Oxidations by the reagent 'H_2O_2–vanadium complex–pyrazine-2-carboxylic acid'. Part 4.[1] Oxidation of alkanes, benzene and alcohols by an adduct of H_2O_2 with urea

Georgiy B. Shul'pin *,[a] and **Georg Süss-Fink** [b]
[a] *N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow 117977, Russia*
[b] *Institut de Chimie, Faculté des Sciences, Université de Neuchâtel, CH-2000, Neuchâtel, Avenue de Bellevaux 51, Switzerland*

In the presence of catalytic amounts of a vanadium complex ($Bu^n_4NVO_3$) and pyrazine-2-carboxylic acid, the adduct H_2O_2·urea, in MeCN solution at 22–60 °C, oxidizes cyclohexane to yield mainly cyclohexyl hydroperoxide which may be easily converted into cyclohexanol by the action of triphenylphosphine (at room temperature after the reduction the ratio cyclohexanol : cyclohexanone is 25 : 1). Linear and branched alkanes are also oxidized by this reagent to give the corresponding alcohols, the regioselectivity being low; *e.g.*, for oxidation of hexane C(1) : C(2) : C(3) = 1.0 : 6.8 : 6.0. The effective activation energy of cyclohexane oxidation is ~ 70 kJ mol^{-1}. Dependencies of initial rate of the reaction on concentration of substrate and the components of the reagent have been obtained. The postulated mechanism includes, as the key stage, the abstraction of a hydrogen atom from alkane, RH, to produce radical R$^•$ which then rapidly reacts with O_2 to afford ROO$^•$. The hydrogen atom is most probably abstracted by hydroxyl radical formed in the interaction of H_2O_2 with the vanadium complex. Benzene is oxidized by the reagent under consideration to yield phenol, and alcohols are transformed into aldehydes or ketones.

Introduction

The transformation of hydrocarbons, the main crude oil and natural gas constituents, into oxygenated derivatives such as alcohols, aldehydes, ketones, carboxylic acids and peroxides has been extensively studied over the last decades, primarily because such products are important intermediates in industrial production.[6–9] However, industrial oxidation processes are usually not selective. For instance, catalytic oxidation of cyclohexane with air in the presence of manganese or cobalt naphthenates to give a mixture of cyclohexanone and cyclohexanol as goal products may produce up to 100 additional substances.[10] Thus, at present one of the aims of metal complex catalysis is the search for new efficient systems which oxidize hydrocarbons and other organic compounds under mild conditions with high selectivities.

In addition to molecular oxygen (and air), hydrogen peroxide is the most attractive oxidation reagent because it is inexpensive and gives only water as by-product. A large number of publications have appeared on oxidations by hydrogen peroxide in the presence of transition metal complexes.[11] Complexes of chromium, molybdenum, titanium, ruthenium, iron, palladium, polyoxometalates and metalloporphyrinates were employed as catalysts in such oxidations. Since the pioneering paper by Milas,[12] vanadium complexes are known to catalyse H_2O_2 oxidations and many papers on this topic have appeared.[13] Alkyl peroxides are also used in vanadium-catalysed oxidations.[14] Vanadium peroxo complexes that easily oxidize hydrocarbons in stoichiometric reactions[15] were postulated as active intermediates in catalytic processes.[13,14] It should also be noted that vanadium-containing complexes catalyse oxidation of organic compounds with molecular oxygen[16] and play an important role in biological systems.[17]

We have recently shown that vanadate anion in the presence of pyrazine-2-carboxylic acid (PCA) catalyses efficient oxidation of organic compounds by aq. (30%) hydrogen peroxide in MeCN. Under the action of this system alkanes are transformed predominantly into alkyl hydroperoxides (as well as smaller amounts of alcohols and ketones or aldehydes),[2,5] alcohols give rise to ketones or aldehydes,[3,5] and benzene and its alkyl derivatives are oxidized to produce phenols and quinones as well as side-chain oxidation derivatives.[3,5] In continuing the study of the synthetic applications of the system 'H_2O_2–vanadium complex–PCA' we attempted to use an adduct of hydrogen peroxide with urea as the oxidizing reagent (hydrocarbon oxygenation by H_2O_2·urea catalysed by CrO_3 was recently described[18]). The merits of this method would include the absence of water in the reaction solution which could destroy some substrates.

Here we report oxidation of saturated hydrocarbons, benzene and aliphatic alcohols by the system 'H_2O_2·urea–VO_3^-–PCA' in MeCN. It should be emphasized that the system under discussion transforms alkanes under mild conditions into alkyl hydroperoxides—valuable products for organic synthesis both in the laboratory and in industry,[19] and which also play a very important role in living cells.[20]

Results and discussion

We carried out oxidation of cyclohexane in MeCN solution by using adduct H_2O_2·urea at various temperatures in the range 22–60 °C (Fig. 1). A combination (Bu^n_4N)VO_3 + PCA in the ratio 1 : 4 was used as catalyst.

