

# Oxygenation of methane with atmospheric oxygen in aqueous solution promoted by H<sub>2</sub>O<sub>2</sub> and catalyzed by a vanadate ion—pyrazine-2-carboxylic acid system

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Methane is oxidized in aqueous solution with atmospheric oxygen and hydrogen peroxide in a reaction catalyzed by a NaVO<sub>3</sub>—pyrazine-2-carboxylic acid system. Methyl hydroperoxide is selectively formed at 50 °C. The turnover number of the catalyst after 24 h amounts to 480, and the yield of methyl hydroperoxide is 24% with respect to H<sub>2</sub>O<sub>2</sub>. Formaldehyde and formic acid are mainly formed at 120 °C.

**Key words:** activation of C—H bond, alkanes, hydroxyl radicals, metallocomplex catalysis, methane, methyl hydroperoxide, formic acid, oxidation, hydrogen peroxide, vanadium complexes, formaldehyde.

The search for new ways of processing methane to obtain valuable chemical products is of great scientific and practical interest due to its considerable reserves, although, on the other hand, methane is the most inert organic compound.<sup>1,2</sup>

Previously, we have shown that hydrocarbons and some other compounds are readily oxidized with atmospheric oxygen in acetonitrile in the presence of hydrogen peroxide and a vanadate anion—pyrazine-2-carboxylic acid (PCA) catalytic system.<sup>3–12</sup> The optimum

VO<sub>3</sub><sup>-</sup>/PCA ratio lies in the 1 : 2 to 1 : 4 range. It has also been shown that under the action of this catalyst H<sub>2</sub>O<sub>2</sub> decomposes under mild conditions to give hydroxyl radicals, which attack the alkane molecules. The alkyl radicals produced add oxygen and are converted into alkyl hydroperoxides. Thus, H<sub>2</sub>O<sub>2</sub> only acts as a promoter and is used in stoichiometric amounts, whereas molecular oxygen is the true oxidant in this reaction.

Since acetonitrile also reacts with hydroxyl radicals, it was of interest to investigate the possibility of oxida-

**Table 1.** Oxidation of methane in aqueous solution in the presence of  $\text{NaVO}_3 + \text{PCA}$  (1 : 4) and in the absence of the catalyst

$T/^\circ\text{C}$	$C \cdot 10^3/\text{mol L}^{-1}$		
	MeOOH	$\text{CH}_2\text{O}$	HCOOH
50	9.6 (0.0)	0.0 (0.0)	0.0 (0.0)
60	9.4 (—)	0.0 (—)	0.0 (—)
70	8.5 (0.9)	0.0 (0.05)	0.0 (0.0)
100	6.0 (0.0)	1.4 (1.3)	3.0 (2.0)
120	0.0 (0.0)	2.4 (2.5)	10.2 (8.5)

*Note.* Duration of the reaction is 4 h. The concentrations of the reagents and the reaction conditions are given in the Experimental. The results obtained in the absence of the catalyst are given in parentheses. Only MeOOH was obtained in the presence of the catalyst (concentrations of MeOOH  $2.4 \cdot 10^{-3}$ ,  $5.1 \cdot 10^{-3}$ , and  $9.3 \cdot 10^{-3}$  mol  $\text{L}^{-1}$  at 20, 30, and 40  $^\circ\text{C}$ , respectively), while none of the products (1, 2, or 3) was observed in the absence of the catalyst.

tion in aqueous medium. In addition to its inertness, water attracts particular attention since it is cheapest and is an ecologically pure solvent.

We found that methane is oxidized in aqueous solution at 20–120  $^\circ\text{C}$  (at a pressure of methane and air of 75 and 10 bar, respectively) in the presence of  $\text{H}_2\text{O}_2$  and catalytic amounts of a  $\text{NaVO}_3 + \text{PCA}$  (1 : 4) system to give three products: methyl hydroperoxide (1), formaldehyde (2), and formic acid (3).

Compound 1 was identified by the  $^1\text{H}$  NMR spectroscopy. A singlet signal of 1 at  $\delta$  3.80 was found in the spectra of both aqueous solution of 1 synthesized from  $\text{Me}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  and the reaction solution after oxidation of methane. This signal disappears after addition of  $\text{NaBH}_4$  to both solutions, and a new singlet at  $\delta$  3.29 due to the protons of methanol obtained in the reduction of 1 appears instead. The quantitative analysis of 1 was performed by GLC after reduction of 1 to MeOH by sodium borohydride (the peak of MeOH was not observed on the chromatogram before reduction).

