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Vanadate Ion–Catalyzed Oxidation of Methane with Hydrogen Peroxide in an Aqueous Solution

V. B. Romakh[a,b], G. Süss-Fink[a], and G. B. Shul'pin[b]

[a] *Institute of Chemistry, University of Neuchâtel, Avenue de Bellevaux 51, Neuchâtel, CH-2009, Switzerland*

[b] *Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina 4, Moscow, 119991 Russia*
e-mail: gbsh@mail.ru

Abstract—It was shown that, unlike methane oxidation with the reagent "hydrogen peroxide–vanadate anion–pyrazine-2-carboxylic acid (PCA)" in acetonitrile, the performance of the process in an aqueous solution is accompanied by the intense parallel degradation of the cocatalyst. Therefore, relatively high yields of methane oxidation products (largely, formic acid) cannot be attained unless a rather high PCA concentration is used. Admixtures of a strong acid (sulfuric, trifluoroacetic, or perchloric) increase the yield of the products. It was found that perchloric acid can also be used as a cocatalyst instead of PCA.

The functionalization of saturated hydrocarbons, the "noble gases" of organic chemistry [1], is an important area of metal-complex catalysis [2–9]. Obtaining products of the partial oxidation of the most inert alkane methane is an especially challenging problem. It is known that vanadium derivatives catalyze the oxidation and oxidative functionalization of alkanes, including methane [10–16].

Earlier, we found that a vanadate anion in an acetonitrile solution catalyzes the effective oxidation of saturated hydrocarbons with air oxygen in the presence of hydrogen peroxide at low temperatures (20–70°C) [17–30]. The presence of pyrazine-2-carboxylic acid (PCA) as a cocatalyst in concentrations that sometimes exceed the concentration of a vanadium complex is a necessary condition for the reaction. The primary product of the reaction is alkyl hydroperoxide, which decomposes during the process yielding the corresponding carbonyl compound (ketone or aldehyde) and alcohol.

A study of the selectivity parameters in the oxidation of various alkanes showed that the oxidizing action of the test system is due to the formation of hydroxyl radicals, which attack C–H bonds in an alkane. It was assumed [26] that the PCA anion coordinated to vanadium facilitates the processes of the proton transfer between ligands in the vanadium coordination sphere and, thus, accelerates the reaction of the generation of hydroperoxyl and hydroxyl radicals. Bell et al. [31] performed a density functional theory (DFT) study of our reagent. They showed that the direct proton transfer from the H_2O_2 molecule to the oxygen atom of a vanadium-containing species indeed has a substantially higher barrier as compared to that of proton migration first from hydrogen peroxide to the carboxyl group of the pyrazine-2-carboxylate anion coordinated to the vanadium ion through the nitrogen atom and only then to the V=O moiety. Recently, on the basis of the results of the study of the electronic absorption spectra of solutions and the kinetics of isopropanol oxidation with this system, it has been concluded [30] that the decomposition of vanadium(V) diperoxocomplex with the PCA anion is the rate-determining step of the process and the species that induces the oxidation of isopropanol is the hydroxyl radical.

It was assumed [28] that H_2O_2 degradation in an organic solvent proceeds as a radical nonchain process. Preliminary data [23, 24] obtained earlier indicate that this system oxygenates alkanes in an aqueous solution as well. Since water is a quite attractive (inexpensive and environmentally friendly) solvent, it was interesting to investigate in more detail the methane oxidation in an aqueous solution.

In the present work, we investigated the behavior of the vanadate ion and PCA during the oxidation of methane in an aqueous solution in the presence of hydrogen peroxide and air at a pressure ranging from atmospheric to 10 bar and a temperature ranging from ambient to 90°C.

EXPERIMENTAL

The experiments with methane were carried out in 100-ml autoclaves. A glass tube containing a solvent, the catalyst, the cocatalyst, and hydrogen peroxide was inserted into a steel autoclave, which was tightly closed and filled with air. After that, methane was supplied into the autoclave under the required pressure. WARNING! Mixing air or molecular oxygen and hydrogen peroxide with organic compounds at elevated temperature can result in an explosion! After the cessation of the reac-

Table 1. Effect of water on methane oxidation in an acetonitrile solution[a]

$[H_2O]_{tot}$, mol/l	Time, h	$[H_2O]_{in}$, mol/l	$[H_2O]_{fin}$, mol/l	[Products], mmol/l	TON[b]
0.7	16	0.20	0.15	18	180[c]
1.6	24	0.20	0.20	< 0.1	< 1[d]

Notes: [a] Reaction conditions: $[NBu_4VO_3]$ = 0.1 mmol/l, [PCA] = 0.4 mmol/l, p (methane) = 75 bar, p (air) = 10 bar, and 23°C.
[b] TON, the turnover number, is the number of moles of products per mole of catalyst.
[c] Determined by the GLC method.
[d] Determined by the GLC and ^{1}H NMR methods.

