



Palladium(II)- or copper(II)-catalysed solution-phase oxyfunctionalisation of methane and other light alkanes by hydrogen peroxide in trifluoroacetic anhydride

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

Both $[\text{Pd}(\text{hfacac})_2]$ **2** and $[\text{Cu}(\text{hfacac})_2(\text{H}_2\text{O})_2]$ **3** ($\text{hfacac} = 1,1,1,5,5,5$ -hexafluoropentane-2,4-dionate) catalyse the oxidation of methane to methyl trifluoroacetate **1** by H_2O_2 in trifluoroacetic anhydride (TFAA), at temperatures as low as 50°C , under 25–30 atm methane partial pressure, the main by-product being CO_2 . Under the same conditions, ethane and propane are oxidized to the corresponding trifluoroacetates. The *iso*-to-*normal* propyl esters ratio varies markedly (7.2 versus 34) on passing from **2** to **3**.

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1. Introduction

The activation and functionalisation of methane, the most abundant member of the hydrocarbon family, has attracted very much attention because of its abundance in natural gas and its low reactivity [1]. In particular, a lot of studies have dealt with the direct conversion of methane into oxygenates, using molecular oxygen and various peroxides in homogeneous systems, in the presence of various catalysts [2]. Some years ago, Sen and co-workers [3] discovered that the oxidation of methane to methyl trifluoroacetate by hydrogen peroxide in trifluoroacetic anhydride (TFAA) can be catalysed by bis(propionate)palladium(II). The authors suggest that the metal centres could

co-ordinate the peroxytrifluoroacetic acid, which arises from the reaction of TFAA with H_2O_2 , thus causing an enhancement of its electrophilic properties. This convincing suggestion prompted us to search for more efficient and selective metal complex-based soluble catalysts for the oxidation of methane and other light alkanes to the corresponding trifluoroacetates by the $\text{H}_2\text{O}_2/\text{TFAA}$ system. We devoted our attention to complexes characterized by the presence of a highly electrophilic transition metal centres and were attracted by the idea of testing the activity of some $16e^- d^8$ -metal centres surrounded by the hexafluoroacetylacetonate anion (hfacac), a strong electron-withdrawing and oxidation-resistant ligand capable to increase the electrophilic properties of the metal centres [4]. We have found that $[\text{Pd}(\text{hfacac})_2]$ **2** and $[\text{Cu}(\text{hfacac})_2(\text{H}_2\text{O})_2]$ **3** exhibit interesting catalytic properties in the oxidation of methane, ethane,

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and propane by H_2O_2 in TFAA. The results of this study are reported here.

2. Experimental

2.1. General

Gas-chromatographic analyses were performed on a Perkin-Elmer 8500 instrument equipped with FID and HWD detectors by using helium as carrier and the following columns: a stainless steel Porapak PS packed column (5 m \times 1/8 in.) (Supelchem) for the analysis of the products arising from methane, ethane, and propane oxidation; a stainless steel 3% SE-30 on Supelcoport packed column (5 m \times 1/8 in.) (Supelchem) for the evaluation of *normal-to-iso* ratio for the propyl trifluoroacetates; a stainless steel Carboxen 1004 micro packed column (2 m \times 1/16 in.) (Supelchem) for the quantitative analysis of methane and carbon dioxide. GC-MS analyses were performed with a Perkin-Elmer 8500 gas-chromatograph connected with a Perkin-Elmer Q-910 mass spectrometer, using a DB-1 capillary column (length, 30 m; i.d., 0.25 mm) and helium as carrier-gas. Bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)palladium(II) [5], diaquobis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)copper(II) [6], and 91% hydrogen peroxide [7] were prepared according to published procedures. Sodium trifluoroacetate, potassium trifluoroacetate, cesium trifluoroacetate, methyl trifluoroacetate, propane (98% pure), ethane (99% pure), and methane (99.0% pure) were purchased from Aldrich and were used as received. TFAA (Aldrich) was stored under a pure atmosphere, at -30°C . Hydrogen peroxide (35%) (Carlo Erba) was stored at -30°C . 1-Propyl trifluoroacetate and 2-propyl trifluoroacetate were prepared by reacting the corresponding alcohols with trifluoroacetic anhydride in diethyl ether at 20°C , following standard procedures [8].

