

Oxidations by the reagent ‘O₂–H₂O₂ – vanadate anion – pyrazine-2-carboxylic acid’.

Part 10¹.

Oxygenation of methane in acetonitrile and water

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Abstract

The oxidation of methane by a combination of air and hydrogen peroxide is effectively catalyzed in solution by a system composed of vanadate and pyrazine-2-carboxylic acid (PCA). In acetonitrile solution, containing the vanadate anion as tetrabutylammonium salt, the reaction gives, over a temperature range of 25 to 50°C, methanol, carbon monoxide, formaldehyde, formic acid and carbon dioxide, the latter three compounds, however, being partially due to the oxidation of the acetonitrile used as the solvent, especially at higher temperatures. In aqueous solution, containing the vanadate anion in the form of the sodium salt, the reaction affords, over a temperature range of 40 to 70°C, selectively methyl hydroperoxide within 4 h. The yield of CH₃OOH attains 24%, based on H₂O₂, after 24 h at 50°C, the catalytic turnover number being 480. The process seems to involve hydroxyl radicals, generated by the catalyst from H₂O₂ even at low temperatures. At 120°C, methane is oxidized by O₂ and H₂O₂ to give formaldehyde and formic acid, even in the absence of the catalyst, presumably due to the formation of HO· radicals from H₂O₂ in the presence of very low concentrations of metal ions from the autoclave under high temperature conditions. © 1998 Elsevier Science B.V.

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1. Introduction

Methane is one of the most important feedstocks for chemical industry although this hydrocarbon is simultaneously the least reactive

organic compound [1,2]. Methane is extremely inert even in comparison with other alkanes [3–6] as its molecule does not contain relatively reactive methylene groups. Almost all transformations of methane occur at high (> 500°C) temperatures and only in the last decades new methods of activation of C–H bonds in methane under mild conditions have been described [7–26]. Selective partial oxidation of methane in solutions into valuable products (e.g., methanol,

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¹ Communications 1–9 see [44–52], respectively. Preliminary communications of previous parts have been also published [53–55].

formaldehyde, formic acid) at temperature < 100°C is a challenging task of contemporary homogeneous catalysis. Molecular oxygen and hydrogen peroxide [27–35] could be potential oxidizing reagents in such reactions. Various soluble metal complexes are known to catalyze these reactions, see for example [36–43].

Earlier we have demonstrated [44–55] that the system ‘vanadate anion — pyrazine-2-carboxylic acid (PCA)’ catalyses efficient oxidation of various organic compounds in acetonitrile solution by hydrogen peroxide in air (Scheme 1). Some other derivatives of vanadium are also active as catalysts. In the absence of PCA the oxidation rate is negligible. It has been shown that saturated hydrocarbons are transformed into alkyl hydroperoxides, ketones (aldehydes) and alcohols. The oxidation of alkanes does not proceed in the absence either of both components of the catalyst or air. The cyclohexane oxidation under an $^{18}\text{O}_2$ atmosphere showed that in alkane oxidation hydrogen peroxide plays the role of promoter while atmospheric oxygen is a true oxidant. It has been concluded on the basis of the results obtained previously that the reagent ‘ H_2O_2 – VO_3^- –PCA’ is an efficient generator of hydroxyl radicals which attack the substrate molecules. At moderate temperatures the combination ‘ VO_3^- –PCA’ is much more efficient in comparison with Fenton’s reagent, where normally a $\text{Fe(II)}/\text{H}_2\text{O}_2$ ratio of 1:1 is employed.

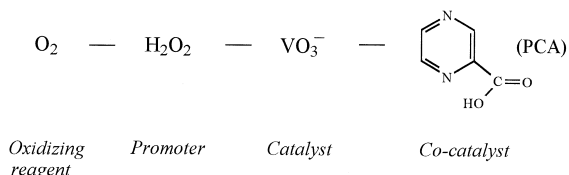
We wish to report here the highly efficient oxygenation of methane by the reagent ‘ O_2 – H_2O_2 – VO_3^- –PCA’ in acetonitrile and water as solvents. The oxidation of acetonitrile both in the presence of methane (and some other hydro-

carbons) and in pure state is also under discussion.