The concentrations of the products formed in 4 h at different temperatures in the 50–120  $^\circ\text{C}$  range are given in Table 1. Compound 1 is the only product at tempera-

**Table 2.** Consumption of hydrogen peroxide and accumulation of methyl hydroperoxide in the oxidation of methane in aqueous solution of the  $\text{NaVO}_3 + \text{PCA}$  (1 : 4) catalyst (at 50  $^\circ\text{C}$ )

$\tau/\text{h}$	$C/\text{mol L}^{-1}$		$\tau/\text{h}$	$C/\text{mol L}^{-1}$	
	$\text{H}_2\text{O}_2$	MeOOH		$\text{H}_2\text{O}_2$	MeOOH
0	0.193	0	8	0.123	0.015
1	0.186	0.001	14.5	0.061	0.031
2	0.171	0.006	20	0.043	0.043
4	0.156	0.010	24	0.020	0.048

*Note.* The concentrations of the reagents and the reaction conditions are given in the Experimental.

tures below 70  $^\circ\text{C}$ , whereas compounds 2 and 3 are also formed at this and higher temperatures. The maximum concentration of 1 after 4 h at 50  $^\circ\text{C}$  is  $9.6 \cdot 10^{-3}$  mol  $\text{L}^{-1}$ , which corresponds to the turnover number of the catalyst of 96 and to a 5% yield of 1 with respect to  $\text{H}_2\text{O}_2$ . Compound 1 is accumulated linearly with time (Table 2), and the turnover number of the catalyst and the yield of 1 after 24 h amount to 480 and 24%, respectively. The initial reaction rate (defined as the yield of 1 over a period of 4 h at 50  $^\circ\text{C}$ ) depends linearly on the initial concentration of  $\text{H}_2\text{O}_2$ :

$\text{H}_2\text{O}_2/\text{mol L}^{-1}$	0.193	0.04	0.02
$[\text{MeOOH}] \cdot 10^2/\text{mol L}^{-1}$	0.96	0.29	0.01

No hydroperoxide 1 is formed in the absence of the catalyst at temperatures below 70  $^\circ\text{C}$ ; however, it is obtained along with compounds 2 and 3 at higher temperatures both in the presence and in the absence of the catalyst ( $\text{NaVO}_3 + \text{PCA}$ , 1 : 4) (see Table 1). It can be assumed that the decomposition of  $\text{H}_2\text{O}_2$  with the formation of hydroxyl radicals at relatively high temperatures in the absence of the vanadium-containing catalyst is due to admixtures of ions of transition metals (for instance, of iron and manganese, which pass into solution from the metal surfaces of the autoclave). In this case the reaction proceeds by the same mechanism that operates in the catalysis by the  $\text{NaVO}_3 + \text{PCA}$  (1 : 4) system; however, most of the  $\text{MeOO}^\cdot$  radicals formed are further converted into more stable products 2 and 3. The advantage of the  $\text{NaVO}_3 + \text{PCA}$  (1 : 4) catalyst is its ability to efficiently decompose  $\text{H}_2\text{O}_2$  to form hydroxyl radicals at much lower temperatures without decomposition of relatively unstable methyl hydroperoxide formed in the reaction. Therefore, the use of this catalyst makes it possible to convert methane into hydroperoxide 1 with high selectivity under mild conditions.

## Experimental

Oxidation of methane was carried out in cylindrical glass vessels placed in stainless steel autoclaves with vigorous stirring at constant temperature. The volume of the reaction solution was 30 mL, and the total volume of the autoclave was 100 mL. At the beginning, air and methane (at a pressure of 10 and 75 bar, respectively) were introduced into the aqueous solution of  $\text{H}_2\text{O}_2$  (0.193 mol  $\text{L}^{-1}$ ; a 35% aqueous solution; Fluka) and the catalyst ( $\text{NaVO}_3$ ,  $1 \cdot 10^{-4}$  mol  $\text{L}^{-1}$ , and PCA,  $4 \cdot 10^{-4}$  mol  $\text{L}^{-1}$ , in all cases) in the autoclave. (Caution: mixtures of air and  $\text{H}_2\text{O}_2$  with organic compounds are potentially explosive at elevated temperatures and pressures!). After completion of the process, the vessel was cooled in ice and opened.

The reaction solutions were analyzed by GLC on a DANI-86.10 chromatograph equipped with a flame ionization detector, a capillary column (Carbowax 20M, 50 m  $\times$  0.25 mm), and an SP-4400 integrator. Helium was used as the carrier gas. Each sample was analyzed twice, before and after addition of excess  $\text{NaBH}_4$ .

Formaldehyde (2) was determined spectrophotometrically after its conversion into 3,5-diacetyl-2,6-dimethyl-1,4-dihydropyridine.<sup>13</sup> The concentration of 3 was measured by titration

with potassium hydroxide. Methyl hydroperoxide (**1**) was synthesized following the known procedure.<sup>14</sup>

Water was distilled twice prior to use in the reaction. Gaseous methane (Carbagas, content 99.95%) was used without preliminary purification.

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