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Oxidation of saturated hydrocarbons with peroxyacetic acid catalyzed by vanadium complexes

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Abstract

Peroxyacetic acid (PAA) oxidizes alkanes in acetonitrile or acetic acid at 60 °C if a soluble vanadium(V) salt, *n*-Bu_4NVO_3 (**1**), is used as a catalyst. Corresponding ketones, alcohols and alkyl hydroperoxides are the main products. Methane, ethane, propane, cyclohexane, and other higher alkanes were substrates in the oxidations. The proposed mechanism involves the formation of a complex between (**1**) and PAA with equilibrium constants 3.3 and 6.8 $dm^3\,mol^{-1}$ for acetonitrile and acetic acid as solvents, respectively. This complex decomposes to produce $CH_3C(=O)OO^\bullet$ radical and a V^{IV} derivative. The latter reacts with PAA to generate a $CH_3C(=O)O^\bullet$ radical which attacks the alkane abstracting its hydrogen atom. An alkyl radical thus formed adds rapidly a molecule of dioxygen which leads finally to the alkyl hydroperoxide and then to the ketone and alcohol. Other vanadium(V) and vanadium(IV) complexes are also active in this oxidation only if the vanadium ion is not shielded with strongly bound bulky ligands.

Keywords: Alkanes; Alkyl hydroperoxides; Cyclohexane; Ethane; Homogeneous catalysis; Methane; Peroxy acids; Peroxyacetic acid; Oxidation; Vanadium complexes

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1. Introduction

Peroxy acids (e.g., peroxyacetic, *m*-chloroperbenzoic acids) including those generated in situ have been widely used in oxidations of various hydrocarbons (see books and reviews [1–3], examples of non-catalyzed oxidations with peroxy acids [4,5], non-metal-catalyzed oxidation with peroxy acids [6], base-induced oxidations with participation of peroxy acids [7–10] and metal-catalyzed oxidations with peroxy acids [11–36]). Earlier we have demonstrated that the "H_2O_2-*n*-Bu_4NVO_3-pyrazine-2-carboxylic acid (PCA)" reagent [37–51] and *tert*-butyl hydroperoxide [52] in air in acetonitrile solution oxidize alkanes and alkyl hydroperoxides are formed as main products which decompose during the course of the reaction to produce the more stable corresponding alcohols and ketones (for other recently published vanadium-catalyzed oxidations see, for example, [53–71]). In the present work we investigated for the first time the alkane oxidation by peroxyacetic acid (PAA) using various vanadium(V) and vanadium(IV) complexes as catalysts.

2. Experimental

Experiments on the higher alkane oxidation were carried out in acetonitrile or acetic acid solution (typically at 60 °C) in thermostated Pyrex cylindrical vessels with vigorous stirring. The total volume of the reaction solution was 10 mL. Initially, a portion of 39% solution of PAA in acetic acid ("Aldrich") was added to the solution of the catalyst and cyclohexane (or other alkane) in acetonitrile. The oxidations of light alkanes (ethane and methane) were carried out in a stainless steel autoclave with intensive stirring (volume of the reaction solution was 10 mL and total volume of autoclave was 100 mL). The autoclave was charged with air (under atmospheric pressure) and then, consecutively, with the reaction solution containing the catalyst in acetonitrile and the alkane to the appropriate pressure.

In order to determine concentrations of all cyclohexane oxidation products the samples of reaction solutions

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were typically analyzed twice (before and after their treatment with PPh_3) by GC (DANI-86.10 instrument; capillary column 50 m × 0.25 mm × 0.25 μm, Carbowax 20M; integrator SP-4400; the carrier gas was helium) measuring concentrations of cyclohexanol and cyclohexanone. This method (an excess of solid triphenylphosphine is added to the samples before the GC analysis) which was used by us earlier [1,37–52,72–80] allows us 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 mainly the corresponding alcohol and ketone.

Synthesis of $n\text{-}Bu_4NVO_3$ (**1**) is described in the literature [49,81]. Preparation and characterization of complexes (**5**), (**6**) and (**7**) was reported elsewhere [82].

3. Results and discussion

Stirring a solution of cyclohexane, CyH, and PAA in acetonitrile at 30 °C in the presence of catalytic amounts of a simple vanadate anion containing *n*-butylammonium cation, $n\text{-}Bu_4NVO_3$ (**1**), gives rise to the relatively slow formation of cyclohexyl hydroperoxide, CyOOH, which decomposes in the course of the reaction to produce cyclohexanone and cyclohexanol (Fig. 1). The reaction occurs with auto-acceleration and reaches the maximum rate after approximately 2 h (curve 4). Total concentration of the oxygenates is 0.8×10^{-2} mol dm^{-3} which corresponds to the turnover number (that is the number of moles of all products per one mole of the catalyst, TON) of 80. The reaction proceeds much more rapidly at 60 °C and TON reaches 90 in this case. The kinetic curve for the accumulation of the sum of all products also exhibits S-shape which can be seen more clearly in Fig. 1.

Fig. 2 demonstrates that PAA is completely consumed after approximately 2 h because after the addition of a new portion of PAA the oxidation reaction begins with approximately the same rate. It is necessary to note that in all our kinetic studies described below, we measured concentrations of cyclohexanone and cyclohexanol after reduction of the reaction mixture with PPh_3. This gives precisely concentrations of all oxygenates which can be used for the obtaining reaction rates.

One might assume that PAA can be generated in situ by mixing solutions of acetic acid and hydrogen peroxide in acetonitrile. To check this proposal we studied the cyclohexane oxygenation with H_2O_2 in the $CH_3CN\text{–}CH_3CO_2H$ (19:1) mixture and in pure acetic acid (Fig. 3). It turned out that although the oxidation in this case proceeds, comparable with that for the PAA oxidation, the selectivities of both reactions are different: predominant products are cyclohexanol in $CH_3CN\text{–}CH_3CO_2H$ and cyclohexyl hydroperoxide in CH_3CO_2H (Fig. 3). Thus, we can conclude that PAA is not apparently produced in sufficient concentration by simple mixing acetic acid and hydrogen peroxide in acetonitrile.

