Carboxylation of Methane

Single-Pot Conversion of Methane into Acetic Acid in the Absence of CO and with Vanadium Catalysts Such as Amavadine**

Patrícia M. Reis, José A. L. Silva, António F. Palavra, João J. R. Fraústo da Silva, Tsugio Kitamura, Yuzo Fujiwara, and Armando J. L. Pombeiro**

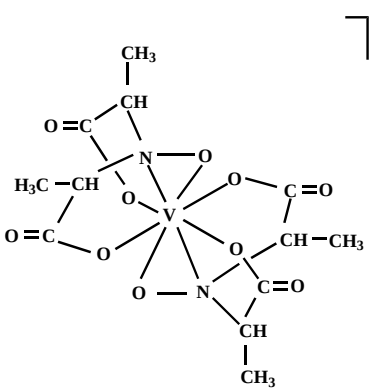
Despite current interest in the biological roles of vanadium, its application in catalysis is still an underdeveloped field of research.[1] We have already reported that amavadine, a natural vanadium complex present in some *Amanita* fungi and whose biological function is still unknown, can exhibit haloperoxidase- and peroxidase-type activities and act as a catalyst for the oxidation of some biological thiols,[2] as well as for the peroxidative halogenation, hydroxylation, and oxo-functionalization of alkanes and aromatic compounds.[3] Following this work, we have been searching for other reactions that could be catalyzed by this and related V complexes, in particular the conversion of methane—the main component of natural gas and the most abundant and least reactive alkane—into functionalized products with added commercial value.[4] Recently attention has focused on the metal-catalyzed transformation of CH_4 and CO into acetic acid,[5–11] as well as the formation of carbonylated products without requiring the use of noxious CO, such as the conversion of CH_4 into methyl esters[12] and into acetic acid (and methanol).[9] The latter, the reaction of CH_4 and CO_2 catalyzed by $NaVO_3$/pyrazine-2-carboxylic acid (in the presence of H_2O_2 in aqueous solution), occurs in very low yield based on CH_4 (ca. 0.01 %) and at a considerable pressure (50 bar) of this gas, although at low temperature (40 °C).[9] The reaction also proceeds with CO, which apparently is the carbonylating agent even when CO_2 is used (CO is then formed by reduction of CO_2 by methyl and/or hydroxyl radicals).[9] We now report the unprecedented (to our knowledge) conversion of CH_4 into CH_3COOH in the absence of either CO or CO_2, in a novel single-pot catalytic reaction [Eq. (1)] under considerably mild conditions and in high yields.

$$CH_4 \xrightarrow[K_2S_2O_8,\ CF_3COOH]{\text{V cat.}} CH_3COOH \qquad (1)$$

[*] Prof. J. J. R. Fraústo da Silva, Prof. A. J. L. Pombeiro, P. M. Reis, Dr. J. A. L. Silva, Prof. A. F. Palavra
Centro de Química Estrutural, Complexo I
Instituto Superior Técnico
Av. Rovisco Pais, 1049-001 Lisboa (Portugal)
Fax: (+351) 21-846-4455
E-mail: pcd1950@popsrv.ist.utl.pt
pombeiro@ist.utl.pt
Prof. T. Kitamura, Prof. Y. Fujiwara
Department of Chemistry and Biochemistry
Graduate School of Engineering
Kyushu University, Fukuoka, 812-8581 (Japan)

[**] This work was supported in part by the Fundação para a Ciência e a Tecnologia (FCT) and the POCTI Programme, Portugal.

The catalytic systems are based on a V^{IV} or V^{V} complex with poly- or bidentate N,O or O,O ligands in the presence of the peroxodisulfate salt $K_2S_2O_8$ as the oxidizing agent and in trifluoroacetic acid as the solvent. The V catalysts include: oxovanadium(v) complexes **1** and **2** of the type [VO(*N,O*-L)];



3

synthetic amavadine **3** and its model **4**, which are Ca^{2+} salts of V^{IV} complexes with N,O ligands; and V^{IV} vanadyl complexes **5–9** of the type [VO(*O,O*-L)$_2$]. Turnover numbers (TONs, moles of acetic acid per mol of metal catalyst) and yields (based on methane) are given in Table 1, and typical conditions include conducting the reaction in CF_3COOH at 80 °C with molar ratios of CH_4:V catalyst and $K_2S_2O_8$:V catalyst of 46:1 (corresponding to CH_4 pressure of 5 atm) and 200:1, respectively. Usually the yields were determined after a reaction time of 20 h, but often much shorter times were sufficient to attain close values (see entries 1 and 11 for yields obtained after 2 h; the former is 92 % of that in entry 2 obtained after 20 h).

