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Oxidations by the Reagent «O_2 – H_2O_2 – Vanadium Complex – Pyrazine-2-carboxylic Acid» - 8.[1]

Efficient Oxygenation of Methane and Other Lower Alkanes in Acetonitrile

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Abstract: Methane, ethane, propane, *n*-butane and isobutane can be readily oxidized in acetonitrile solution by air and H_2O_2 at 20-75 °C using the catalytic system [*n*-Bu_4N]VO_3/pyrazine-2-carboxylic acid. Apart from alkyl hydroperoxides which are the primary oxidation products, more stable derivatives (alcohols, aldehydes or ketones and carboxylic acids) are obtained with high total turnover numbers (e.g., at 75 °C after 4 h: 420 for methane and 2130 for ethane). It was shown in the case of ethane and cyclohexane that alkanes do not yield oxygenated products in the absence of air. The cyclohexane oxidation under an $^{18}O_2$ atmosphere showed a high degree of ^{18}O incorporation into the oxygenated products. Thus in the oxidation reaction described here H_2O_2 is only the promoter while O_2 is the "true" oxidant.

The direct transformation of saturated hydrocarbons, whose inertness (especially of methane) is well-known, to valuable products such as alkyl hydroperoxides, ketones, alcohols, carboxylic acids is a challenging task for both the academic science and chemical industry.[4] The oxidation of saturated hydrocarbons with hydrogen peroxide and molecular oxygen catalyzed by transition metal complexes in solutions under relatively mild conditions constitutes a convenient route for such transformations. Complexes of vanadium are known to exhibit a catalytic activity in the oxidation of various organic compounds by hydrogen peroxide and organic peroxides.[5] Recently we have demonstrated that hydrogen peroxide oxidizes hydrocarbons and alcohols in acetonitrile in air if a combination of tetrabutylammonium vanadate and pyrazine-2-carboxylic acid (PCA) is used as catalyst.[1] Almost no reaction occurs in the absence of PCA. Acetonitrile has been found to be the best solvent. At ambient temperature, the reaction with higher alkanes gives rise predominantly to the formation of alkyl hydroperoxides which are of great importance in organic chemistry.[6] Substantially lower amounts of corresponding alcohols and ketones (aldehydes) are formed simultaneously. However, at elevated (> 50 °C) temperatures alcohols and carbonyl derivatives become the main products.

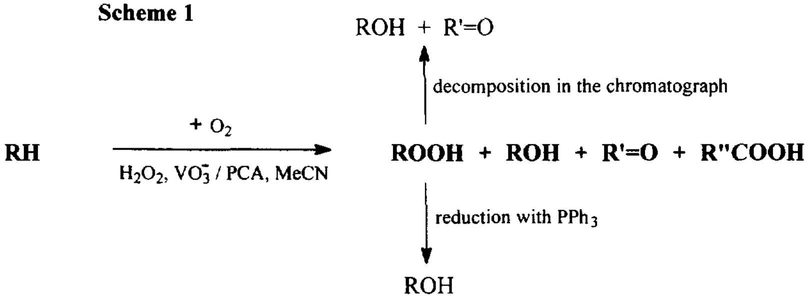
It should be noted that the reagent under discussion oxidizes higher alkanes and arylalkanes more efficiently than many other systems based on hydrogen peroxide and transition metal complex.[4,7] It is noteworthy that in the oxidation of linear alkanes the site selectivity is low [e.g. for *n*-heptane C(1):C(2):C(3):C(4) ≈ 1:4:4:4] and therefore the relative amount of the product of methyl group oxygenation is high. Taking into account the latter feature of the reaction one could propose that the reagent under discussion will easily oxidize methane which is known to be the least reactive organic compound. Since methane is simultaneously the most abundant hydrocarbon it might become the main feedstock for chemical industry. It is only necessary to find a cheap method to convert this hydrocarbon into products under relatively mild conditions.