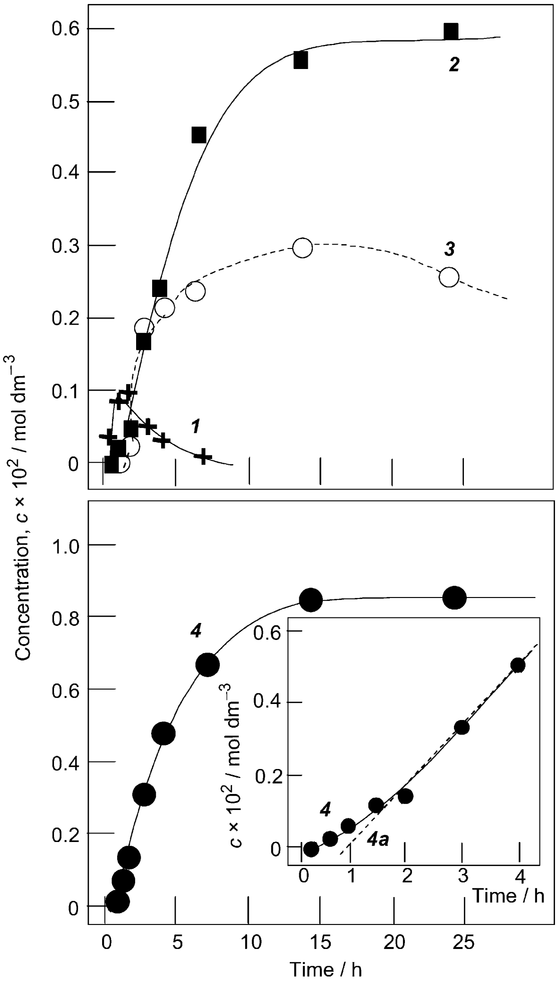


Fig. 1. Accumulation of oxygenates (cyclohexyl hydroperoxide, curve 1; cyclohexanone, curve 2; cyclohexanol, curve 3; and the sum of all products, curve 4) in the reaction of cyclohexane (0.46 mol dm^{-3}) with PAA (0.30 mol dm^{-3}) in MeCN at 30 °C catalyzed by $n\text{-}Bu_4VO_3$ (1×10^{-4} mol dm^{-3}). The initial oxidation rate was determined from the slope of the dashed straight line 4a which corresponds to the maximum rate in the initial period of the reaction.

Studies of the dependence of the initial rate of the PAA oxidation on the initial catalyst concentration under different conditions showed that the curves for this dependence have rather complex shape (Fig. 4, curves 1 and 2). The oxidation exhibits first order for PAA at $[PAA]_0 < 0.2$ mol dm^{-3} and the rate is independent of PAA concentration at $[PAA]_0 > 0.4$ mol dm^{-3} (Fig. 4, curve 3). The curve for the dependence on initial cyclohexane concentration also exhibits saturation (at $[CyH]_0 > 1$ mol dm^{-3}) (Fig. 4, curve 4). Addition of acetic acid accelerates the reaction (Fig. 4, curve 5).

The reaction in pure acetic acid gives only cyclohexanone and cyclohexanol with total TON = 50 after 0.5 h (Fig. 5). The catalyst is stable under the used conditions and after addition of a new PAA portion the oxidation can be continued with the same initial rate. The curve for dependence

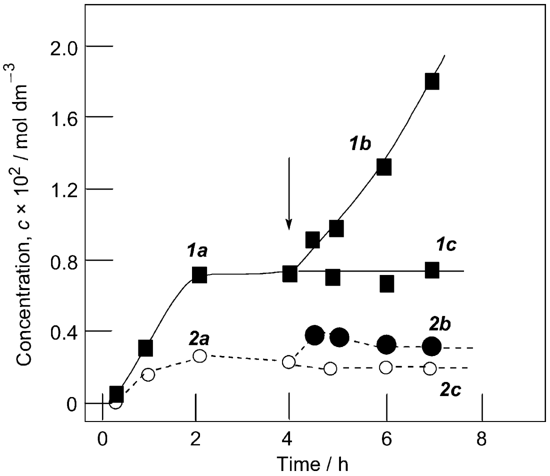


Fig. 2. Accumulation of oxygenates (cyclohexanone, curve 1a; cyclohexanol, curve 2a) in the reaction of cyclohexane (0.46 mol dm^{-3}) with PAA (0.30 mol dm^{-3}) in MeCN at 60 °C catalyzed by n-Bu_4VO_3 (1×10^{-4} mol dm^{-3}). At the moment marked by an arrow (4 h) either additional amount of PAA (0.30 mol dm^{-3}) was added to the reaction mixture (further accumulation of cyclohexanone and cyclohexanol is denoted by curves 1b and 2b, respectively) or additional amount of n-Bu_4VO_3 (1×10^{-4} mol dm^{-3}) was added (further accumulation of cyclohexanone and cyclohexanone is denoted by curves 1c and 2c, respectively). In this experiment concentrations of cyclohexanone and cyclohexanol were measured only after addition of PPh_3.

of the initial oxidation rate on the initial concentration of vanadate ion is shown in Fig. 5. Dependencies of the initial rate on the initial concentration of cyclohexane and PAA are shown in Fig. 6. The situation in all cases is similar with that found for the reaction in acetonitrile (compare with Fig. 4); at low concentration of a component the reaction exhibits a linear dependence on the component, whereas at relatively high concentration the reaction rate does not depend on the component concentration.

Light alkanes (methane, ethane and propane) can be also oxidized by PAA both in acetonitrile and acetic acid (Table 1). The propane oxidation in acetonitrile gives predominantly acetone with total TON up to 165.