$[VO(N(CH_2CH_2O)_3)]$ **1**

$[VO(N(CH_2CH_2O)_2(CH_2COO)]$ **2**

$Ca[V(ON(CH(CH_3)COO)_2)_2]$ **3**

$Ca[V(ON(CH_2COO)_2)_2]$ **4**

$[VO(maltolate)_2]$ **5**
(maltolate = basic form of 3-hydroxy-2-methyl-4-pyrone)

$[VO(HOCH_2CH_2N(CH_2CO_2)_2)]$ **6**

$[VO(CF_3COO)_2]$ **7**

$[VO(CF_3SO_3)_2]$ **8**

$VOSO_4$ **9**

The most active catalysts, which can give yields over 50 % and TONs close to 30, are complex **1** within the type [VO(*N,O*-L)], both amavadine (**3**) and its model **4** of the [V(*N,O*-L) salts, and complexes **5, 7**, and **8** of the type [VO(*O,O*-L)$_2$]. In contrast **2, 6**, and **9** exhibit much lower

Table 1: Conversion of methane into acetic acid.[a]

Entry	Cat.	$p(CH_4)$ [atm][b]	$p(CO)$ [atm][b]	t [h]	TON[c]	Yield [%][d]
1	**1**	5	–	2	9.2	19.7
2	**1**	5	–	20	10.0	21.4
3	**1**	5	5	20	10.9	23.5
4	**1**	5	15	20	10.4	22.2
5	**1**	3	15	20	5.1	18.5
6	**1**	8	15	20	24.7	33.7
7	**1**	12	15	20	28.2	25.6
8[e]	**1**	5	15	20	10.4	35.3
9[f]	**1**	5	5	20	3.9	42.7
10	**2**	5	–	20	2.2	4.8
11	**3**	5	–	2	7.0	15.3
12	**3**	5	–	20	13.4	29.4
13	**3**	5	5	20	9.7	21.2
14	**3**	5	15	20	8.1	17.3
15[g]	**3**	5	15	20	12.0	54.3
16	**4**	5	–	20	9.6	20.9
17	**4**	5	15	20	9.6	20.6
18	**4**	12	15	20	27.9	25.4
19[h]	**4**	5	15	20	5.4	24.5
20	**5**	5	–	20	6.8	14.9
21	**5**	5	15	20	8.2	17.6
22	**6**	5	–	20	2.0	4.5
23	**7**	5	–	20	1.8	3.8
24	**7**	5	5	20	10.5	23.0
25	**7**	5	20	20	8.8	19.0
26	**8**	5	–	20	6.7	14.6
27	**8**	5	5	20	10.1	22.1
28	**8**	5	20	20	12.1	29.0
29	**9**	5	–	20	1.0	2.2
30	**9**	5	20	20	2.3	5.0