RESULTS AND DISCUSSION

We report here on the highly efficient oxidation of lower alkanes with hydrogen peroxide catalyzed by the combination VO_3^-/PCA and the demonstration of crucial role of molecular oxygen in this reaction. The reaction of gaseous alkanes (methane, ethane, propane, isobutane and *n*-butane) as well as liquid cyclohexane were carried out at various temperatures and pressures.

The process was monitored by withdrawing aliquots at specific intervals and analyzing each sample twice, i.e. before and after the addition of an excess of solid triphenylphosphine. Such a method which has been extensively used by us previously in various alkane oxidations [2,3,8] (see also Refs. 9) allows to detect alkyl hydroperoxides present in the reaction solution and estimate its concentrations. Usually alkyl hydroperoxides are decomposed in the chromatograph to produce corresponding alcohol and ketone. If PPh_3 is added to the reaction solution 10-20 min before the GC analysis, the alkyl hydroperoxide present is completely reduced to corresponding alcohol. As a result in the chromatogram the alcohol peak rises, while the intensity of the ketone peak decreases. Comparing the intensities of peaks due to the alcohol and ketone before and after the reduction, it is possible to estimate the *real* concentrations of the three products (i.e. alcohol, ketone and

Scheme 1



alkyl hydroperoxide) present in the reaction solution. This method allows to determine organic peroxides in the presence of hydrogen peroxide. Using a GC quartz lined injector and a fused silica capillary column we have obtained [2g,h] direct evidence for the formation of alkyl hydroperoxides in the oxidation of higher alkanes (RH: *n*-heptane, 2- and 3-methylhexanes, cyclohexane, cyclooctane): peaks of alkyl hydroperoxides were detected in the chromatograms of the reaction mixture untreated with PPh_3; the retention times of these peaks are longer than that for corresponding alcohols. If the sample of the reaction solution is treated with PPh_3, the peaks of ROOH disappear and the peaks of the corresponding alcohols grow markedly in intensity. However, it is difficult to measure precisely the concentration of alkyl hydroperoxide in the solution on the basis of its peak intensity, since partial decomposition (ca. 5-10%) of the peroxide occurs on the GC column. Therefore it is preferable to determine the concentration of ROOH (and of ROH and R'=O as well) by the 'difference analysis' before and after reduction of the reaction mixture with PPh_3.[2,3,8] Thus, the reagent under discussion oxidizes alkanes in MeCN to produce alkyl hydroperoxides, alcohols and carbonyl compounds; their interconversions are shown in Scheme 1.

In the present work we have found that the [*n*-Bu_4N]VO_3 – H_2O_2 – PCA reagent oxidizes methane in acetonitrile solution in the presence of air (glass-lined stainless steel autoclave) to produce methyl hydroperoxide, formaldehyde and formic acid (Table 1). No methanol peak has been detected in these experiments prior the reduction with PPh_3. After the reduction with PPh_3 the MeOH appears, while the concentration of HCHO in the solution drops. It is evidently that at 40 °C the primary product methyl peroxide gradually decomposes to produce formaldehyde. The concentration of the latter drops after 17 h, while the

Table 1. Oxidation of methane by the reagent '[*n*-Bu_4N]VO_3/PCA/H_2O_2/air' (in glass) [a]

Temperature °C	Time h	Products (concentration, × 10^2, *M*) MeOOH	HCHO	HCOOH	TON [b]
23	6	0.5	0.04	0	54
	16	1.3	0.13	0	143
	24	1.6	0.16	0	176
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

[a] Reaction conditions: autoclave (100 mL), glass inlet tube (solution volume 10 mL); methane, 75 bar; air, 10 bar; [*n*-Bu_4N]VO_3, 1.0×10^{-4} *M*; PCA, 4.0×10^{-4} *M*; H_2O_2 (used as 35% aqueous solution), 0.2 *M*. At 75 °C (methane, 40 bar; air, 10 bar) the following compounds were produced after 4 h: HCHO (0.2×10^{-2} *M*), HCOOH (4.0×10^{-2} *M*) (total turnover 420). [b] TON = moles of all detected products per mole of vanadate ion.

content of formic acid increases noticeably. Average rates of oxidation at 20, 40, and 75 °C are 7.5, 30 and 105 turnovers h^{-1}, respectively.