2.2. General procedure for the catalytic reactions and for the isolation of reaction products

All reactions were carried out in a Pyrex glass reactor (capacity, ca. 16 cm^3) (Fig. 1) which was projected in collaboration with Mr. Raffaele Disa and supplied by R. Disa & F. Ili (Milan, Italy). The gas seal (maxi-

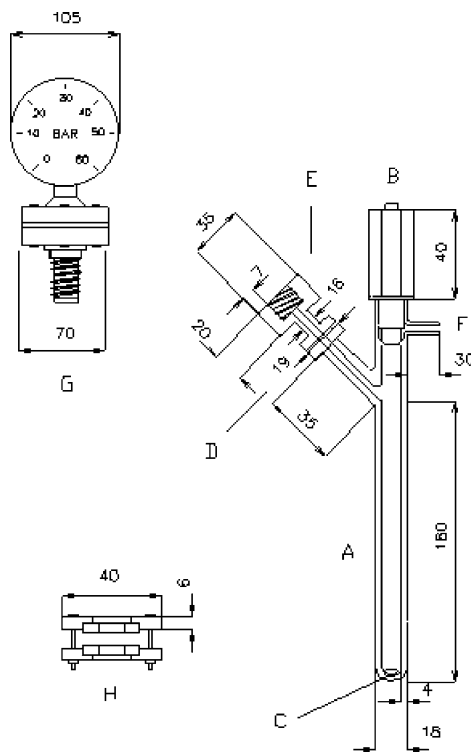


Fig. 1. Pressure reactor employed for the oxidation of methane, ethane, and propane (dimensions in mm): (A) Pyrex glass tubular vessel; (B) Bibby Quickfit Rotaflo Teflon tap; (C) 3/8 in. \times 3/16 in. egg-shaped Teflon-covered magnetic stirring-bar; (D) flange joint, whose gas pressure seal is provided by a perfluorinated rubber "O"-ring; (E) Teflon-made connector; (F), gas inlet/outlet nozzle; (G) Teflon-coated membrane manometer; (H) flange metallic holdfast.

um pressure, 35 atm) of such an apparatus was tested by introducing increasing amounts of liquid dinitrogen which was then left to warm up to room temperature. Gas loss was observed through the nozzle F when the internal pressure was as high as 37 atm. The reactor was charged under argon with the appropriate amount of catalyst precursor and with TFAA (typically 2 ml), at room temperature. To the resulting mixture, previously kept at 77 K, hydrogen peroxide 35% (typically 2.5 mmol) was added and then the gaseous hydrocarbon (typically 17 mmol) was fed through the nozzle F at atmospheric pressure by a mercury gas-burette. The Teflon tap was closed and the reactor was immersed into a thermostatted ($\pm 0.2^\circ\text{C}$) oil bath making the reaction mixture level to be only 5–10 mm below

oil level. The reaction mixture was then kept at the desired temperature for the appropriate reaction time, under vigorous stirring by a Teflon coated magnetic bar. At the end of reaction the reactor was immersed into a dry ice/acetone bath maintained at -60°C . The Teflon tap was opened and the volatile components (typically, unreacted hydrocarbon and carbon dioxide) were allowed to flow through the nozzle F and were conveyed to an evacuated Schlenk tube (capacity, 250 cm^3) equipped with a silicon-rubber serum-cap and immersed in liquid dinitrogen. After the addition of a known amount of a gaseous standard (typically 10 cm^3 at 40 psi of ethane, in the case of methane oxidation) by a gastight sampling syringe incorporating an on/off valve (Hamilton), the gases were analysed by gas-chromatography (HWD). Analogously, after the addition of a known amount of a liquid standard (typically 6 mg of *n*-heptane), the liquid phase was analysed by gas-chromatography.

The use of the reactor of Fig. 1 allowed us to operate under conditions of high reproducibility and chemical purity.

Catalyst re-cycling experiments were performed by drying the reaction mixtures under reduced pressure (0.1 mmHg), at 50°C , just connecting the reactor to a vacuum line. In all cases a microcrystalline solid residue remained on the bottom of the reactor which was again charged with all the reactants exactly as reported above.

3. Results and discussion

3.1. Oxidation of methane

The oxidation of methane to methyl trifluoroacetate **1** by hydrogen peroxide in trifluoroacetic anhydride (TFAA) is a scarcely selective reaction if carried out in the absence of any catalyst, carbon dioxide being the most abundant product (Eq. (1)). At least in part, CO_2 derives from the thermal decomposition of TFAA, as already observed [9]. For this reason we did not evaluate the amount of CO_2 .