[a] Reaction conditions (unless stated otherwise): metal complex catalyst (0.0625 mmol), $K_2S_2O_8$ (12.5 mmol, i.e. 200:1 molar ratio of $K_2S_2O_8$ to metal catalyst), CF_3COOH (23 mL), 80 °C, in an autoclave (39-mL capacity). Amounts of CH_4 or CO gas correspond to 0.572 mol atm^{-1}, with pressure measured at 25 °C; for example, 2.86 and 8.58 mmol gas for pressures of 5 and 15 atm, respectively. The catalyst complexes were prepared according to the literature: **1**,[14] **3**,[15] **4**,[15] **5**,[16] **8**.[17] New complexes **2, 6**, and **7** were prepared by processes similar to those for **1**, of[18], and for **8**, respectively, but with the appropriate ligand. $VOSO_4$, CF_3COOH, and $K_2S_2O_8$ were purchased from Merck or Aldrich.
[b] Measured at 25 °C. [c] Turnover number (moles of acetic acid per mol of metal catalyst) determined by GLC or GC-MS; the reaction mixture, with an internal standard, was filtered to remove the ionic species and the metal complex, diethyl ether was added (which leads to further precipitation), and the reaction mixture was filtered again. [d] Molar yield [%] based on CH_4, i.e. moles of acetic acid per 100 moles of methane. [e] Less CH_4 was used (1.84 mmol) than in the conditions described in footnote [a] by using a higher volume of CF_3COOH (28 mL). [f] Five times more metal catalyst (0.312 mmol) was used. [g] Less CH_4 was used (1.02 mmol) than in the conditions described in footnote [a] by using a smaller reactor (23.5 mL): metal catalyst (0.046 mmol), $K_2S_2O_8$ (9.2 mmol i.e. 200:1 molar ratio of $K_2S_2O_8$ to metal catalyst), CF_3COOH (17 mL). [h] Less CH_4 was used (1.02 mmol) than in the conditions described in footnote [a] by using a higher volume of CF_3COOH (32 mL).

activities. Of the oxo-V complexes with aminoalcohol ligands (basic forms), **1** is the most active, whereas the activity decreases on replacement of alcoholato by carboxylato groups; that is, **2** and **6** are less active than **1** (Table 1, entries 10, 22, 2). The active species, at least for the [VO(*N,O*-L)] and [V(*N,O*-L)]$^{2-}$ types, are believed to have the metal in the +5 oxidation state (the starting blue V^{IV} complexes **3** and **4** are oxidized by $K_2S_2O_8$ to the respective red V^{V} forms).

Interestingly, the carboxylation of CH_4 does not require CO. With amavadine (**3**) and its model **4**, as well as with complex **1**, yields of acetic acid within the 20–30% range (TON ca. 10–13) are commonly obtained under standard conditions (entries 12, 16, and 2). CH_4 is the carbon source for the methyl group of acetic acid as we demonstrated by using ^{13}C-labeled CH_4. The product, $^{13}CH_3COOH$, was determined by the $^{13}C\{^1H\}$ and ^{13}C NMR spectra of the reaction solution. The carbon source of the carboxylic acid group, in the absence of CO, is CF_3COOH, which is known[4d] to undergo radical reactions with $K_2S_2O_8$ derivatives to form, for example, CO_2. However, our reactions do not appear to proceed via a free CO_2 intermediate or free CH_3OH, since the former does not promote the carboxylation and the latter is not converted into the acid under our experimental conditions.

Although the mechanistic details are still unknown, the carboxylation of methane may possibly involve the formation of the methyl radical and the derived methyl cation (upon hydrogen abstraction from CH_4 followed by oxidation, for example, by a V^{V}-oxo or V^{V}-peroxo species) which would react[12] with CF_3COOH. The role of the chelating N,O and O,O ligands still remains unclear, but one can postulate their involvement (upon decoordination of a single N or O atom of the ligand) in proton-transfer steps, for example, among oxo- or hydroxo-V species and CF_3COOH or $K_2S_2O_8$ (which, acting as an oxidant, can give[12] HSO_4^- and $HSO_4^{\bullet}$). A related role in promoting proton transfer from coordinated H_2O_2 to oxo ligands has been suggested[13] for some vanadium systems such as nBu$_4$NVO$_3$/H_2O_2/O_2, whose activity towards alkane oxygenation requires[9,13] particular N,O additives as cocatalysts (e.g. heteroaromatic aminocarboxylic acids like pyrazine-2-carboxylic acid). Moreover, in amavadine (**3**) and its model **4**, the hydroxyimino(1−) groups of the ligands, η^2-(O-N<)$^-$, are isoelectronic with peroxo(2−), and their possible behavior as peroxo-like ligands also deserves consideration.