2. Experimental

All reactions were carried out in thermostated glass-lined stainless steel autoclaves with intensive stirring (volume of the reaction solution was 30 ml, total volume of the autoclave was 100 ml). Some experiments were performed directly in stainless steel autoclaves without glass inlet tubes. Acetonitrile or water were employed as solvents. Usually the following amounts of the reagents were introduced into the reaction mixtures: $n\text{-Bu}_4\text{NVO}_3$ (in acetonitrile solutions) or NaVO_3 (in aqueous solutions), 0.03×10^{-4} mol (concentration 1.0×10^{-4} mol l^{-1}); PCA, 0.12×10^{-4} mol (concentration 4.0×10^{-4} mol l^{-1}); H_2O_2 (35% aq), 60×10^{-4} mol (concentration 0.2 mol l^{-1}). Before the oxidation the autoclave was charged with air (10 bar) and then with gaseous methane (75 bar; 0.23 mol) (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 concentration of methanol in the reaction solution was analyzed by GLC (DANI-86.10, capillary column 50 m \times 0.25 mm \times 0.25 μm , Carbowax 20 M; integrator SP-4400). The same instrument was used for measuring the concentrations of products of cyclohexane oxidation as well as for quantitative determination of gaseous products of acetonitrile and methane oxidation (CO and CO_2) (column Carboxen 1000). In the case of liquid products each sample was analyzed twice, i.e. before and after the addition of the excess of solid PPh_3 in the cases when the reaction was carried out in acetonitrile, and the addition of NaBH_4 if the oxidation was in aqueous solution. Since alkyl hydroperoxides formed are quantitatively transformed under the action of the reducing agent into corresponding alcohols, this method allowed to



Scheme 1. Components of the reagent described in the present paper.

calculate real concentrations not only of peroxides but also amounts of alcohols, ketones and other compounds present in the solution at a given moment [44–66]. 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 [67,68]. The concentrations of formic acid were determined by titration with tetrabutylammonium hydroxide (in MeCN) and potassium hydroxide (in H₂O). Methyl hydroperoxide was prepared from H₂O₂ and Me₂SO₄ according to Ref. [69]. In experiments with this compound NMR spectrometer Varian (200 MHz) was used to detect MeOOH and MeOH.

Bidistilled water was used as a solvent and acetonitrile was distilled twice over phosphorus pentoxide prior the reaction. Methane (Carbogas, 99.95%) was introduced into the reactions as received. Compound *n*-Bu₄NVO₃ was prepared starting from V₂O₅ and *n*-Bu₄NOH according to a method described in Ref. [70].

Additional details of the experiments are also given in the figure captions.

3. Results and discussion

Previously we have shown that the crucial step in reactions of the reagent ‘O₂–H₂O₂–VO₃[–]–PCA’ is the attack of hydroxyl radicals on C–H bond of a substrate, RH. This interaction proceeds as abstracting of the hydrogen atom and gives rise to the formation of radical R[•]. It is important to note that the analysis of distribution of the oxygenates formed in oxidation of *cis*-decalin demonstrated the different nature of active species in alkane oxidation in acetonitrile by the reagent ‘O₂–H₂O₂–VO₃[–]–PCA’ on the one hand and by Mimoun’s complex [71], VO(O₂)(picolinate)·2H₂O, on the other hand. One can assume that, while the first system is a generator of hydroxyl radicals, in the case of the latter complex, hydrogen atom

from alkane is abstracted by oxygen-centered vanadium-containing radical, e.g., V^{IV}V–OO[•] [71]. Hydroxyl radicals are known to be extremely reactive species, so it does not seem surprising that even very inert methane can be involved into transformations under the action of the reagent ‘O₂–H₂O₂–VO₃[–]–PCA’ [51,55]. High reactivity of hydroxyl radicals might, however, lead to a significant oxidation of acetonitrile used as a solvent in a competitive reaction with inert methane whose concentration in the solution is relatively low. The aim of the present work is to investigate the possible competitive oxidation of acetonitrile and to use the oxidation-resistant water as an alternative solvent.