Parameters of regio-selectivity determined for the oxidations of n-hexane, isooctane and isomers of 1,2-dimethylcyclohexane (Table 2) are close to that found for oxidations by the "H_2O_2-n-Bu_4NVO_3-PCA" reagent which has been shown by us earlier to operate via a radical mechanism [37–51].

Observed dependencies of the initial reaction rate on initial concentrations of cyclohexane and PAA (Figs. 4,6) are similar to analogous curves found by us previously for the cyclohexane oxidation by the "H_2O_2-n-Bu_4NVO_3-PCA" reagent [37–51] and by the "$tert$-BuOOH-n-Bu_4NVO_3" system [52]. The dependence mode of the rate on the PAA initial concentration indicates that a vanadium monoperoxy complex, *comp*, takes part in the generation of species which induces the CyH oxidation:

$$V^V + CH_3C(=O)OOH \rightleftharpoons comp \qquad (1)$$

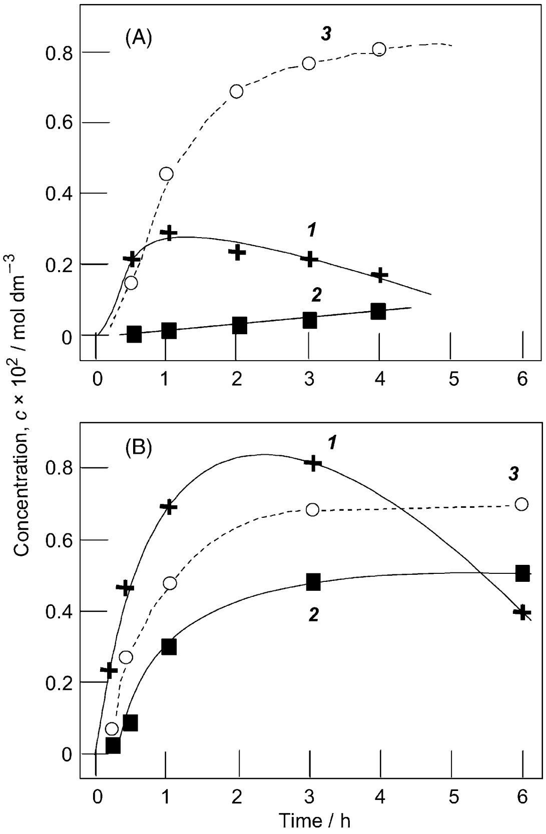


Fig. 3. Accumulation of oxygenates (cyclohexyl hydroperoxide, curve 1; cyclohexanone, curve 2; cyclohexanol, curve 3) in the reaction of cyclohexane (0.46 mol dm^{-3}) with H_2O_2 (0.30 mol dm^{-3}) at 60 °C catalyzed by n-Bu_4VO_3 (1×10^{-4} mol dm^{-3}) in MeCN (total volume of the reaction solution was 10 mL) containing $MeCO_2H$ (0.5 mL) (graph A) and in $MeCO_2H$ (graph B).

Table 1
Oxidation of light alkanes by PAA[a]

Alkane (p, bar)	Solvent	Products ($\times 10^3$, mol dm^{-3})	TON[b]
Methane (30)[c]	MeCN	Formaldehyde (0.1) Methanol (0.4) Methyl acetate (3.0)	35
	$MeCO_2H$	Formaldehyde (2.0) Methanol (0.17)	21
Ethane (25)	MeCN	Acetaldehyde (2.3) Ethanol (1.0) Ethyl acetate (0.43)	34
	$MeCO_2H$	Acetaldehyde (1.0) Ethyl acetate (0.2)	12
Propane (5)	MeCN	Acetone (10) Isopropanol (3) Isopropyl acetate (3) n-Propanol (0.5)	165

[a] Conditions: n-Bu_4VO_3, 1×10^{-4} mol dm^{-3}; PAA, 0.30 mol dm^{-3}; total volume, 10 mL; 60 °C; 3 h.

[b] Numbers of product moles per one mole of a catalyst.

[c] All product concentrations are given after subtraction of corresponding concentrations obtained in blank (without methane) experiments.