The formation of CH_3COOH from CH_4 can be enhanced by the presence of CO at sufficiently low pressures, which suggests that CO can behave as a carboxylating agent, as was clearly observed for **7** (Table 1, entries 23–25) and **8** (entries 26–28). For **1** this enhancing effect is very small (Figure 1), whereas for **3** and **4** (entries 12–14 and 16, 17) it was not detected at all. Moreover, higher CO pressures often result in an inhibiting effect (Figure 1 for **1** and entries 23–25 for **7**), conceivably because ligation of CO lowers the activity of the catalyst; we are investigating this possibility.

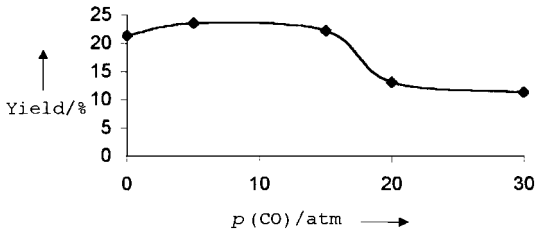


Figure 1. Effect of CO pressure on the yield of acetic acid derived from methane (at 5 atm) by using catalyst **1** and $K_2S_2O_8$ in CF_3COOH (see Table 1).

  0044-8249/03/11507-0846 $ 20.00+.50/0

The increase of CH_4 pressure (up to 12 atm in our work) can have a notorious enhancing effect on the TONs (entries 5–7 and 17, 18), whereas the yield tends to decrease after reaching a maximum (entries 5–7). Higher yields can be obtained when less CH_4 is used but at the same pressure (e.g., entry 8 vs. 4 and entry 15 vs. 14), or when more metal catalyst is employed (entry 9 vs. 3).

The reaction does not occur in the absence of $K_2S_2O_8$, CF_3COOH (which is replaced by ethanol or water as the solvent), or the V catalyst. Related complexes with other metals, even of the same periodic group, display little or no catalytic activity. The carboxylation by CO is also strongly hampered when acetonitrile is used instead of CF_3COOH.

This direct one-pot synthesis of CH_3COOH from CH_4 without required CO is a process whose simplicity and low energy requirements contrast with the features of the industrial route.[4e] The established synthesis involves three separate stages: the metal-catalyzed high-temperature steam-reforming of CH_4, conversion of the derived synthesis gas to CH_3OH, and final carboxylation of CH_3OH with CO and either an expensive Rh catalyst (Monsanto process) or an Ir catalyst (BP–Amoco modified process). The route we now report has also the advantage of requiring a cheap V catalyst, but we are still searching for less expensive solvents, carboxylating agents, and oxidants. The V catalysts used in this work are also effective in the carboxylation of other alkanes apart from CH_4 to give the corresponding carboxylic acids, and the study of these catalytic reactions is underway. Of particular interest is the behavior of amavadine, whose catalytic activity is now extended to such interesting reactions. Can they take place in natural conditions and also be of biological significance?

Received: September 24, 2002 [Z50224]

[1] a) J. J. R. Fraústo da Silva, R. J. P. Williams, *The Biological Chemistry of the Elements*, 2nd ed., Clarendon Press, Oxford, **2001**; b) "Vanadium Compounds": *ACS Symp. Ser.* **1998**, *711*; c) D. Rehder, *Coord. Chem. Rev.* **1999**, *182*, 297.

[2] a) C. M. M. Matoso, A. J. L. Pombeiro, J. J. R. Fraústo da Silva, M. F. C. G. da Silva, J. A. L. Silva, J. L. Baptista-Ferreira, F. Pinho-Almeida, *ACS Symp. Ser.* **1998**, *711*, 241–247; b) M. F. C. G. da Silva, J. A. L. Silva, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, C. Amatore, J.-N. Verpeaux, *J. Am. Chem. Soc.* **1996**, *118*, 7568.

[3] P. M. Reis, J. A. L. Silva, J. J. R. Fráusto da Silva, A. J. L. Pombeiro, *Chem. Commun.* **2000**, 1845.