Table 2. Oxidation of methane in an aqueous solution at various PCA concentrations[a]

Solvent	$[KVO_3]$, mmol/l	[[PCA], mmol/l	Temperature, °C	Time, h	$[H_2O]_{in}$, mol/l	$[H_2O]_{fin}$, mol/l	[Products], mmol/l	TON[b]
D_2O–H_2O	0.1	0.1–0.4	50	4–24	0.20	0.19–0.20	<0.1	<1[b]
D_2O–H_2O (pH 8–9)	0.1–1.0	0.4–4.0	50	4–24	0.20	0.05–0.20	<0.1	<1[c]
D_2O	1.0	4.0	80	4	0.20	0.17	4.0	4[c]
D_2O	0.1	10.0	80	4	0.20	0.17	4.5	45[c]

Notes: [a] Reaction conditions: $[NBu_4VO_3]$ = 0.1 mmol/l, [PCA] = 0.4 mmol/l, p(methane) = 75 bar, p(air) = 10 bar, and 23°C.
[b] Determined by GLC ^{1}H NMR.
[c] Determined by ^{1}H NMR.

tion, the autoclave was ice cooled and the pressure was released. Samples of the gas mixture were placed into a container of 200-ml capacity and analyzed by the GLC technique. Aliquots of the reaction solution were analyzed by the GLC and ^{1}H NMR (Varian Gemini 200 BB and Bruker AMX 400 instruments) techniques.

Twice-distilled water and an hydrogen peroxide aqueous solution (30%, nonstabilized, Fluka) were used. The concentration of hydrogen peroxide was determined by titration with potassium permanganate and from electronic absorption spectra (230 nm, ε = 81 $mol^{-1}cm^{-1}$). PCA (98%) and potassium vanadate (99.5%) were purchased from Fluka and Aldrich, and tetrabutylammonium vanadate was synthesized according to a procedure described in [32].

A DANI-86.10 chromatograph with a SR-WAX52CB-coated capillary column of 25 m × 0.32 mm × 0.25 μm (helium as the carrier gas) and an SP-4400 integrator was used for the analysis. The chromatograms were calibrated with the authentic samples of the substrates and oxidation products. Gas mixtures (O_2, N_2, CH_4, CO, and CO_2) were analyzed with the use of a 500-μl syringe (Supelco Carboxen-1000 60/80 column, 4.5 m × 3.1 mm).

RESULTS AND DISCUSSION

Products of methane oxidation were determined by means of both the GLC and ^{1}H NMR techniques, because the latter technique provided information not only on the products formed from methane, but also on the behavior of PCA during the reaction. We have shown that the main product of methane oxidation in an aqueous solution is formic acid. The total amount of methylhydroperoxide, methanol, and formaldehyde does not exceed 10–20% of the quantity of formic acid. The formation of CO and CO_2 was undetectable under the given conditions. In special experiments, it was shown that the products of methane oxidation at temperatures below 90°C are formed only in trace quantities in the absence of PCA.

The results of two experiments on the oxidation of methane at ambient temperature in acetonitrile in the presence of different concentrations of water are presented in Table 1. The vanadate ion–PCA combination in a 1 : 4 ratio was used. Earlier, it was shown [26] that the highest rate of alkane oxidation in acetonitrile was achieved at this catalyst-to-cocatalyst ratio. From the data presented in Table 1, it follows that an increase in the concentration of water from 0.7 mol/l (1.3 vol %) to 1.6 mol/l (2.8 vol %) results in the complete suppression of the oxidation of methane.

