless, in the case of Co^{III} trifluoroacetate the origin of CO_2 was recognized definitively, methyl trifluoroacetate being obtained in *ca.* 90% yield based on Co^{III} (see Table 1), according to equation (1). In the absence of methane, CF_3CO_2Me was found to be relatively stable towards oxidation by Co^{III} under the same experimental conditions: *ca.* 100% of the CF_3CO_2Me introduced (0.1 M in CF_3CO_2H solution) was recovered after the maximal period (6 h) for the oxidation of CH_4. These facts led us to the conclusion that methane was oxidized stoicheiometrically by Co^{III} to give CF_3CO_2Me [equation (1)], without CO_2 formation. This partial oxidation of methane is thought to be more selective than the known reactions involving transition metal ions.[1—4,6,7]

Table 1. Yield of CF_3CO_2Me from partial oxidation of methane by metal trifluoroacetates in CF_3CO_2H solution ($p_{init}^{CH_4}$ 30 atm, 180 °C, 3 h).

Metal salt	CF_3CO_2Me yield, % based on metal oxid. equivalent
$Pd(OCOCF_3)_2$	≤0.1
$Mn(OCOCF_3)_3$	30 ± 5
$Fe(OCOCF_3)_3$	0
$Co(OCOCF_3)_3$	90 ± 10
$Cu(OCOCF_3)_2$	~0.1
$Pb(OCOCF_3)_4$	10 ± 3

$$CH_4 + 2\,Co(OCOCF_3)_3 \rightarrow CH_3OCOCF_3 + 2\,Co(OCOCF_3)_2 + CF_3CO_2H \quad (1)$$

Further experiments with $Co(OCOCF_3)_3$ showed that addition of O_2 (1—5 atm) to CH_4 resulted in a yield of CF_3CO_2Me exceeding that expected for the stoicheiometric reaction of equation (1). Cobalt(II) trifluoroacetate was also found to be a suitable starting form of the catalyst for CH_4 oxidation to CF_3COOMe when O_2 was added. Under CH_4 + O_2 atmosphere, methyl trifluoroacetate was formed at approximately the same rate in CF_3CO_2H solutions containing either Co^{III} or Co^{II} salts. These facts could be explained by the re-oxidation of Co^{II} to Co^{III} by dioxygen [equation (2)].

$$2\,Co(OCOCF_3)_2 + 1/2\,O_2 + 2\,CF_3CO_2H \rightarrow 2\,Co(OCOCF_3)_3 + H_2O \quad (2)$$

The combination of this reaction with the reduction of Co^{III} by methane [equation (1)] results in a catalytic oxidation of CH_4 by O_2 to give methyl trifluoroacetate [equation (3)]. The

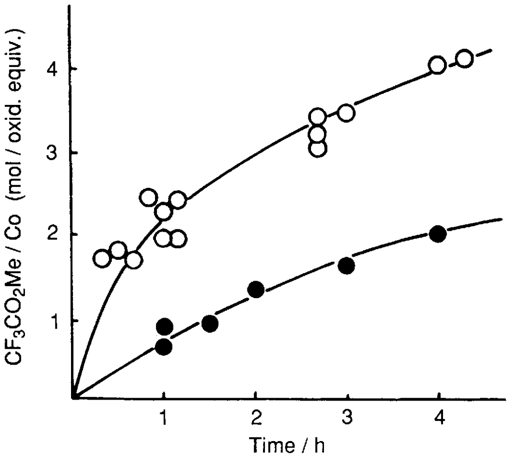

Figure 1. Formation of CF_3CO_2Me during the oxidation of CH_4 by O_2 in a CF_3CO_2H solution of $Co(OCOCF_3)_2$: [Co] 0.90 × 10^{-4} M, O_2 initial pressure 3 atm, 180 °C; (○) CH_4 initial pressure 20 atm; (●) CH_4 initial pressure 10 atm.