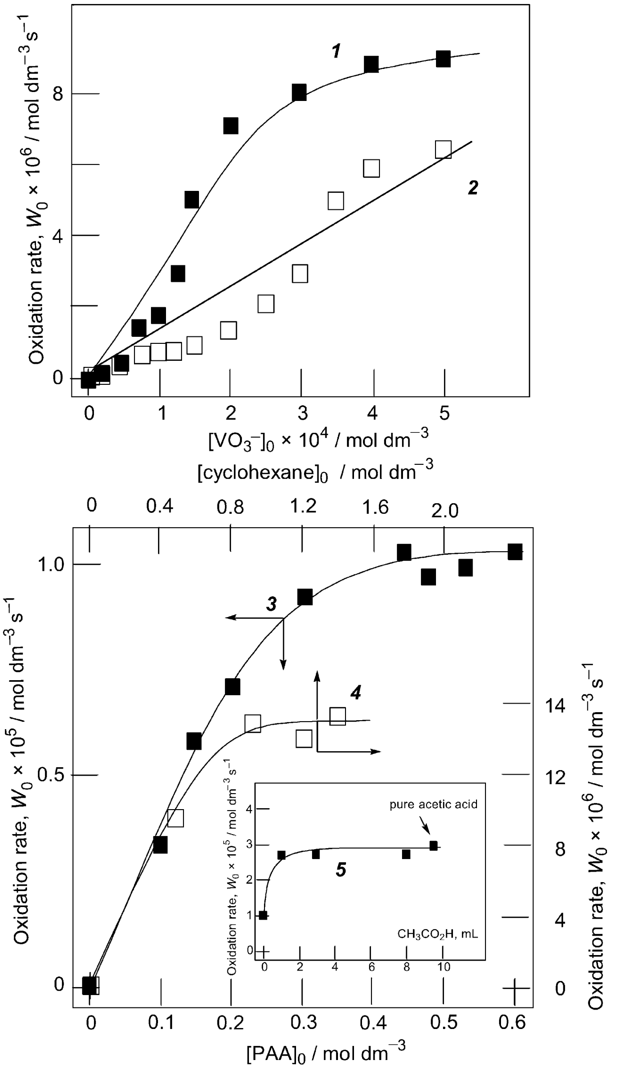


Fig. 4. Initial rate of cyclohexane ($0.46\,mol\,dm^{-3}$) oxidation with PAA in MeCN vs. initial concentration of n-Bu_4VO_3 under different conditions: at 60 °C and $[PAA]_0 = 0.30\,M$ (curve 1) and at 40 °C and $[PAA]_0 = 0.45\,mol\,dm^{-3}$ (curve 2) and °C vs. initial concentration of PAA (curve 3) at $[n\text{-}Bu_4VO_3] = 1 \times 10^{-4}\,mol\,dm^{-3}$ as well as vs. initial concentration of cyclohexane (curve 4) at $[n\text{-}Bu_4VO_3] = 4 \times 10^{-4}\,mol\,dm^{-3}$ and $[PAA]_0 = 0.3\,mol\,dm^{-3}$.

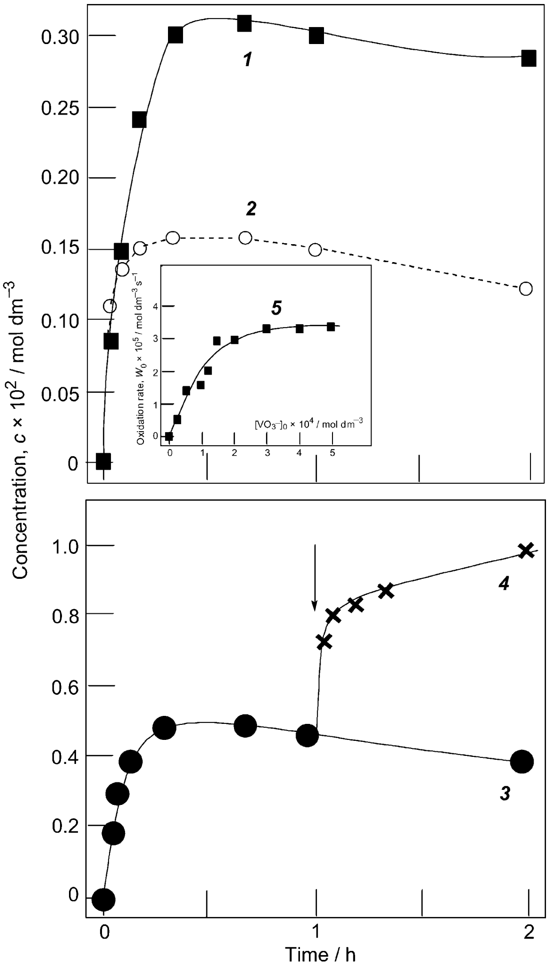


Fig. 5. Accumulation of oxygenates (cyclohexanone, curve 1; cyclohexanol, curve 2; and the sum of all products, curve 3) in the reaction of cyclohexane ($0.46\,mol\,dm^{-3}$) with PAA ($0.30\,mol\,dm^{-3}$) in MeCOOH at 60 °C catalyzed by n-Bu_4VO_3 ($1 \times 10^{-4}\,mol\,dm^{-3}$). In a special experiment at the moment denoted by an arrow an additional amount of PAA ($0.30\,mol\,dm^{-3}$) was added. Accumulation of products in this case is shown by curve 4. In this experiment, concentrations of cyclohexanone and cyclohexanol were measured before and after addition of PPh_3, however, the formation of cyclohexyl hydroperoxide was not detected. Dependence of initial rate of cyclohexane ($0.46\,mol\,dm^{-3}$) oxidation with PAA ($0.3\,mol\,dm^{-3}$) in MeCOOH vs. initial concentration of n-Bu_4VO_3 is shown as curve 5.

$$comp \rightarrow V^{IV} + CH_3C(=O)OO^{\bullet} + H^{+} \quad (2)$$

$$V^{IV} + CH_3C(=O)OOH \rightarrow V^{V} + CH_3C(=O)O^{\bullet} + HO^{-} \quad (3)$$

The mode of the cyclohexane concentration effect on its oxidation rate is in agreement with an assumption about the competition between the processes of $CH_3C(=O)O^{\bullet}$ + CyH interaction, Eq. (4) on the one hand and a $CH_3C(=O)O^{\bullet}$ destruction on the other hand. The deactivation of $CH_3C(=O)O^{\bullet}$ radicals can occur either via its reaction with the solvent (5) or as its monomolecular decarboxylation [18] (6) followed by the interaction of carbon-centered radicals with molecular oxygen to produce an inactive in the oxidation peroxy radical (7):

$$CH_3C(=O)O^{\bullet} + CyH \rightarrow Cy^{\bullet} \quad (4)$$

$$CH_3C(=O)O^{\bullet} + \text{solvent} \rightarrow \text{products} \quad (5)$$

$$CH_3C(=O)O^{\bullet} \rightarrow CH_3^{\bullet} + CO_2 \quad (6)$$

$$CH_3^{\bullet} + O_2 \rightarrow CH_3O_2^{\bullet} \quad (7)$$

The analysis of experimental data presented in Figs. 4 (curve 3) and 6 (curve 2) using the kinetic scheme (1)–(3) allowed us to determine the equilibrium constants for the *comp* formation. They turned out to be equal to 3.3 and $6.8\,dm^3\,mol^{-1}$ for acetonitrile and acetic acid as solvents, respectively.