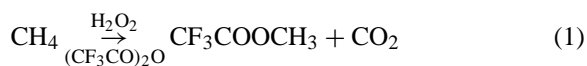


Table 1

Oxidation of methane by H_2O_2 in TFAA in the absence of catalysts: influence of the reaction temperature^a

T ($^{\circ}\text{C}$)	CH_4 conversion (%)	1 ($\times 10^6$ mol)
30	0.3	15
50	2.3	14
75	2.5	14.5
90	ND	15
110	2.8	17
140	3.0	20

^a Reaction conditions: CH_4 , 16.8 mmol; TFAA, 1.8 cm^3 ; 35% H_2O_2 , 0.2 cm^3 (2.3 mmol); reaction time, 4 h.

The data reported in Table 1 and Fig. 2 indicate clearly that both the **1**/ CH_4 and the **1**/ H_2O_2 molar ratios vary little on varying either the reaction temperature or the reaction time. At temperatures lower than 50°C , very poor methane conversions are reached, while, at 50°C as well as at higher temperatures, even adopting low reaction times, the observed methane conversions are quite high as it can be understood easily taking into account either the absolute amount of the starting hydrogen peroxide either the fact that four moles of H_2O_2 are necessary to convert one mole of methane in CO_2 .

On the base of the data of Table 1 we can conclude that: (a) the modest amounts of **1** ($(15\text{--}20) \times 10^{-3}$ mmol) that are formed from the oxidation of methane in the absence of catalysts are scarcely dependant upon the reaction time, at least in the examined range; (b) the methane conversion does not vary significantly on varying reaction time (0.5–2 h), and, consequently, results to be low and almost constant the amount of **1** produced per mole of H_2O_2 ; (c) in the examined range, the amount of **1** increases almost linearly on increasing the reaction temperature, remaining anyway low (0.0012% yield, on the base of the starting CH_4 , and 0.88% yield, on the base of the starting H_2O_2); (d) the oxidation of methane to CO_2 is much more favoured than the partial oxidation to **1**.

This scenario changes dramatically operating in the presence of $[\text{Pd}(\text{hfacac})_2]$ **2** or $[\text{Cu}(\text{hfacac})_2(\text{H}_2\text{O})_2]$ **3**. First of all, the reaction temperature influences now the reaction course much more markedly than it does in the case of the non-catalysed reactions. Indeed, the **1**/catalyst molar ratio increases by increasing the reaction temperature thus reaching the maximum values at 50 and 75°C , in the case of the reactions catalysed

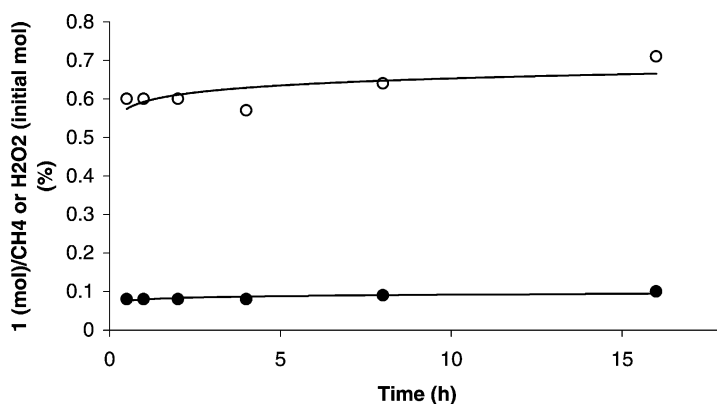


Fig. 2. Variation of methyl trifluoroacetate **1** to methane (●) or hydrogen peroxide (○) ratios as a function of the reaction time for the oxidation of methane by H₂O₂ in TFAA in the absence of catalyst, at 75 °C. Reaction conditions: CH₄, 16.8 mmol; TFAA, 1.8 cm³; H₂O₂ 35%, 0.2 cm³ (2.3 mmol).

by **2** and **3**, respectively (Table 2). In both the cases, a dramatic lowering of the yields in **1** is observed at $T \geq 90$ °C.

The H₂O₂ concentration plays a key role, the best results being obtained using 35% H₂O₂. Indeed, the use of more concentrated H₂O₂ leads to very low methyltrifluoroacetate **1** yields. Under the same experimental conditions ($T = 75$ °C; 4 h; TFAA, 1.8 ml; CH₄, 16.8 mmol; **2**, 6 mmol) the **1/2** molar ratio varies from 39 to 1, using 35% H₂O₂ and 91% H₂O₂, respectively.