In a D_2O solution, no products of methane oxygenation were found, even when the reaction was run for 24 h at 50°C and a vanadate to PCA ratio of 1 : 4 (Table 2). An increase in the pH to 8.0–9.0 resulted in the substantial degradation of hydrogen peroxide yielding molecular oxygen. When the temperature was elevated to 80°C and the vanadate and PCA concentrations were simultaneously increased, the formation of oxygenates with a turnover number (TON) of 4 per vanadate ion was observed. It turned out that the system most effectively operates at a low (0.1 mM) vanadate concentration, although a 100-fold excess of PCA over

Table 3. Buildup of products and PCA decomposition during methane oxidation in an aqueous solution at various temperatures[a]

Temperature, °C	Time, h	$[PCA]_{fin}$, mmol/l	[Products], mmol/l	TON
50	4	5.5	<0.1	<1
60	4	5.5	<0.1	<1
70	4	5.0	1.0	10
80	4	1.5	4.5	45
90	4	1.0	6.9	69
90	8	0.5	7.9	79
90[b]	4	10.0	0.00	

Notes: [a] Reaction conditions: $[KVO_3]$ = 0.1 mmol/l, $[PCA]_{initial}$ = 10 mmol/l, $[H_2O_2]_{in}$ = 0.2 mol/l, p(methane) = 75 bar, p(air) = 10 bar, and solvent D_2O. Concentration of products were determined by the ^1H NMR method;
[b] $[H_2O_2]_{in}$ = 0.

the vanadate ion is needed. In this case, the TON reaches 45 (formic acid is preferably formed).

The reason for the necessity for the use of a large excess of PCA in the reaction solution became clear after the study of the behavior of PCA during the process. The ^1H NMR data have shown that, unlike the case of the acetonitrile solution, PCA undergoes intensive oxidative degradation during the oxidation of methane with this system in water and, thus, the system rapidly loses its oxidizing power for methane. The results are summarized in Table 3. At temperatures of 50 and 60°C, the concentration of PCA decreases by almost one-half for 4 h. In this case, competing with methane in the oxidation process, PCA is oxidized much more quickly than the alkane and the alkane oxidation products are barely detectable. At 80°C when the PCA concentration decreases by a factor of 7 for 4 h, the system has enough time to form a significant amount of methane oxidation products (TON = 45). The competing oxidation of methane and PCA occurs even more intensively at 90°C: the concentration of PCA decreases by a factor of 20 for 8 h; however, the TON of methane oxidation reaches 79. It is obvious that PCA is oxidized with hydrogen peroxide, because a decrease in the PCA concentration was not observed even at 90°C in the absence of hydrogen peroxide (last line in Table 3).

We found that some strong inorganic and organic acids added to the aqueous solution substantially increase the yield of formic acid as the main product of methane oxygenation (Table 4). It is interesting that the yield depends on the order of the mixing of PCA and sulfuric acid. When sulfuric acid is added to the reaction solution first and PCA is added after that, the yield is twice as high as that in the case of the reverse order. The best result was achieved with the joint use of PCA and sulfuric acid as cocatalysts, although sulfuric acid itself is an effective oxidation promoter as well (last line in Table 4).

Thus, the behavior of the hydrogen peroxide–vanadate anion–PCA system in an aqueous solution radically differs from its behavior in acetonitrile. For the oxidation of an inert compound, such as methane, a significant excess of PCA, which intensively decomposes in the oxidative mode in water, is required.

Table 4. Oxidation of methane in an aqueous solution in the presence of PCA and various strong acids[a]

[PCA], mol/l	Temperature, °C	Time, h	Acid (mol/l)	[Products], mmol/l	TON
10	90	4	No	6.9	69
10	90	4	Sulfuric (0.1)[b]	8.8	88
10	90	4	Sulfuric (0.1)[c]	14.9	149
10	90	4	Trifluoroacetic (0.1)	10.2	102
10	90	4	Perchloric (0.1)	29.4	294
0	50	24	Perchloric (0.1)	14.8	148

Notes: [a] Reaction conditions: $[KVO_3]$ = 0.1 mmol/l, $[PCA]_{initial}$ = 10 mmol/l, $[H_2O_2]_{in}$ = 0.2 mol/l, p(methane) = 75 bar, p(air) =10 bar, and solvent D_2O. Concentrations of products were determined by the ^1H NMR method.
[b] PCA was added first to the reaction solution and, then, sulfuric acid.
[c] Sulfuric acid was added first to the reaction solution and, then, PCA.

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