In order to evaluate the practical significance of the proposed method of methane oxidation, some additional experiments were carried out directly in larger (300 mL) stainless steel autoclaves without glass lining. Comparison of the data presented in Tables 1 and 2 shows that the selectivity of the oxidation strongly depends on the reaction conditions and especially on the material and construction of the reaction vessel. Methyl hydroperoxide and formaldehyde have not been detected when the oxidation was carried out in steel autoclave at higher concentration of the catalyst. One may assume that the catalyst present and walls of the autoclave can induce the decomposition and oxidation of relatively unstable products. Even if the reaction is carried out in a glass inlet tube placed into the autoclave, it is impossible to avoid completely the contact of the reaction mixture with walls of autoclave. The oxidation by pure molecular oxygen (Table 3) is more efficient in comparison with the reaction in the presence of air. It is noteworthy that PCA is the most powerful co-catalyst among other substituted pyrazinecarboxylic acids (Table 4). When a substituent is situated in close proximity to carboxylic group of substituted PCA (e.g. as in pyrazine-2,3-dicarboxylic acid), no oxidation of methane proceeds. Our preliminary experiments on the oxidation of cyclohexane demonstrated that picolinic acid is approximately 7 times less active as co-catalyst. Recently picolinic acid has been used as strongly accelerating co-catalyst in the oxidation of higher alkanes by Gif systems (the optimal ratio iron complex/picolinic acid 1:4 was used as in our case of vanadium-catalyzed reaction).

Table 2. Oxidation of methane by the reagent '$[n\text{-}Bu_4N]VO_3/PCA/H_2O_2$/air' (in steel) [a]

Temperature	Time	$[H_2O_2]$ (30%)	Products (yields based on CH_4, %)		Total yield based on H_2O_2 [b]	
°C	h	*M*	MeOH	HCOOH	%	TON [c]
25	12	0.2 [d]	0	0.3	15.4	154
	24	0.5	0	1.3	25.0	62
	24	2.0	1.5	2.6	16.8	206
40	12	0.2 [d]	0	0.6	31.3	313
	24	0.5	0.04	1.7	33.8	86
	24	2.0	2.3	5.2	31.9	376

[a] Reaction conditions: autoclave without glass lining (300 mL, solution volume 100 mL); methane, 75 bar; air, 10 bar; $[n\text{-}Bu_4N]VO_3$, 1.0×10^{-3} *M*; PCA, 4.0×10^{-3} *M*. [b] Moles of all detected products per mole of H_2O_2 (%). [c] TON = moles of all detected products per mole of vanadate ion. [d] $[n\text{-}Bu_4N]VO_3$, 1.0×10^{-4} *M*; PCA, 4.0×10^{-4} *M*.

Table 3. Oxidation of methane by the reagent '[*n*-Bu_4N]VO_3/PCA/H_2O_2/O_2' [a]

Temperature	Time	$[H_2O_2]$ (30%)	Products (yields based on CH_4, %)		Total yield based on H_2O_2 [b]	
°C	h	*M*	MeOH	HCOOH	%	TON [c]
25	24	0.001	0	0	0	0
	12	0.5	0	1.6	31.2	78
	24	0.5	0.7	1.9	44.8	129
	24	2.0	3.5	3.6	26.7	353
40	24	0.5	0.6	1.8	42.6	121
	24	0.5 [d]	0	1.5	0	75
	12	2.0	5.5	5.4	35.5	476
	24	2.0	5.1	7.5	50.4	630
	24	2.0 [d]	1.2	3.4	12.0	230

[a] Reaction conditions: autoclave (300 mL, solution volume 100 mL); methane, 75 bar; O_2, 10 bar; [*n*-Bu_4N]VO_3, 1.0×10^{-3} *M*; PCA, 4.0×10^{-3} *M*. [b] Moles of all detected products per mole of H_2O_2 (%). [c] TON = moles of all detected products per mole of vanadate ion. [d] The reaction in autoclave in a glass inlet tube.