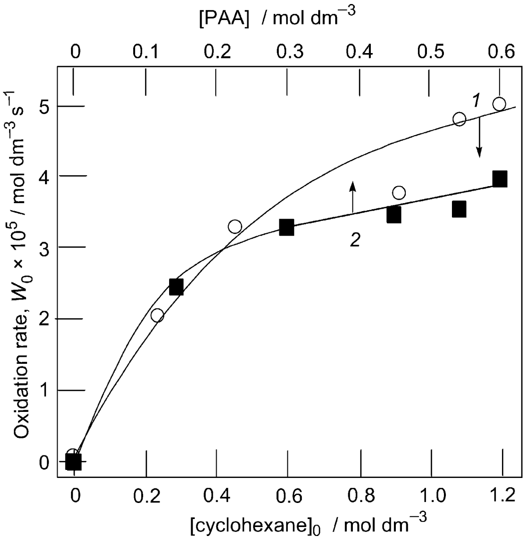


Fig. 6. Initial rate of cyclohexane (0.46 mol dm^{-3}) oxidation with PAA catalyzed by n-Bu_4VO_3 in MeCOOH vs. initial concentration of PAA (curve 1) as well as initial rate of cyclohexane oxidation with PAA (0.3 mol dm^{-3}) in MeCOOH vs. initial concentration of cyclohexane (curve 2). In both experiments [n-Bu_4VO_3] = 4 × 10^{-4} mol dm^{-3}; 60 °C.

Table 2
Selectivity parameters in alkane oxidations by various systems

Substrate	System	Selectivity
n-Hexane		C(1):C(2):C(3)[a]
	VO_3^--PAA in MeCN	1:2.8:2.5
	VO_3^--H_2O_2 in MeCN–$MeCO_2H$[b]	1:4.2:4.1
	VO_3^--H_2O_2 in $MeCO_2H$[c]	1:5.8:4.8
	VO_3^--PCA-H_2O_2 in MeCN[d]	1:8:7
Isooctane[e]		1°:2°:3°[e]
	VO_3^--PAA in MeCN	1:7:38
	VO_3^--H_2O_2 in MeCN–$MeCO_2H$	1:3.8:7.3
	VO_3^--H_2O_2 in $MeCO_2H$	1:1.4:5.2
	VO_3^--PCA-H_2O_2 in MeCN[d]	1:4:9
cis-1,2-DMCH[f]		*trans*/*cis*[f]
	VO_3^--PAA in MeCN	0.46
	VO_3^--PCA-H_2O_2 in MeCN[d]	0.70
trans-1,2-DMCH[f]		*trans*/*cis*[f]
	VO_3^--PAA in MeCN	1.2
	VO_3^--PCA-H_2O_2 in MeCN[d]	0.8

[a] Parameter C(1):C(2):C(3) is normalized (i.e., calculated taking into account the number of hydrogen atoms at each position) relative reactivities of hydrogen atoms in positions 1, 2 and 3 of the hydrocarbon chain, respectively.

[b] Hydrogen peroxide (30% aqueous) in a 9:1 (v/v) mixture MeCN–$MeCO_2H$ at 60 °C.

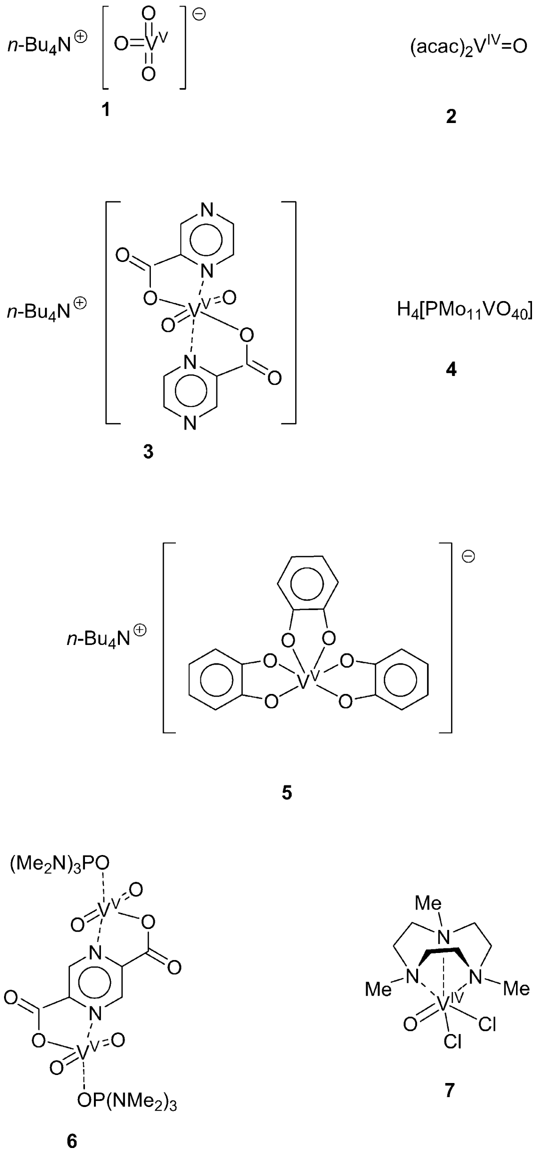
[c] Hydrogen peroxide (30% aqueous) in pure $MeCO_2H$ at 60 °C.

[d] PCA is pyrazine-2-carboxylic acid (for this system, see [37–51]).

[e] Parameter 1°:2°:3° is normalized relative reactivities of hydrogen atoms at primary, secondary and tertiary carbons of 2,2,4-trimethylpentane (isooctane), respectively.

[f] Parameter *trans*/*cis* is the *trans*/*cis* ratio of isomers of *tert*-alcohols formed in the oxidation of *cis*- or *trans*-1,2-dimethylcyclohexane (DMCH).

