Catalytic oxidation of methane to methyl hydroperoxide and other oxygenates under mild conditions

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Methane is oxidized by air in acetonitrile solution to give methyl hydroperoxide (easily reduced to methanol), formaldehyde and formic acid in the presence of [NBu$_4$]VO$_3$–pyrazine-2-carboxylic acid as the catalyst and H_2O_2 as a promoter.

The oxidation of saturated hydrocarbons with hydrogen peroxide and molecular oxygen catalysed by transition-metal complexes constitutes a convenient route for the direct transformation of these inert compounds to valuable products such as peroxides, ketones, alcohols and carboxylic acids.[1] Complexes of vanadium are known to catalyse the oxidation of various organic compounds by peroxides.[2,3]

We report here on the efficient oxidation of methane with air catalysed by the combination [NBu$_4$]VO$_3$–pyrazine-2-carboxylic acid (PCA) in the presence of hydrogen peroxide. The reactions of methane (and of cyclohexane as well) were carried out at various temperatures and pressures.§ The process was monitored by withdrawing aliquots at specific intervals and analysing each sample twice, *i.e.* before and after the addition of an excess of solid triphenylphosphine. This method described by us earlier[3,4] (and used then also by other workers[5]) allows one to detect alkyl hydroperoxides and to measure also the real concentrations of all three products (alkyl hydroperoxide, alcohol and aldehyde or ketone) present in the reaction solution, because usually alkyl hydroperoxides are decomposed in the gas chromatograph to produce the corresponding alcohol and ketone.¶

We have found that the combination of [NBu$_4$]VO$_3$ and PCA catalyses the oxidation of methane in acetonitrile solution in the presence of air and hydrogen peroxide to produce methyl hydroperoxide, formaldehyde and (after an induction period) formic acid (Table 1). Methyl hydroperoxide slowly decomposes to give methanol and formaldehyde. No methanol peak has been detected after opening the autoclave prior to the reduction with PPh$_3$. After the reduction with PPh$_3$ the MeOH peak appeared, while the concentration of HCHO in the solution dropped. The average rates of oxidation at 20, 40 and 75 °C are 7.5, 30 and 105 turnovers h^{-1}, respectively.

Table 1 Oxidation of methane by air in the presence of [NBu$_4$]VO$_3$–PCA–H_2O_2[a]

Pressure/bar				Products (concentration/ 10^2 mol dm^{-3})			
Methane	Air	*T*/°C	*t*/h	MeOOH	HCHO	HCO$_2$H	Total turnover[b]
75	10	23	6	0.5	0.04	0	54
			16	1.3	0.13	0	143
			24	1.6	0.16	0	176
75	10	40	1	1.6	0.18	0	178
			4	1.0	0.32	0.5	182
			6	0.5	0.37	1.5	207
			17	0.1	0.03	5.0	513
40	10	75	4	0	0.20	4.0	420

[a] Conditions and concentrations of components, see Footnote §. Standard deviations of analytic methods ±20%; value 0 means below detection limit (0.01×10^{-2} for MeOH, MeOOH and HCHO; 0.1×10^{-2} mol dm^{-3} for HCO$_2$H). [b] Moles of all detected products per mole of vanadate ion.

The oxidation of methane, catalysed by [NBu$_4$]VO$_3$–PCA, requires the presence of air and hydrogen peroxide. We believe that hydrogen peroxide, although present in stoichiometric amounts, acts only as a promoter, while molecular oxygen is the oxidant. In order to prove the implication of O_2 from air in the oxidation process, we studied the analogous reaction with liquid cyclohexane in the place of methane. When the reaction was carried out in the presence of H_2O_2 but in the absence of air (N_2 atmosphere, 40 °C, 2 h) no formation of oxygenated products was observed. However, when the reaction vessel was opened to air, the reaction started immediately with the same rate as observed in the presence of air.

Finally, the cyclohexane oxidation under an $^{18}O_2$ atmosphere unambiguously showed a high degree of ^{18}O incorporation into the oxygenated products.‖ Thus, according to the GCMS analysis, the measured extent of ^{18}O incorporation into cyclohexanol after the reduction with triphenylphosphine is *ca.* 75%. Prior to the reduction with PPh$_3$, the ^{18}O labelling of cyclohexanol was noticeably lower (*ca.* 50%), and only *ca.* 5% of ^{18}O was found in cyclohexanone. The triphenylphosphine oxide formed from the reduction of the reaction mixture with PPh$_3$ also contained ^{18}O. On the basis of these results one can assume that all oxygen present in the primary product of the oxidation (alkyl hydroperoxide, ROOH) stems from atmospheric dioxygen. Unlabelled oxygen (*ca.* 25%) detected in the cyclohexanol after the reduction with PPh$_3$ could originate from gaseous $^{16}O_2$, formed by catalytic decomposition of $H_2{}^{16}O_2$ in the reaction vessel. Such a decomposition proceeds rapidly in the injector of the chromatograph at high temperature. Cyclohexanone seems to be formed in the injector from cyclohexyl hydroperoxide completely *via* a mechanism involving the generation of alkyl radicals, R•, which react then with $^{16}O_2$.