Ethane was oxidized to yield ethanol, acetaldehyde and acetic acid in addition to ethyl hydroperoxide (Table 5), acetic acid being obviously a secondary product. The rate of oxidation is 530 turnovers h^{-1} at 75 °C which is substantially higher than that for methane. After 4 h, the total amount of products slightly exceeds the amount of hydrogen peroxide introduced into the reaction. Consequently, it should be concluded that molecular oxygen takes part in the oxidation. Indeed, when air was absent in the reaction system, no oxidation products were detected after 3 h at 40 °C (for details, see Experimental).

The product distribution of the propane oxidation (Table 6) strongly depends on temperature and reaction times. At high temperatures more deeply oxidized products are detected in the reaction solution. Thus if the reaction mixture after 6 h at 20 °C contains significant amounts of *n*-propanol and *n*-propyl hydroperoxide, the reaction at 75 °C even after 3 h gives mainly acid and ketone.

The oxidation of isobutane (Table 7) proceeds with partial C–C bond splitting of the initially formed *tert*-butyl hydroperoxide to give acetone and formaldehyde in approximately equal quantities. When the same amounts of the reactants were used, *n*-butane gave after 1 h at 40 °C (in parentheses: concentration × 10^2, *M*): *n*-$PrCH_2OOH$ (0.2), *n*-$PrCH_2OH$ (0.1), *n*-PrCHO (0.4), MeCH(OOH)Et (0.1), MeCH(OH)Et (1.8) and MeCOEt (0.2); the total turnover being 280.

Table 4. Oxidation of methane by air and H_2O_2 catalyzed by the combinations of $[n\text{-Bu}_4\text{N}]\text{VO}_3$ with various substituted pyrazinecarboxylic acids [a]

	Products (yields based on CH_4, %)		Total yield based on H_2O_2,[b]	
Chelating ligand L	MeOH	HCOOH	%	TON[c]
Pyrazine-2-carboxylic acid (PCA)	2.3	5.2	31.9	376
Pyrazine-2,5-dicarboxylic acid	1.4	5.1	29.0	325
5-Methylpyrazine-2-carboxylic acid	0.12	0.90	4.9	52
Pyrazine-2,3-dicarboxylic acid monoamide	0.06	0.84	4.3	45
Pyrazine-2,3-dicarboxylic acid	0	0	0	0
3-Aminopyryzine-2-carboxylic acid	0	0	0	0

[a] Reaction conditions: autoclave (300 mL, total volume of the solution 100 mL); methane, 75 bar; air, 10 bar; $[n\text{-Bu}_4\text{N}]\text{VO}_3$, 1.0×10^{-3} *M*; L, 4.0×10^{-3} *M*; H_2O_2 (used as 30% aqueous solution), 2.0 *M*; temperature 40 °C; time 24 h. [b] Moles of all detected products per mole of H_2O_2 (%). [c] TON = moles of all detected products per mole of vanadate ion.

Table 5. Oxidation of ethane by the reagent '$[n\text{-Bu}_4\text{N}]\text{VO}_3/\text{PCA}/\text{H}_2\text{O}_2/\text{air}$' [a]

Temperature	Time	Products (concentration, $\times 10^2$, *M*)				
°C	h	EtOOH	EtOH	MeCHO	MeCOOH	TON [b]
40	1	1.0	0.8	1.2	0	300
	2	1.8	1.3	2.1	0	520
	4	3.0	2.0	4.1	1.0	1010
	8	5.1	2.7	5.5	4.0	1730
75	1	1.0	1.3	2.5	0	480
	2	2.0	2.6	4.8	2.8	1700
	4	4.0	4.7	7.3	5.3	2130

[a] Reaction conditions: ethane, 25 bar; air, 10 bar; $[n\text{-Bu}_4\text{N}]\text{VO}_3$, 1.0×10^{-4} *M*; PCA, 4.0×10^{-4} *M*; H_2O_2 (used as 35% aqueous solution), 0.2 *M*. [b] TON = moles of all detected products per mole of vanadate ion.