Using kinetic scheme (4)–(7) and experimental parameters given in Figs. 4 (curve 4) and 6 (curve 1), we calculated that the ratio of the rate constant for $CH_3C(=O)O^\bullet$ + CyH interaction to the effective decomposition first order constant equals approximately one for the two solvents. It should be noted that this value is >5 times lower than the corresponding parameter calculated for the reaction between cyclohexane and hydroxyl radicals. This fact testifies that, in our case, an oxidizing species is not the hydroxyl radical but it is a more selectively attacking species, i.e. $CH_3C(=O)O$=. Finally, the rate dependence on the vanadate concentration (see Fig. 4, curves 1 and 2 and Fig. 5, curve 5) surprisingly turned out to be more complex than for previously studied systems [49–52]. This is apparently due to very complex equilibrium transformations of vanadate ion in a medium containing considerable concentrations of acetic acid.



Scheme 1.

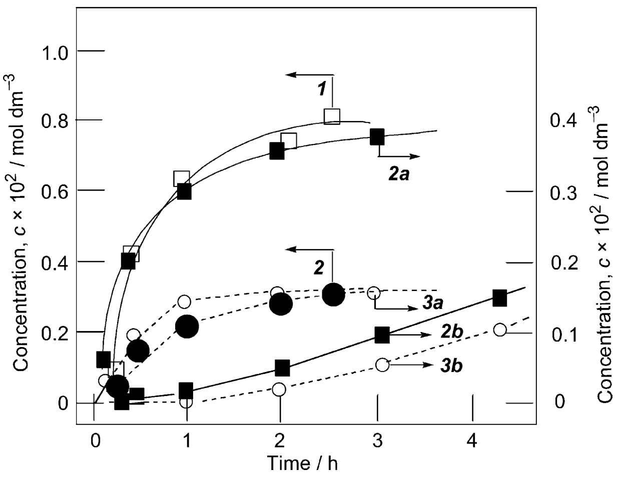


Fig. 7. Accumulation of oxygenates (cyclohexanone, curve 1 and cyclohexanol, curve 2) in the reaction of cyclohexane (0.46 mol dm^{-3}) with PAA (0.30 mol dm^{-3}) in MeCN at 60 °C catalyzed by VO(acac)$_2$ (**2**) (1 × 10^{-4} mol dm^{-3}) as well as accumulation of oxygenates (cyclohexanone, curve 2 and cyclohexanol, curve 3) in the reaction of cyclohexane (0.46 mol dm^{-3}) with PAA (0.30 mol dm^{-3}) in MeCN at 60 °C catalyzed by compound (**3**) (1 × 10^{-4} mol dm^{-3}; curves marked a) and compound $H_4PMo_{11}VO_{40}$ (**4**) (1 × 10^{-4} mol dm^{-3}; curves marked b). In these experiments concentrations of cyclohexanone and cyclohexanol were measured only after addition of PPh_3.

We studied the behaviour of certain other vanadium complexes shown in Scheme 1 as catalysts in the cyclohexane oxidation in acetonitrile. The results are demonstrated in Figs. 7 and 8. Comparing these data with that for catalysis by compound **1** shows that a vanadium(IV) derivative **2** is not less efficient as a catalyst (Fig. 7, curves 1 and 2). At the same time, the activity of complex **7** which contains V^{IV} ion strongly bound to N_3-chelating ligand is very low (Fig. 8) apparently due to great sterical hindrance. Less voluminous N,O-chelating ligands coordinated to V^V in complexes **3** (Fig. 7) and **6** (Fig. 8) provide the activity comparable with that for simple vanadate **1**.

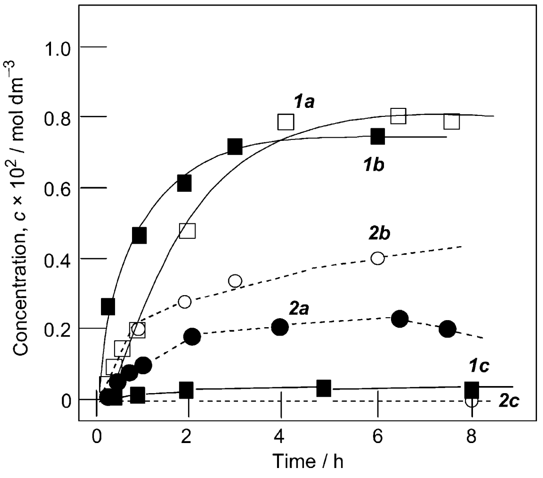


Fig. 8. Accumulation of oxygenates (cyclohexanone, curve 1 and cyclohexanol, curve 2) in the reaction of cyclohexane (0.46 mol dm^{-3}) with PAA (0.30 mol dm^{-3}) in MeCN at 60 °C catalyzed by compound (5) (1 × 10^{-4} mol dm^{-3}; curves marked a) by compound (6) (1 × 10^{-4} mol dm^{-3}; curves marked b) and by compound (7) (1 × 10^{-4} mol dm^{-3}; curves marked c). In these experiments concentrations of cyclohexanone and cyclohexanol were measured only after addition of PPh_3.

The activity of V^V-containing polyoxometalate **4** in which the vanadium ion is surrounded by a few molybdenum ions is very low (Fig. 7). In this case, the oxidation proceeds with auto-acceleration which is possibly due to a gradual decomposition of a bulky polyoxometalate ion with the formation of relatively small fragments [61]. High activity of O_2-chelate-containing complex **5** (Fig. 8) can be explained by easily occurring decomposition of the starting compound via oxidation of the catecholate ligand which gives rise to the formation of a reactive species. Thus it can be concluded that complexes of vanadium(V) and vanadium(IV) are active in the alkane oxidation with PAA only if these complexes do not contain strongly bound bulky surroundings.

Acknowledgements

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References

[1] A.E. Shilov, G.B. Shul'pin, Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes, [Chapter 10: Homogeneous catalytic oxidation of hydrocarbons by peroxides and other oxygen atom donors], Kluwer Academic Publishers, Dordrecht, 2000.

[2] G.B. Shul'pin, in: M. Beller, C. Bolm (Eds.), Transition Metals for Organic Synthesis, vol. 2, second ed., Wiley-VCH, New York, 2004.