3.1. Oxidation in acetonitrile

We have found that the oxidation of methane in acetonitrile solution under conditions described in Section 2 and in caption for Fig. 1, affords methanol, formaldehyde, formic acid as well as carbon monoxide and carbon dioxide. Fig. 1a demonstrates the dependence of the product amounts on the reaction temperature. It may be stated that rising the temperature leads to increasing both of the relative and absolute amounts of HCHO, HCOOH, CO₂ and CO, while the yield of MeOH is only slightly decreases. As follows from Fig. 1b, products HCHO, HCOOH and CO₂ are formed under the same conditions also in the absence of methane (acetonitrile as the sole organic substrate was oxidized by the reagent under discussion, the pressure of air being as usually 10 bar). The subtraction values presented in Fig. 1b from the corresponding values given in Fig. 1a allowed us to estimate the amounts of products derived only from methane (Fig. 1c). It can be concluded that at relatively low temperatures (< 35°C) methanol is the main product, while at elevated temperatures its content becomes lower and formaldehyde and formic acid are produced in substantial concentrations. Carbon monoxide

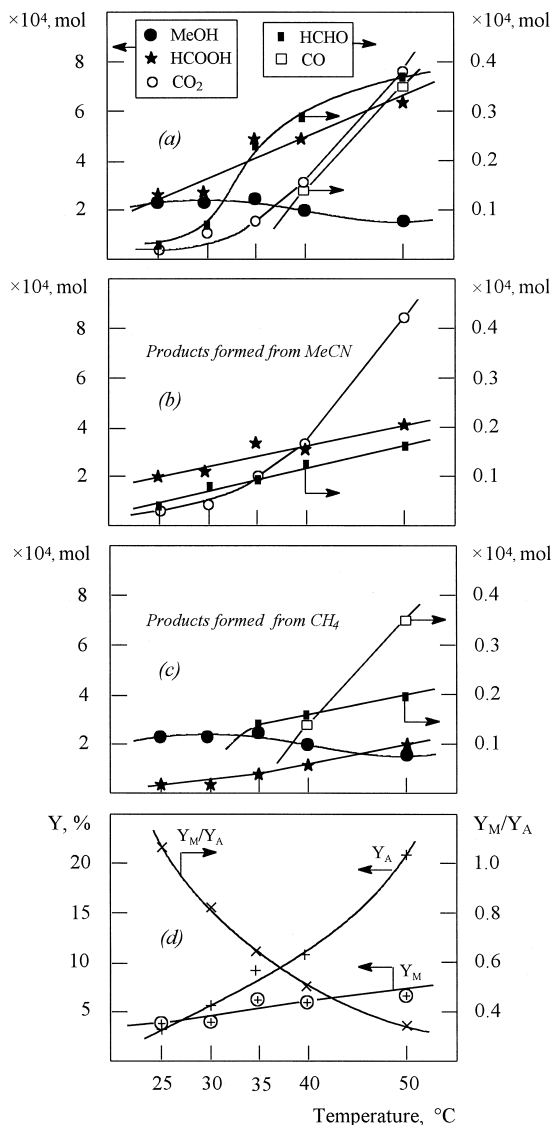


Fig. 1. Oxidation of methane in acetonitrile solution (stainless steel autoclave, reaction time 4 h; for other conditions, see Section 2) at various temperatures. Amounts of oxidation products (×10⁴, mol) are presented: (a) determined experimentally in oxidation of methane in MeCN; (b) determined experimentally in oxidation of MeCN under the same conditions, but without methane. Amounts of oxidation products of only methane (c) have been calculated by subtraction of the parameters for oxidation of MeCN presented in (b) from the corresponding parameters given in (a). The dependencies of the following parameters on temperature are also given (d): the total yield (%) of all products formed from acetonitrile calculated from parameters shown in (b) and based on H₂O₂, Y_A; the total yield of products formed from methane calculated from parameters shown in (c) and based on H₂O₂, Y_M; the ratio Y_M/Y_A.