We presume that in the presence of catalytic amounts of [NBu$_4$]VO$_3$–PCA, hydrogen peroxide is an efficient generator of hydroxyl radicals. The radicals HO• thus formed attack the alkane molecule, RH, abstracting a hydrogen atom. As a result, alkyl radicals, R•, are produced which rapidly react with molecules of oxygen to yield peroxyl radicals ROO• (see ref. 6). These latter species can then be transformed into ROOH. Stoichiometric quantities of H_2O_2 are presumably required in order to reactivate the catalyst system.

Thus it may be concluded that in the system described in the present work, hydrogen peroxide is only the promoter of the oxygenation, while molecular oxygen is the true oxidant. Such a scheme seems to be operative in many alkane oxidations with H_2O_2 in air (small amounts of molecular oxygen necessary for the addition to alkyl radicals can be formed by the decomposition of H_2O_2 even if the reaction is carried out in an inert atmosphere[6]). Indeed, previously we have found that alkyl hydroperoxides are formed as main products when higher alkanes are oxidized with H_2O_2 in air under the catalysis not only by the vanadium system studied in the present work,[3] but also by manganese porphyrinates, palladium complexes and iron salts,[4c] as well as by methyltrioxorhenium.[7] The reagent described in this paper is one of the most efficient ones (in terms of catalytic turnovers) for methane oxidation[8] under mild conditions (temperatures below 100 °C).

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Footnotes

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§ The oxidations were carried out in glass-lined stainless-steel autoclaves with vigorous stirring (volume of the reaction solution = 10 ml, total volume of autoclave = 100 ml). Usually the following concentrations of the reagents were used: $[NBu_4]VO_3$, 1.0×10^{-4} mol dm^{-3}; PCA, 4.0×10^{-4} mol dm^{-3}; H_2O_2 (35% aq), 0.2 mol dm^{-3}. Before the oxidation the autoclave was charged with air and then with methane under appropriate pressures. (**CAUTION**: the combination of air and H_2O_2 with organic compounds at elevated pressures and temperatures may be explosive!) The reactions were stopped by cooling with ice and the reaction solution was analysed by GC (DANI-86.10; fused silica capillary column 60 m × 0.25 mm × 0.25 μm, SPB-1; integrator SP-4400). The concentration of formaldehyde was measured spectrophotometrically after its transformation into 2,6-dimethyl-3,5-diacetyl-1,4-dihydropyridine according to method described in ref. 9.

¶ If an excess of solid PPh_3 is added to the reaction solution 10–20 min before the GC analysis, the alkyl hydroperoxide present is completely reduced to the corresponding alcohol. As a result, the chromatogram differs completely from that of a sample not subjected to the reduction (the alcohol peak increases, while the intensity of the ketone peak decreases). If there is no difference between chromatograms of the same sample before and after reduction, this testifies to the absence of an alkyl hydroperoxide in the solution. If, by contrast, the chromatogram prior to the reduction exhibits the peaks for the ketone and the alcohol, whereas after the reduction with PPh_3 only a peak for the alcohol is observed, one may conclude that only the alkyl hydroperoxide was present in the solution. This method allows one to determine alkyl hydroperoxides in the presence of hydrogen peroxide.

‖ The reaction was carried out in a sealed ampoule (10 ml) at 20 °C under an atmospheric pressure of $^{18}O_2$ (content 98%, Cambridge Isotope Laboratories) over 3 days; concentrations: cyclohexane, 0.46 mol dm^{-3}; H_2O_2 (35% aq), 0.2 mol dm^{-3}; $[NBu_4]VO_3$, 1.0×10^{-4} mol dm^{-3}, PCA, 4.0×10^{-4} mol dm^{-3}. The resulting solution was analysed by GCMS (NERMAG R 30-10, capillary column 50 m × 0.25 mm × 0.25 μm, Carbowax 20M).

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