[3] A.E. Shilov, G.B. Shul'pin, Chem. Rev. 97 (1997) 2879–2932.

[4] D. Ma, C. Xia, H. Tian, Tetrahedron Lett. 40 (1999) 8915–8917.

[5] M. Freccero, R. Gandolfi, M. Sarzi-Amadè, A. Rastelli, Tetrahedron 57 (2001) 9843–9848.

[6] M. Picard, J. Gross, E. Lübbert, S. Tölzer, S. Krauss, K.-H. van Pée, A. Berkessel, Angew. Chem. Int. Ed. 36 (1997) 1196–1199.

[7] W.C. Frank, Tetrahedron: Asymmetry 9 (1998) 3745–3749.

[8] S. Ueno, K. Yamaguchi, K. Yoshida, K. Ebitani, K. Kaneda, Chem. Commun. (1998) 295–296.

[9] K. Yamaguchi, K. Ebitani, K. Kaneda, J. Org. Chem. 64 (1999) 2966–2968.

[10] H.-D. Brauer, B. Eilers, A. Lange, J. Chem. Soc., Perkin Trans. 2 (2002) 1288–1295.

[11] S.-I. Murahashi, Y. Oda, N. Komiya, T. Naota, Tetrahedron Lett. 35 (1994) 7953–7956.

[12] S. Banfi, F. Montanari, S. Quici, S.V. Barkanova, O.L. Kaliya, V.N. Kopranenkov, E.A. Luk'yanets, Tetrahedron Lett. 36 (1995) 2317–2320.

[13] M. Kodera, H. Shimakoshi, K. Kano, Chem. Commun. (1996) 1737–1738.