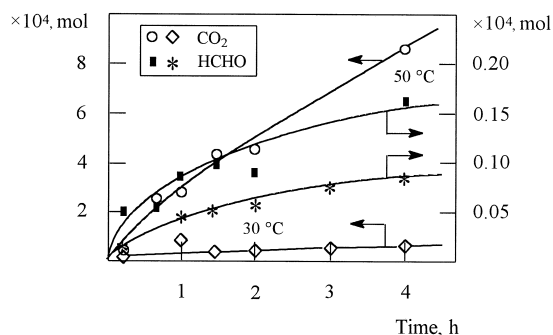


Fig. 2. Kinetics of accumulation of CO₂ and HCHO in the catalyzed oxidation of MeCN at temperatures 30 and 50 °C (stainless steel autoclave, air pressure 10 bar).

is detected only at temperature > 35 °C and only when methane is present in the reaction mixture. On the contrary, carbon dioxide seems to be produced exclusively from acetonitrile. On going from 25 to 50 °C the total yield (based on H₂O₂) of products derived from acetonitrile Y_A grows more rapidly than the corresponding yield Y_M calculated for methane. As a consequence the ratio Y_M/Y_A monotonically decreases when the temperature increases (Fig. 1d). Thus it may be concluded that the lower the temperature the higher relative efficiency of the reagent in respect to methane, while at higher temperatures (especially at > 50 °C) the reagent under discussion oxidizes predominantly acetonitrile.

In the oxidation of acetonitrile, the product distribution depends on the temperature of the reaction (see Fig. 2; in experiments shown in Figs. 2 and 3 only formaldehyde and carbon dioxide originated from acetonitrile were quantified and the amounts of formic acid were not measured). If at 30 °C formaldehyde significantly prevails over carbon dioxide, at 50 °C both products are produced in approximately equal amounts. The fact of relatively extensive oxidation of acetonitrile used as a solvent in the reaction with methane found in present work prompted us to investigate also a competitive oxidation by the reagent under discussion of a mixture of acetonitrile (solvent) and cyclohexane. The latter is known to be much more reactive in comparison with methane and more-

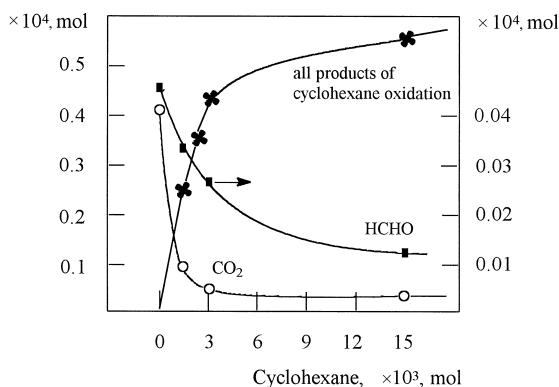


Fig. 3. Dependence of product distribution on amount of cyclohexane in the oxidation of a mixture of cyclohexane and acetonitrile (stainless steel autoclave, air pressure 10 bar, 50°C, reaction time 15 min; for other conditions, see Section 2).

over it can be involved into the reaction in higher concentration. Fig. 3 demonstrates that products of acetonitrile oxidation (HCHO and CO₂) are produced in relatively large amounts only if cyclohexane is not present in the solution or present in low concentration. If concentration of cyclohexane is relatively high (> 0.05 mol l⁻¹) as it was used in all our previous works, acetonitrile is oxidized only in small extent.

