Carboxylation of methane with CO or CO_2 in aqueous solution catalysed by vanadium complexes

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Reaction of methane with CO or CO_2 in aqueous solution in the presence of O_2 (catalysed by $NaVO_3$) or H_2O_2 (catalysed by $NaVO_3$–pyrazine-2-carboxylic acid) at 25–100 °C affords acetic acid and in some cases also methanol, methyl hydroperoxide and formaldehyde.

The direct conversion of methane, the least reactive representative of the very inert saturated hydrocarbon family, into valuable chemical products under mild conditions is a challenging problem of metal complex catalysis.[1] A very small number of publications have appeared that describe the homogeneous carboxylation of methane in the absence[2a] or in the presence[2b–e] of soluble metal compounds (see also recent works on theoretical study of carbonylation[3a] and carboxylation with the participation of solid metals[3b]).

We have found that heating an aqueous solution of sodium vanadate in the presence of methane, carbon monoxide and air gives rise to the formation of acetic acid, as well as, in smaller amounts, of methanol and formaldehyde (Table 1).† The yield of acetic acid attains 3700% based on vanadium after 50 h at 100 °C, the total turnover number being 49. In the absence of either V^V or CH_4, no products have been detected. When a larger concentration of vanadate (1.0×10^{-3} mol dm^{-3}) was used, in the absence of air, only 0.2×10^{-3} mol dm^{-3} of $MeCO_2H$ was formed after 16 h at 100 °C. While in the course of the reaction with air the solution remains pale yellow, in the case when air is absent the colour of the solution becomes blue indicating the formation of a V^{IV} derivative. Thus it can be concluded that atmospheric oxygen is capable of reoxidizing the V^{IV} species formed in the reaction between methane, VO_3^- and CO. The yield of acetic acid and its relative content in the mixture of the products increases with the increase of partial CO pressure (Table 2). A comparison to Sen's catalytic system ($RhCl_3$/KI), which gives 790% of acetic acid (based on Rh) after 20 h at 80 °C,[2e] shows that the inexpensive sodium vanadate is more active giving a yield of 3300% of acetic acid (based on V) after 25 h at 100 °C.

Table 1 Carboxylation of methane by carbon monoxide in the presence of air catalysed by $NaVO_3$ in aqueous solution[a]

		Products (concentration/10^3 mol dm^{-3})		
T/°C	*t*/h	$MeCO_2H$	MeOH	HCHO
80	5	0.3	0.2	0.03
	15	0.6	0.4	0.1
	25	1.0	0.6	0.5
100	6	2.0	0.9	0.6
	25	3.3	1.1	1.0
	50	3.7	1.9	1.2

[a] Conditions, see Footnote †. Pressures and concentrations: CH_4, 50 bar; CO, 15 bar; synthetic air, 15 bar; $NaVO_3$, 1.0×10^{-4} mol dm^{-3}; initial pH = 7.30.

Hydrogen peroxide can be used instead of molecular oxygen as reoxidizing agent in the carboxylation using pyrazine-2-carboxylic acid (PCA)[4] as a co-catalyst; no products are detected in the absence of PCA. In this case the selectivity of the reaction depends strongly on temperature and CO pressure (Table 3),‡ the carboxylation at room temperature and relatively high CO pressure yielding acetic acid as a sole product. The initial rate of acetic acid accumulation depends linearly on the initial pressure of methane (when this pressure < 50 bar) and on initial concentration of hydrogen peroxide (when $[H_2O_2] < 0.1$ mol dm^{-3}). The role of PCA in aqueous solution is not completely clear; on the basis of preliminary investigations we can assume that PCA stabilises an active vanadium peroxo species, while the protons from PCA simultaneously facilitate the substitution of coordinated water ligands by H_2O_2 in the coordination sphere of vanadium. The reaction of ethane (20 bar) with CO (5 bar) and H_2O_2 (0.1 mol dm^{-3}) in the presence of $NaVO_3$ (1.0×10^{-4} mol dm^{-3}) gave after 2 h at 40 °C propionic acid (3.0×10^{-4} mol dm^{-3}) and acetic acid (3.3×10^{-3} mol dm^{-3}).

Interestingly, the carboxylation of methane also occurs, when carbon dioxide is used instead of carbon monoxide. Under the conditions described in Table 3, the yield of acetic acid is 2000% based on vanadium after 30 h at 40 °C; methanol was also observed (10^{-4} mol dm^{-3}). No acetic acid can be detected, when the reaction was carried out in the absence of either CH_4 or CO_2.