[14] S.V. Barkanova, V.M. Derkacheva, O.V. Dolotova, V.D. Li, V.M. Negrimovsky, O.L. Kaliya, E.A. Luk'yanets, Tetrahedron Lett. 37 (1996) 1637–1640.
[15] M. Yamaguchi, H. Kousaka, T. Yamagishi, Chem. Lett. (1997) 769–770.
[16] M. Yamaguchi, T. Iida, T. Yamagishi, Inorg. Chem. Commun. 1 (1998) 299–301.
[17] J.R. Lindsay Smith, G.B. Shul'pin, Tetrahedron Lett. 39 (1998) 4909–4912.
[18] J.R. Lindsay Smith, G.B. Shul'pin, Russ. Chem. Bull. 47 (1998) 2313–2315.
[19] G.B. Shul'pin, J.R. Lindsay Smith, Russ. Chem. Bull. 47 (1998) 2379–2386.
[20] U. Beifuss, A. Herde, Tetrahedron Lett. 39 (1998) 7691–7692.
[21] T. Konoike, Y. Araki, Y. Kanda, Tetrahedron Lett. 40 (1999) 6971–6974.
[22] S. Banfi, M. Cavazzini, G. Pozzi, S.V. Barkanova, O.K. Kaliya, J. Chem. Soc., Perkin Trans. 2 (2000) 871–877.
[23] S. Banfi, M. Cavazzini, G. Pozzi, S.V. Barkanova, O.K. Kaliya, J. Chem. Soc., Perkin Trans. 2 (2000) 879–885.
[24] N. Komiya, S. Noji, S.-I. Murahashi, Chem. Commun. (2000) 65–66.
[25] C.J. Moody, J.L. O'Connell, Chem. Commun. (2000) 1311–1312.
[26] S.V. Barkanova, E.A. Makarova, J. Mol. Catal. A: Chem. 174 (2001) 89–105.
[27] S.V. Barkanova, O.K. Kaliya, E.A. Luk'yanets, Mendeleev Commun. 11 (2001) 116–118.
[28] S.-I. Murahashi, N. Komiya, Y. Hayashi, T. Kumano, Pure Appl. Chem. 73 (2001) 311–314.
[29] W. Nam, I. Kim, Y. Kim, C. Kim, Chem. Commun. (2001) 1262–1263.
[30] J. Le Bras, J. Muzart, J. Mol. Catal. A: Chem. 185 (2002) 113–117.
[31] H.R. Khavasi, S.S.H. Davarani, N. Safari, J. Mol. Catal. A: Chem. 188 (2002) 115–122.
[32] T. Sooknoi, J. Limtrakul, Appl. Catal. A: Gen. 233 (2002) 227–237.
[33] M. Yamaguchi, Y. Ichii, S. Kosaka, D. Masui, T. Yamagishi, Chem. Lett. (2002) 434–435.
[34] W. Nam, J.Y. Ryu, I. Kim, C. Kim, Tetrahedron Lett. 43 (2002) 5487–5490.
[35] N. Grootboom, T. Nyokong, J. Mol. Catal. A: Chem. 179 (2002) 113–123.
[36] G. Ingrosso, N. Midollini, J. Mol. Catal. A: Chem. 204–205 (2003) 425–431.
[37] G.B. Shul'pin, D. Attanasio, L. Suber, Russ. Chem. Bull. 42 (1993) 55–59.
[38] G.B. Shul'pin, D. Attanasio, L. Suber, J. Catal. 142 (1993) 147–152.
[39] G.B. Shul'pin, A.N. Druzhinina, G.V. Nizova, Russ. Chem. Bull. 42 (1993) 1327–1329.
[40] G.V. Nizova, G.B. Shul'pin, Russ. Chem. Bull. 43 (1994) 1146–1148.
[41] G.B. Shul'pin, G. Süss-Fink, J. Chem. Soc., Perkin Trans. 2 (1995) 1459–1463.
[42] G.B. Shul'pin, R.S. Drago, M. Gonzalez, Russ. Chem. Bull. 45 (1996) 2386–2388.
[43] M.C. Guerreiro, U. Schuchardt, G.B. Shul'pin, Russ. Chem. Bull. 46 (1997) 749–754.
[44] G.B. Shul'pin, M.C. Guerreiro, U. Schuchardt, Tetrahedron 52 (1996) 13051–13062.
[45] G.V. Nizova, G. Süss-Fink, G.B. Shul'pin, Tetrahedron 53 (1997) 3603–3614.
[46] U. Schuchardt, M.C. Guerreiro, G.B. Shul'pin, Russ. Chem. Bull. 47 (1998) 247–252.
[47] G. Süss-Fink, G.V. Nizova, S. Stanislas, G.B. Shul'pin, J. Mol. Catal. A: Chem. 130 (1998) 163–170.
[48] G.B. Shul'pin, Y. Ishii, S. Sakaguchi, T. Iwahama, Russ. Chem. Bull. 48 (1999) 887–890.
[49] G.B. Shul'pin, Yu.N. Kozlov, G.V. Nizova, G. Süss-Fink, S. Stanislas, A. Kitaygorodskiy, V.S. Kulikova, J. Chem. Soc., Perkin Trans. 2 (2001) 1351–1371.
[50] Yu.N. Kozlov, G.V. Nizova, G.B. Shul'pin, Russ. J. Phys. Chem. 75 (2001) 770–774.
[51] M.H.C. de la Cruz, Yu.N. Kozlov, E.R. Lachter, G.B. Shul'pin, New J. Chem. 27 (2003) 634–638.
[52] G.B. Shul'pin, Yu.N. Kozlov, Org. Biomol. Chem. 1 (2003) 2302–2306.
[53] J.-M. Brégeault, Catalyse homogène par les complexes des métaux de transition, Masson, Paris, 1992.
[54] A. Butler, M.J. Clague, G.E. Meister, Chem. Rev. 94 (1994) 626–638.
[55] V. Conte, F. Di Furia, G. Licini, Appl. Catal. A: Gen. 157 (1997) 335–361.
[56] E.P. Talsi, V.D. Chinakov, V.P. Babenko, K.I. Zamaraev, J. Mol. Catal. 81 (1993) 235–254.
[57] E.P. Talsi, K.V. Shalyaev, J. Mol. Catal. A: Chem. 92 (1994) 245–255.
[58] N.I. Moiseeva, A.E. Gekhman, I.I. Moiseev, J. Mol. Catal. A: Chem. 117 (1997) 39–55.
[59] C. Bolm, G. Schlingloff, F. Bienewald, J. Mol. Catal. A: Chem. 117 (1997) 347–350.
[60] F. van de Velde, I.W.C.E. Arends, R.A. Sheldon, J. Inorg. Biochem. 80 (2000) 27–33.
[61] J.-M. Brégeault, F. Launay, A. Atlamsani, C. R. Chim. 4 (2001) 11–26.
[62] K.P. Bryliakov, E.P. Talsi, T. Kühn, C. Bolm, New. J. Chem. 27 (2003) 609–614.
[63] G.S. Mishra, A. Kumar, J. Mol. Catal. A: Chem. 192 (2003) 275–280.
[64] K.P. Bryliakov, E.P. Talsi, S.N. Stas'ko, O.A. Kholdeeva, S.A. Popov, A.V. Tkachev, J. Mol. Catal. A: Chem. 194 (2003) 79–88.
[65] G.B. Shul'pin, E.R. Lachter, J. Mol. Catal. A: Chem. 197 (2003) 65–71.
[66] E. Battistel, R. Tassinari, M. Fornaroli, L. Bonoldi, J. Mol. Catal. A: Chem. 202 (2003) 107–115.
[67] J.E. Remias, T.A. Pavlovsky, A. Sen, J. Mol. Catal. A: Chem. 203 (2003) 179–192.
[68] P.M. Reis, J.A.L.A.F. Silva Palavra, J.J.R. Fraústo da Silva, T. Kitamura, Y. Fujiwara, A.J.L. Pombeiro, Angew. Chem. Int. Ed. 42 (2003) 821–823.
[69] S. Seelan, A.K. Sinha, Appl. Catal. A: Gen. 238 (2003) 201–209.
[70] E.D. Park, Y.-S. Hwang, C.W. Lee, J.S. Lee, Appl. Catal. A: Gen. 247 (2003) 269–281.
[71] T. Joseph, M. Hartmann, S. Ernst, S.B. Halligudi, J. Mol. Catal. A: Chem. 207 (2004) 129–135.
[72] G.B. Shul'pin, A.N. Druzhinina, React. Kinet. Catal. Lett. 47 (1992) 207–211.
[73] G.B. Shul'pin, G.V. Nizova, React. Kinet. Catal. Lett. 48 (1992) 333–338.
[74] G.B. Shul'pin, A.N. Druzhinina, Petrol. Chem. 33 (1993) 247–251.
[75] G.B. Shul'pin, A.N. Druzhinina, L.S. Shul'pina, Petrol. Chem. 33 (1993) 321–325.
[76] G.B. Shul'pin, M.M. Bochkova, G.V. Nizova, J. Chem. Soc., Perkin Trans. 2 (1995) 1465–1469.
[77] G.B. Shul'pin, G.V. Nizova, Yu.N. Kozlov, New J. Chem. 20 (1996) 1243–1256.
[78] G.B. Shul'pin, Alkane oxidation: estimation of alkyl hydroperoxide content by GC analysis of the reaction solution samples before and after reduction with triphenylphosphine (2001) 1–6, http://preprint.chemweb.com/orgchem/0106001.
[79] G.B. Shul'pin, J. Mol. Catal. A: Chem. 189 (2002) 39–66.
[80] G.B. Shul'pin, C. R. Chim. 6 (2003) 163–178.
[81] V.W. Day, W.G. Klemperer, A. Yagasaki, Chem. Lett. (1990) 1267–1268.
[82] G. Süss-Fink, L. Gonzalez Cuervo, B. Therrien, H. Stoeckli-Evans, G.B. Shul'pin, Inorg. Chim. Acta 357 (2004) 475–484.