3.2. Oxidation in water

We have also found that methane is oxidized by the reagent 'O₂-H₂O₂-VO₃⁻-PCA' if water is used as a solvent. Three products, methyl hydroperoxide, formaldehyde and formic acid, have been detected in the reaction mixture after 4 h. Methyl hydroperoxide was identified by comparison of the reaction solution with the spectrum of a solution of the MeOOH authentic sample prepared from H₂O₂ and Me₂SO₄. In both cases MeOOH gives in the ¹H NMR spectrum a singlet with δ = 3.80 p.p.m., and in both cases, if NaBH₄ is added to the solution, a new singlet at δ = 3.29 p.p.m. due to MeOH appears in the spectrum in expense of previous signal. Methyl hydroperoxide was determined quantitatively by GLC in the form of MeOH after reduction of the reaction solution with NaBH₄.

If the reaction is carried out in the presence of the catalyst, NaVO₃ + 4PCA, in water at temperature < 70°C in a glass inlet tube, only methyl hydroperoxide can be detected in the reaction solution after 4 h (see Fig. 4a). Maximum amount of MeOOH has been found after 4

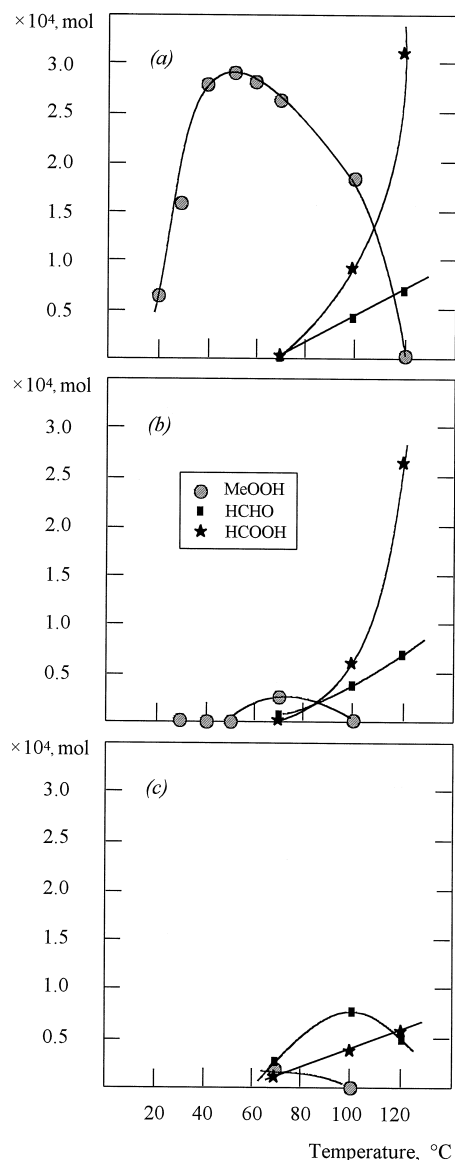


Fig. 4. Oxidation of methane in aqueous solution at various temperatures (reaction time 4 h) in the presence of the catalyst (a) and in the absence of any catalyst (b and c) in glass inlet tube (a and b) and without glass tube directly in stainless steel autoclave (c).

h at 50°C. This amount is equal to 2.88 mol. the concentration of the product is $9.6 \times 10^{-3} \text{ mol l}^{-1}$ which corresponds to the catalyst turnover number 96 and the yield 5% based on H_2O_2 introduced into the reaction. A linear dependence is observed between time of the reaction and the yield of MeOOH in the interval 0–24 h (Fig. 5), after 24 h turnover number attains 480, the yield based on H_2O_2 is 24%. There is a linear dependence between initial concentration of H_2O_2 and the amount of MeOOH formed after 4 h at 50°C (Fig. 6). In the presence of catalytic amounts of $\text{NaVO}_3 + 4\text{PCA}$, if the temperature of the process is $> 70^\circ\text{C}$ formaldehyde and formic acid are produced in substantial concentrations; the yields of these products increase markedly with increasing the temperature (Fig. 4a). At 120°C after 4 h no methyl hydroperoxide has been detected in the mixture of products. As it follows from Fig. 4b, at temperature $> 70^\circ\text{C}$ formaldehyde and formic acid are produced even in the absence of $\text{NaVO}_3 + 4\text{PCA}$, the yields of these substances being approximately equal to that obtained in the catalyzed reaction. If the reaction is carried out without a glass inlet tube, formaldehyde and