In order to get additional evidence for the participation of O_2 from air in the formation of oxygenated products from alkanes, we carried out the same reaction with the liquid cyclohexane since in the case of higher alkane the experiments are easier to fulfill and they are less dangerous. We suppose that the results obtained with cyclohexane can be extrapolated to the light alkanes (*vide supra*, the reaction with ethane in the absence of air). It turned out that no oxygenation of cyclohexane occurred in a nitrogen atmosphere (40 °C, 2 h). However, when the reaction vessel was opened to air, the reaction started immediately with the rate equal to that observed in air. Oxidation of cyclohexane in an autoclave at various pressures of dioxygen evaluated that

Table 6. Oxidation of propane by the reagent '[*n*-Bu_4N]VO_3/PCA/H_2O_2/air' [a]

Temperature	Time	Products (concentration, × 10^2, *M*)						
°C	h	$EtCH_2OOH$	EtCHO	EtCOOH	Me_2CHOOH	Me_2CHOH	Me_2CO	TON [b]
23	6 [c]	0.2	0.15	0	0.5	0.6	0.2	180
	17 [d]	0.7	0.4	0	0.7	1.2	0.6	390
40	2	0.4	0.1	0	0.8	0.1	0.2	160
	4	0.8	0.2	0	1.2	0.3	0.4	290
	6	1.1	0.3	0	1.6	0.7	0.7	440
	9	1.1	0.2	0.1	1.6	1.1	0.8	490
75	1	0.3	0.3	3.0	0.6	0.3	0.5	500
	2	0.1	0.3	6.0	0.3	0.2	0.8	770
	3	0	0.2	9.8	0	0.1	1.0	1110

[a] Reaction conditions: propane, 7 bar; air, 5 bar; [*n*-Bu_4N]VO_3, 1.0 × 10^{-4} *M*; PCA, 4.0 × 10^{-4} *M*; H_2O_2 (used as 35% aqueous solution), 0.2 *M*. [b] TON = moles of all detected products per mole of vanadate ion. [c] Also *n*-PrOH, 0.15 × 10^{-2} *M*. [d] Also *n*-PrOH, 0.3 × 10^{-2} *M*.

Table 7. Oxidation of isobutane by the reagent '[*n*-Bu_4N]VO_3/PCA/H_2O_2/air' [a]

Temperature	Products (concentration, × 10^2, *M*)						
°C	Me_2CHCH_2OOH	Me_2CHCH_2OH	Me_2CHCHO	Me_3COOH	Me_3COH	Me_2CO	TON [b]
23 [c]	0.7	0.2	1.5	0.4	2.4	0.1	530
40	0.2	0.4	0.5	0.3	0.9	0.1 [d]	240
75	0.5	0.5	1.1	1.6	3.1	0.3 [d]	710

[a] Reaction conditions: isobutane, 2.5 bar; air, 25 bar; time 2.5 h; [*n*-Bu_4N]VO_3, 1.0 × 10^{-4} *M*; PCA, 4.0 × 10^{-4} *M*; H_2O_2 (used as 35% aqueous solution), 0.2 *M*. [b] TON = moles of all detected products per mole of vanadate ion. [c] After 17 h. [d] Approximately equal concentrations of formaldehyde have been also detected in the solution.

at low oxygen pressures the reaction rate is proportional to the pressure, and when the pressure of $O_2 > 3$ bar this rate is independent of the amount of oxygen. It is noteworthy that the ratio cyclohexanol/cyclohexanone determined after reduction with phosphine slightly changes with increasing the air pressure (Fig. 1).