[4] a) C. Jia, T. Kitamura, Y. Fujiwara, *Acc. Chem. Res.* **2001**, *34*, 633; b) R. H. Crabtree, *J. Chem. Soc. Dalton Trans.* **2001**, 2437; c) A. E. Shilov, G. B. Shul'pin, *Chem. Rev.* **1997**, *97*, 2879; d) Y. Fujiwara, K. Takaki, Y. Taniguchi, *Synlett* **1996**, 591; e) *Catalytic Activation and Functionalisation of Light Alkanes* (Eds.: E. G. Derouane, J. Haber, F. Lemos, F. R. Ribeiro, M. Guisnet), Kluwer, Dordrecht, **1998**; e) R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, Wiley, New York, **2001**, chap. 12.

[5] Y. Taniguchi, T. Hayashida, H. Shibasaki, D.-G. Piao, T. Kitamura, T. Yamaji, Y. Fujiwara, *Org. Lett.* **1999**, *1*, 557.

[6] a) T. Nishiguchi, K. Nakata, K. Takaki, Y. Fujiwara, *Chem. Lett.* **1992**, 1141; b) M. Asadullah, Y. Taniguchi, T. Kitamura, Y. Fujiwara, *Appl. Catal. A* **2000**, *194–195*, 443.

[7] a) M. Asadullah, T. Kitamura, Y. Fujiwara, *Angew. Chem.* **2000**, *112*, 2609; *Angew. Chem. Int. Ed.* **2000**, *39*, 2475; b) M. Asadullah, T. Kitamura, Y. Fujiwara, *Appl. Organomet. Chem.* **1999**, *13*, 539.

[8] M. Asadullah, T. Kitamura, Y. Fujiwara, *Chem. Lett.* **1999**, 449.

[9] G. V. Nizova, G. Süss-Fink, S. Stanislas, G. B. Shul'pin, *Chem. Commun.* **1998**, 1885.

[10] a) M. Lin, A. Sen, *Nature* **1994**, *368*, 613; b) M. Lin, A. Sen, *J. Chem. Soc. Chem. Commun.* **1992**, 892.

[11] A. Bagno, J. Bukala, G. A. Olah, *J. Org. Chem.* **1990**, *55*, 4284.

[12] a) D.-G. Piao, K. Inoue, H. Shibasaki, Y. Taniguchi, T. Kitamura, Y. Fujiwara, *J. Organomet. Chem.* **1999**, *574*, 116; b) G. Yin, D.-G. Piao, T. Kitamura, Y. Fujiwara, *Appl. Organomet. Chem.* **2000**, *14*, 438.

[13] a) G. B. Shul'pin, *J. Mol. Catal. A* **2002**, *189*, 39; b) G. B. Shul'pin, Y. N. Kozlov, G. V. Nizova, G. Süss-Fink, S. Stanislas, A. Kitaygorodskiy, V. S. Kulikova, *J. Chem. Soc. Perkin Trans. 2* **2001**, 1351.

[14] D. C. Crans, H. Chen, O. P. Anderson, M. M. Miller, *J. Am. Chem. Soc.* **1993**, *115*, 6769.

[15] R. E. Berry, E. M. Armstrong, R. L. Beddoes, D. Collison, S. N. Ertok, M. Helliwell, C. D. Garner, *Angew. Chem.* **1999**, *111*, 871; *Angew. Chem. Int. Ed.* **1999**, *38*, 795.

[16] P. Caravan, L. Gelmini, N. Glover, F. G. Herring, H. Li, J. H. McNeill, S. J. Rettig, I. A. Setyawati, E. Shuter, Y. Sun, A. S. Tracey, V. G. Yuen, C. Orvig, *J. Am. Chem. Soc.* **1995**, *117*, 12759.

[17] C. T. Chen, J. H. Kuo, C. H. Li, N. B. Barhate, S. W. Hon, T. W. Li, S. D. Chao, C. C. Liu, Y. C. Li, I. H. Chang, J. S. Lin, C. J. Liu, Y. C. Chou, *Org. Lett.* **2001**, *3*, 3729.

[18] B. J. Hamstra, A. L. P. Houseman, G. J. Colpas, J. W. Kampf, R. LoBrutto, W. D. Frasch, V. L. Pecoraro, *Inorg. Chem.* **1997**, *36*, 4866.