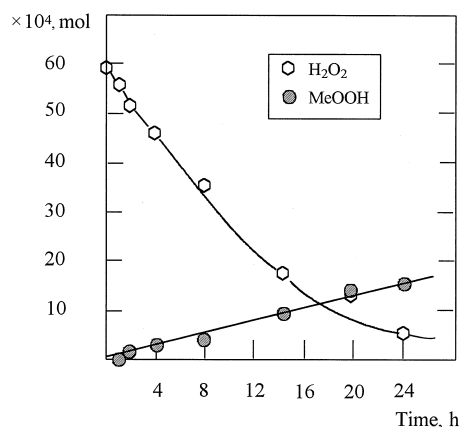


Fig. 5. Kinetics of the H_2O_2 consumption and MeOOH accumulation in oxidation of methane in aqueous solution at 50°C in the presence of the catalyst. Concentration of MeOOH was measured by GLC after reduction of the reaction solution into MeOH with NaBH_4 . Concentration of sum MeOOH + H_2O_2 was determined by titration and concentration of H_2O_2 was calculated from these data.

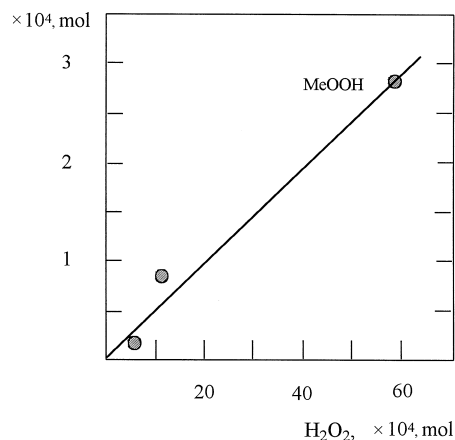


Fig. 6. Plot of yield of MeOOH after 4 h vs. initial amount of H_2O_2 in the oxidation of methane in aqueous solution at 50°C .

formic acid are also formed at higher temperatures even in the absence of $\text{NaVO}_3 + 4\text{PCA}$, although slightly different distribution of products has been observed (Fig. 4c).

The formation of formaldehyde and formic acid from methane in aqueous solution of H_2O_2 in the absence of $\text{NaVO}_3 + 4\text{PCA}$ at relatively high temperatures is apparently due to the decomposition of H_2O_2 catalyzed by subanalytical admixtures of transition metals present in water (e.g. iron ions originated from the autoclave). Hydroxyl radicals thus formed attack methane molecules to yield methyl radicals which react rapidly with molecular oxygen giving rise to the formation of peroxy radicals, $\text{MeOO}\cdot$. The latter at high temperatures, and possibly under the action of transition metal ions, are transformed into stable products, formaldehyde and formic acid. In the presence of $\text{NaVO}_3 + 4\text{PCA}$ the process occurs according to the same scheme, but the system ' $\text{H}_2\text{O}_2\text{-VO}_3\text{-PCA}$ ' efficiently produces hydroxyl radicals even at low temperatures. At once, the combination $\text{NaVO}_3 + 4\text{PCA}$ does not seem to be active in decomposition of $\text{MeOO}\cdot$ or MeOOH. Due to this it is possible to oxidize methane selectively into methyl hydroperoxide using the reagent ' $\text{O}_2\text{-H}_2\text{O}_2\text{-VO}_3\text{-PCA}$ ' the optimal temperature interval being $40\text{--}70^\circ\text{C}$.

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