We believe that the reaction involves hydrogen atom abstraction from methane by a radical or radical-like species. In the case of hydrogen peroxide as an oxidising agent, this species could be a hydroxyl radical or vanadium peroxo complex.[4] The vanadate anion (like permanganate or chromate ions) can also add hydrogen from an alkane to one of oxygen atoms reducing V^V into V^{IV}.[5] The methyl radicals thus formed will react[6] with CO to give the radicals $RCO^\bullet$ and then, after interaction with O_2, produce the radicals $RCOOO^\bullet$ and peroxyacetic acid. If carbon dioxide is used as carboxylating reagent, in the first stage CO_2 is apparently reduced into CO by methyl or/and hydroxyl

Table 2 Carboxylation of methane by carbon monoxide in the presence of air catalysed by $NaVO_3$ in phosphate aqueous buffer solution at various pressures of CO[a]

	Products (concentration/10^3 mol dm^{-3})		
Pressure CO/bar	$MeCO_2H$	MeOH	HCHO
5	0.0	1.3	0.1
10	0.2	1.4	0.3
15	0.4	1.4	0.3
30	0.5	0.6	0.1

[a] Conditions, see Footnote †. Pressures and concentrations: CH_4, 50 bar; synthetic air, 15 bar; $NaVO_3$, 1.0×10^{-4} mol dm^{-3}; pH = 7.01 constant in the course of the reaction; 100 °C; 15 h.

Table 3 Carboxylation of methane by carbon monoxide in the presence of H_2O_2 catalysed by $NaVO_3$ and PCA in aqueous solution[a]

			Products (concentration/10^3 mol dm^{-3})	
Pressure CO/bar	*T*/ °C	*t*/h	$MeCO_2H$	MeOOH
5	25	2	0.9	0.0
		8	1.1	0.0
		16	1.3	0.0
		48	1.6	0.0
	40	2	1.1	0.8
		4	1.3	1.4
		8	1.7	1.7
		16	1.8	2.1
		48	1.9	2.6
	60	2	0.4	0.9
		4	0.5	1.6
		7	0.5	2.3
		16	0.5	2.8
30	25	2	0.4	0.0
		4	0.7	0.0
		8	0.9	0.0
		16	1.1	0.0
		50	1.6	0.0
	40	2	0.5	0.0
		4	0.8	0.0
		8	1.2	0.0
		16	1.4	0.0
		50	2.2	0.0

[a] Conditions, see Footnote ‡. Pressures and concentrations: CH_4, 50 bar; H_2O_2, 0.1 mol dm^{-3}; $NaVO_3$, 1.0×10^{-4} mol dm^{-3}; PCA, 4.0×10^{-4} mol dm^{-3}. Value 0.0 means below detection limit (0.5×10^{-4} mol dm^{-3}).

radicals (dry CO_2 reforming of methane in the presence of solid catalyst at high temperatures is well-known process[7]).

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Notes and References

† The oxidations were carried out in a stainless steel autoclave with intensive stirring (volume of the reaction solution = 30 ml and total volume of autoclave = 100 ml). The autoclave was charged with synthetic air (78% N_2, 21% O_2, 1% Ar), and consecutively with carbon monoxide and methane to the appropriate pressures. The reactions were stopped by cooling with ice, and the reaction solution was analysed for $MeCO_2H$ and MeOH by GC (DANI-86.10; fused silica capillary column 25 m × 0.32 mm × 0.25 μm, CP-WAX52CB; integrator SP-4400), as well as by GC–MS (NERMAG R 30-10, capillary column 25 m × 0.32 mm × 0.25 μm, CP-WAX52CB) and ^1H NMR (Varian spectrometer, 200 MHz; in D_2O; in this case GC–MS analysis testified partial H–D exchange in methyl groups of $MeCO_2H$ and MeOH formed). The concentration of formaldehyde was measured spectrophotometrically after its transformation into 2,6-dimethyl-3,5-diacetyl-1,4-dihydropyridine as described previously.[4b]

‡ The reaction was carried out in a glass tube placed into the stainless steel autoclave (100 ml, volume of the solution = 10 ml). (**CAUTION**: the combination of air and H_2O_2 with organic compounds at elevated pressures and temperatures may be explosive!). The resulting solution was analysed by GC (the concentration of MeOOH was measured as concentration of MeOH after reduction of the solution with sodium tetrahydroborate[4]), as well as by GC–MS and ^1H NMR.

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