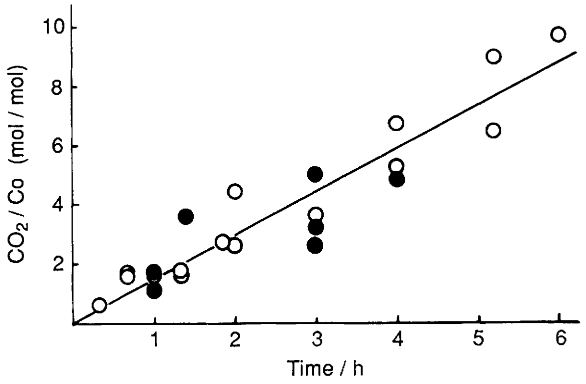

Figure 2. Time course of CO_2 accumulation in the gaseous phase over a CF_3CO_2H solution of $Co(OCOCF_3)_2$: [Co] 0.90×10^{-4} M, O_2 initial pressure 3 atm, 180 °C; (○) no CH_4 added; (●) CH_4 initial pressure 20 atm.

mechanism of the reaction may be more complicated than just a sum of the reactions (1) and (2). In addition to Co^{III} and Co^{II} trifluoroacetates, other cobalt compounds, *e.g.* Co^{IV} peroxo complexes, are thought to be involved in the reaction.

Smaller yields of CF_3CO_2Me were obtained using $Mn(OCOCF_3)_2$ as a catalyst.

$$CH_4 + 1/2\ O_2 + CF_3CO_2H \rightarrow CH_3OCOCF_3 + H_2O \quad (3)$$

The reaction catalysed by Co^{II} trifluoroacetate was studied in more detail. Figure 1 shows that *ca.* 400% yield of CF_3CO_2Me based on the Co^{III} oxidative equivalent can be achieved, in agreement with the catalytic nature of the reaction. The decrease in the rate of CF_3CO_2Me accumulation may be caused by the precipitation of inactive Co^{II} fluoride compounds rather than by the further oxidation of CF_3CO_2Me. This assumption is supported by the previous experiments confirming the stability of CF_3CO_2Me towards oxidation both by Co^{III} and by O_2 in the presence of Co^{II} trifluoroacetate.

Comparable yields of CO_2 and CF_3CO_2Me were obtained, as shown in Figures 1 and 2. Under O_2 atmosphere, the quantities of CO_2 formed were independent of the presence of methane (Figure 2), so that methane cannot be the source of the CO_2 formed in either the catalytic [equation (1)] or the stoicheiometric [equation (3)] oxidation of methane.

Both pure CF_3CO_2H and CF_3CO_2H solutions of Co^{II} or Mn^{II} trifluoroacetates were found to undergo only slow decarboxylation under anaerobic atmosphere at 150—180 °C ($\leqslant 0.2$ mol CO_2 per mol M^{II} for 6 h), unlike CF_3CO_2H solutions of Co^{III} or Mn^{III} trifluoroacetates. The rate of CO_2 evolution from the CF_3CO_2H solution of $Co(OCOCF_3)_2$ was found to increase with increasing O_2 partial pressure. These facts may be explained by homo- or hetero-lytic oxidative splitting of the $M^{III\text{ or }IV}$–$OCOCF_3$ bond, resulting finally in CO_2 formation. This reaction, accompanied by the formation of a series of organofluorides, is not thought to be directly related to the oxidation of methane.

Received, 4th April 1990; Com. 0/01521K

References

1 A. E. Shilov, 'Activation of Saturated Hydrocarbons by Transition Metal Complexes,' D. Reidel, Dordrecht, 1984.
2 R. Pitchai and K. Klier, *Catal. Rev., Sci. Eng.*, 1986, **28**, 13.
3 E. Gretz, T. F. Oliver, and A. Sen, *J. Am. Chem. Soc.*, 1987, **109**, 8109.
4 A. Sen, E. Gretz, T. F. Oliver, and Z. Jiang, *New J. Chem.*, 1989, **13**, 755.
5 N. M. Emanuel, E. T. Denisov, and Z. K. Maizus, 'Liquid-Phase Oxidation of Hydrocarbons,' Plenum, New York, 1967.
6 E. S. Rudakov, 'Reactions of Alkanes with Oxidants, Metal Complexes and Radicals in Solutions,' Naukova Dumka, Kiev, 1985.
7 V. S. Belova, A. M. Khenkin, and A. E. Shilov, *Kinet. Katal.*, 1988, **29**, 1279.