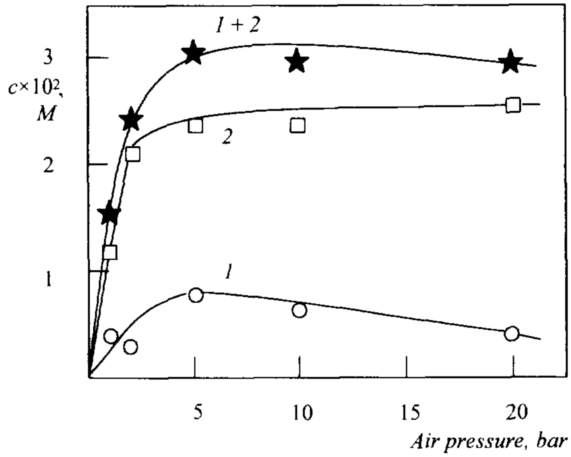


Figure 1. Oxidation of cyclohexane (0.46 *M*) at 40 °C with H_2O_2 (0.2 *M*) catalyzed by VO_3^- – PCA in autoclave (total volume 100 mL; volume of the solution 10 mL). Dependences of concentrations of cyclohexanone (*1*), cyclohexanol (*2*) and their sum (*1* + *2*) after 1 h on the air pressure are shown.

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 GC-MS 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 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, the alkyl hydroperoxide, ROOH, stems from atmospheric dioxygen. Unlabeled oxygen (ca. 25%) detected in the cyclohexanol after the reduction with PPh_3 could originate from atmospheric $^{16}O_2$, 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 $^{16}O_2$. It is interesting to note that the oxygen atom of a ketone formed in the Gif oxidation of the corresponding alkane with H_2O_2 promoted by iron compounds in pyridine–acetic acid, is largely derived from O_2 and not from H_2O_2.[10b-d]

We presume that in the presence of catalytic amounts of 'VO_3^- – PCA' hydrogen peroxide is an efficient generator [11] of hydroxyl radicals (Scheme 2, eq. 1). In the beginning of the oxidation, the anion VO_3^- seems to be converted into either a peroxo complex of V(V) [5l,o, 12] or a derivative of V(IV).[2h] Both species might be uncharged and stabilized by PCA; the role of $(n\text{-}Bu)_4N^+$ cation is only to introduce the vanadium derivative into the reaction solution. This anion is possibly completely oxidized in the course of the process. The radicals $HO^•$ formed attack the alkane molecule, RH, abstracting the hydrogen atom (eq. 2). As a result, alkyl radicals, $R^•$, are produced which rapidly react with molecules of oxygen to yield peroxyl radicals $ROO^•$ (eq. 3). These latter species are assumed to be reduced and after addition of the proton converted into alkyl hydroperoxide (eq. 4) which can be detected as the primary relatively unstable product. The abstraction of hydrogen from an alkane molecule by $R^\bullet$ to give the alkyl hydroperoxide and an alkyl radical (eq. 5) to maintain the chain reaction is not probable at least in the cases of methane and ethane since the energy of C–H bonds in these hydrocarbons is very high and the oxidations were carried out at low temperatures. The recombination of alkyl and hydroxyl radicals (eq. 6) is also not very probable because the local concentrations of $HO^\bullet$ and $R^\bullet$ are low. This explains why in the absence of air the yields of ROH were below our limits for their GC detection. A pronounced dependence of the oxidation in the case of methane on the material of the reaction vessel supports the conclusion about involvement of various radical particals into the process.