It is interesting to underline that neither the reactions catalysed by **2** nor those catalysed by **3** result to be affected by the presence of 2,6-di-*tert*-butyl-4-methylphenol (BHT), a powerful radical scavenger. Instead, the methyl trifluoroacetate yields are reduced to

a half when the palladium-catalysed reaction are carried out in the presence of a trifluoroacetate excess ($\text{CF}_3\text{CO}_2^-/\mathbf{2} = 10/1$) (introduced as $\text{CF}_3\text{CO}_2\text{M}$; M: Li, Na, K, or Cs), and result to be lowered by ca. 20%, in the case of the reactions catalysed by the copper complex **3**.

Tables 3 and 4 show the influence exerted by the reaction time on the oxidation of methane by TFAA/H₂O₂ in the presence of **2** and **3**, respectively.

It can be first observed that in both cases a quite similar profile is observed, although **2** is clearly more active than **3**. The mol of **1** formed per mol of catalyst increase on increasing the reaction time thus reaching a maximum after 2 h, in the cases of reactions catalysed by **2**, and after 4 h, in the case of the reactions carried out in the presence of **3**. Afterwards, in

Table 2

Oxidation of methane by H₂O₂ in TFAA catalysed by [Pd(hfacac)₂] **2**^a or [Cu(hfacac)₂(H₂O)₂] **3**^b: influence of the reaction temperature on methane conversion and on the amount of methyl trifluoroacetate **1** produced per mol of catalyst

T (°C)	[Pd(hfacac) ₂] 2		[Cu(hfacac) ₂ (H ₂ O) ₂] 3	
	CH ₄ conversion (%)	1/2 (mol/mol)	CH ₄ conversion (%)	1/3 (mol/mol)
30	4.8	22.0	3.6	1.2
50	6.0	50.1	7.9	11.5
75	13.7	39.0	12.4	12.4
90	ND	19.8	13.7	8.6
110	12.2	15.1	9.7	5.5
140	10.5	9.7	11.7	5.6

^a Reaction conditions: CH₄, 16.8 mmol; TFAA, 1.8 ml; 35% H₂O₂, 0.2 ml (2.3 mmol); reaction time, 4 h; **2**, 8.7×10^{-6} mol.

^b Reaction conditions: CH₄, 16.8 mmol; TFAA, 1.8 ml; 35% H₂O₂, 0.2 ml (2.3 mmol); reaction time, 4 h; **3**, 7.7×10^{-6} mol.

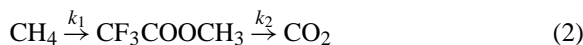
Table 3

Oxidation of methane by H₂O₂ in TFAA catalysed by [Pd-(hfacac)₂] **2**: influence of the reaction time^a

Reaction time (h)	CH ₄ conversion (%)	1 ($\times 10^6$ mol)	1/2 (mol/mol)
0.5	3.8	258	29.7
1	4.1	335	38.5
2	4.2	346	39.8
4	13.7	340	39.0
6	ND	305	35.0
8	ND	210	24.1
10	ND	140	16.2
16	ND	78	8.95

^a Reaction conditions: CH₄, 16.8 mmol; TFAA, 1.8 ml; 35% H₂O₂, 0.2 ml (2.3 mmol); temperature, 75 °C; **2**, 8.7×10^{-6} mol.

both cases the yields of **1** decrease fast. Such a reaction trend is typically observed in the case of consecutive reactions and is frequently encountered within oxidation processes [10], owing to the fact that the primary oxidation products undergo further oxidation (Eq. (2)).



A process of this type will be more or less selective towards partial oxidation, i.e. the formation of **1**, depending upon the relative values for k_1 and k_2 . The role of a catalyst may be crucial making a favourable discrimination between a k_1 and k_2 to occur. This seems to occur in the present study, as it was supported by

Table 4

Oxidation of methane by H₂O₂ in TFAA catalysed by [Cu-(hfacac)₂(H₂O)₂] **3**: influence of the reaction time^a

Reaction time (h)	CH ₄ conversion (%)	1 ($\times 10^6$ mol)	1/3 (mol/mol)
0.5	ND	27	3.5
1	2.8	28	3.6
2	ND	55	7.1
3	ND	85	11.0
4	3.1	100	13.0
6	ND	94	12.2
8	ND	63	8.2
12	ND	39	5.1
17	ND	23	3.0

^a Reaction conditions: CH₄, 16.8 mmol; TFAA, 1.8 ml; 35% H₂O₂, 0.2 ml (2.3 mmol); temperature, 75 °C; **3**, 7.7×10^{-6} mol.

observing the course of the oxidation of methane in the presence of methyl trifluoroacetate **1** in the absence of catalyst as well as in the presence of **2** or **3**, as a function of the reaction time (Fig. 3). The reproducibility of the data was verified by repeating all runs three times. It is evident that both **2** and **3** make the oxidation of methane to methyl trifluoroacetate **1** to be kinetically favoured over the consecutive oxidation of **1**. Indeed, in both cases the concentration of methyl trifluoroacetate first increases and then decreases. Instead, in the absence of catalyst, the reaction starting implicates a fast lowering of the concentration of **1**. In this connection, our data appear to disagree with what reported by Sen and co-workers [3] ‘... CF₃CO₂CH₃

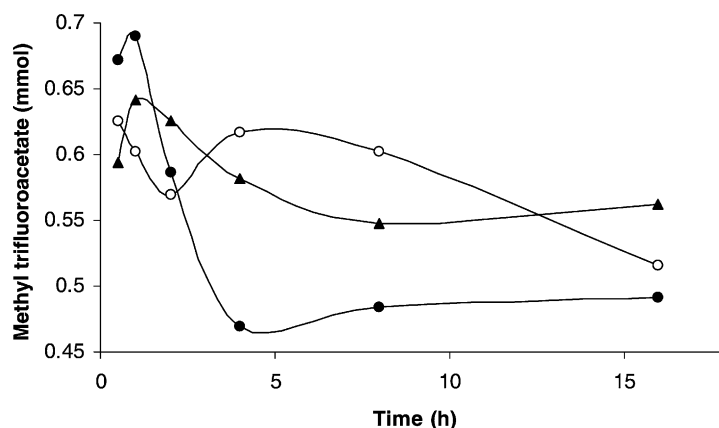
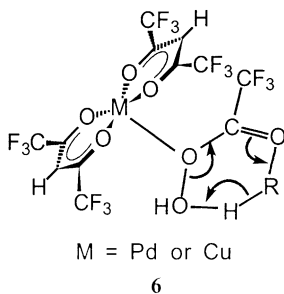


Fig. 3. Variation of methyl trifluoroacetate **1** as a function of the reaction time for the oxidation of a mixture of methyl trifluoroacetate and methane by H₂O₂ in TFAA catalysed by **2** (●), by **3** (▲), or carried out in the absence of any catalyst (○). Reaction conditions: **1**, 0.597 mmol; CH₄, 16.8 mmol; TFAA, 1.8 ml; 35% H₂O₂, 0.2 ml (2.3 mmol); T, 75 °C; **2**, 6.7×10^{-6} mol; **3**, 6.8×10^{-6} mol.

presence of bis(propionate)palladium(II), at 90 °C and 63 atm. Under these reaction conditions 5 mol of methyl trifluoroacetate per mole of palladium complex are formed in 3 h.

This study shows that both bis(hexafluoroacetylacetonate)palladium(II) **2** and diaquobis(hexafluoroacetylacetonate)copper(II) **3** are suitable catalysts for the above reaction. These catalysts operate under smoother reaction conditions than those adopted by Sen and exhibit quite higher activities. In the best conditions, 19.9 and 3.3 mol of methyl trifluoroacetate are formed per mol of **2** and **3**, per hour, respectively. As already pointed out, in the case of the oxidation of ethane and propane these figures result to be significantly higher.

The fact that neither the reactions catalysed by **2** nor those catalysed by **3** result to be affected by the presence of a radical scavenger seems to be in agreement with the hypothesized electrophilic rather than radicalic mechanism for these reactions [3]. Accordingly, the oxidation of hydrocarbons by peroxytrifluoroacetic acid (the product of the reaction of TFAA with H₂O₂) could take place through a transition state like **6**, where an incipient OH⁺ activates a hydrocarbon C–H bond. The co-ordination of peroxytrifluoroacetic acid to palladium(II) or copper(II) electrophilic centres of **2** and **3** should result in a marked enhancement of the electrophilic properties of such a strong oxidant.



In this connection, the fact that the methyl trifluoroacetate yields are reduced when the catalysed reactions are carried out in the presence of Li, Na, K, or Cs trifluoroacetate (see above) has some relevance, since free trifluoroacetate anion could compete with trifluoroacetic acid in the co-ordination to the metal centres.

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