Scheme 2

$$H_2O_2 \xrightarrow{VO_3^- / PCA} HO^\bullet \qquad (1)$$

$$HO^\bullet + RH \rightarrow H_2O + R^\bullet \qquad (2)$$

$$R^\bullet + O_2 \rightarrow ROO^\bullet \qquad (3)$$

$$ROO^\bullet + e^- + H^+ \rightarrow ROOH \qquad (4)$$

$$ROO^\bullet + RH \rightarrow ROOH + R^\bullet \qquad (5)$$

$$R^\bullet + HO^\bullet \rightarrow ROH \qquad (6)$$

$$2ROO^\bullet \rightarrow ROOOOR \rightarrow ROH + R'{=}O \qquad (7)$$

One may assume that the route consisting of steps (1)-(3) operates at least in some of known alkane oxidations with H_2O_2 catalyzed by metal complexes. In this case the peroxyl radicals may give rise to the formation of either alkyl hydroperoxides (e.g., via reaction 4) or alcohol and ketone via a Russell-type termination (eq. 7). Alkyl hydroperoxides can decompose completely in chromatograph (see Scheme 1) and in many works only alcohols and ketones thus formed have been detected by GC. The method of alkyl hydroperoxide determination by comparison of chromatograms of the reaction samples before and after reduction with phosphine [2, 3, 8] permits to detect ROOH easily and consequently to elucidate the reaction path. Recently it has been demonstrated [13] that alkane, RH, oxygenation with alkyl hydroperoxides, R'OOH, in air catalyzed by iron complexes proceeds, at least in part, via the reaction between $R'O^\bullet$ and RH to generate R'OH and $R^\bullet$. Such a scheme is very similar with the route including steps (1)-(3).

Only little is known at present about oxidation of methane and other lower alkanes with hydrogen peroxide and/or molecular oxygen as well as some other oxidants in solutions under mild conditions (low temperature and pressure) when a metal complex is used as a catalyst.[14] The reagent described in this paper seems to be one of the most efficient for such an oxidation.

EXPERIMENTAL

The oxidations (results summarized in Tables 1, 5, 6 and 7) were carried out in glass-lined stainless steel autoclaves with intensive stirring (volume of the reaction solution was 10 mL, total volume of the autoclave was 100 mL). Usually the following concentrations of the reagents were used: [*n*-Bu_4N]VO_3, 1.0 × 10^{-4} *M*; PCA, 4.0 × 10^{-4} *M*; H_2O_2 (35% aq), 0.2 *M*. The large-scale oxygenations (Tables 2, 3 and 4) were carried out in stainless steel autoclaves without a glass inlet tube; in these cases total volume of the autoclave was 300 mL and the volume of the reaction mixture was 100 mL, and the concentrations of the components were 10 times higher (see footnotes to Tables 2, 3 and 4). Before the oxidation the autoclave was charged with air and then with gaseous alkane under appropriate pressures. (CAUTION: the combination of air or molecular oxygen 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 analyzed by GC (DANI-86.10, capillary columns 50 m × 0.25 mm × 0.25 μm, Carbowax 20M and 60 m × 0.25 mm × 0.25 μm, SPB-1; integrator SP-4400; also HP 5880A, capillary column Porapak-N, 2 m). Each sample was analyzed twice, *i.e.* before and after the addition of the excess of solid PPh_3. The concentration of formic acid in experiments given in Tables 2, 3 and 4 was also determined by titration with tetrabutylammonium hydroxide. The concentration of formaldehyde was measured spectrophotometrically after its transformation into 2,6-dimethyl-3,5-diacetyl-1,4-dihydropyridine according to the method described in Refs. 15.

In experiments on ethane oxidation under anaerobic conditions, before adding hydrogen peroxide, the air in the autoclave containing the reaction solution was thoroughly replaced with nitrogen (30 bar), and then nitrogen was replaced with ethane (25 bar). In experiment with labeled dioxygen, the reaction was carried out in a sealed ampoule (10 mL) at 20 °C under atmospheric pressure of $^{18}O_2$ (content 98 %, Cambridge Isotope Laboratories) during 3 days; concentrations: cyclohexane, 0.46 *M*; H_2O_2, 30% aq, 0.2 *M*; [*n*-Bu_4N]VO_3, 1.0 × 10^{-4} *M*, PCA, 4.0 × 10^{-4} *M*. The resulting solution was analyzed by GC-MS (NERMAG R 30-10, capillary column 50 m × 0.25 mm × 0.25 mμ, Carbowax 20M).

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