The process was monitored by withdrawing aliquots at specific intervals and analysing them by means of GLC. If the reaction solution was injected in the chromatograph without any preliminary treatment, the formation of cyclohexanol and cyclohexanone in approximately equal amounts was detected. It should be emphasized that neither product can be formed in substantial amounts from cyclohexane and hydrogen peroxide directly in the injector or the chromatographic column since in the initial moment of the reaction, when the concentrations of both starting reagents are high, GLC detects only minor amounts of the oxidation products. However, if an excess of triphenylphosphine is added to the reaction solution 10–20 min

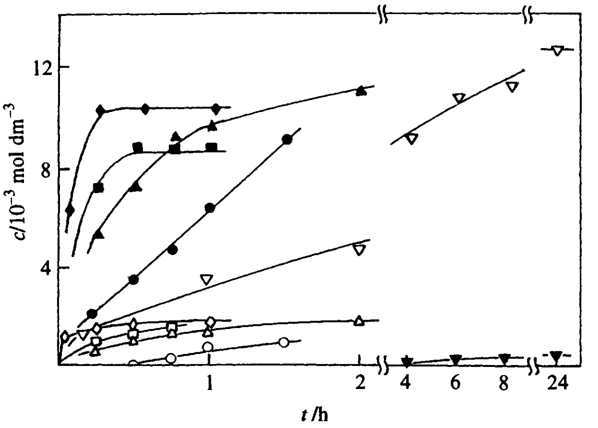


Fig. 1 Kinetics of oxidation of cyclohexane (0.56 mol dm^{-3}) by adduct H_2O_2·urea (0.07 mol dm^{-3}) in MeCN catalysed by $(Bu^n_4N)VO_3$ (0.125×10^{-3} mol dm^{-3}) and PCA (0.5×10^{-3} mol dm^{-3}) at various temperatures: 22 (curves ▽,▼), 30 (○,●), 40 (△,▲), 50 (□,■) and 60 °C (◇,◆). Open symbols, cyclohexanol; closed symbols, cyclohexanone. Triphenylphosphine was added to an aliquot before the GLC analysis (the same as in the cases shown in Figs. 2–7).

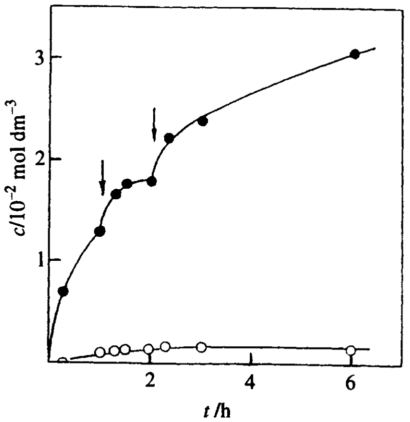


Fig. 2 Oxidation of cyclohexane (0.09 mol dm^{-3}) in the presence of VO_3^- (0.125×10^{-3} mol dm^{-3}) and PCA (0.5×10^{-3} mol dm^{-3}). ●, Cyclohexanol; ○, cyclohexanone. At time t = 0 and at moments denoted by arrows, portions of solid adduct H_2O_2·urea (0.14 mol dm^{-3}) were added. Temperature 40 °C.

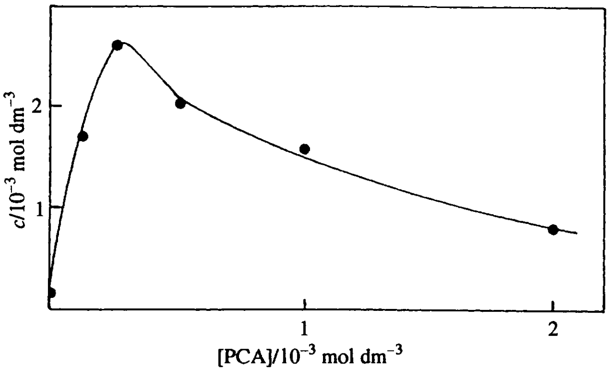


Fig. 3 Plot of initial rate of the reaction W_0 [determined as concentration, c, of the cyclohexane oxidation products (sum of cyclohexanol and cyclohexanone after the reduction of an aliquot by triphenylphosphine) after 15 min of the reaction] *versus* concentration of PCA. Conditions: $[CyH]_0$ = 0.37 mol dm^{-3}; $[H_2O_2\cdot urea]_0$ = 0.07 mol dm^{-3}; $[VO_3^-]$ = 0.125×10^{-3} mol dm^{-3}; 30 °C.

before the GLC analysis, the resulting chromatogram differs drastically from that of a sample not subjected to reduction by triphenylphosphine. In this case, the cyclohexanol peak rises markedly, while the intensity of the cyclohexanone peak decreases. The sum of alcohol and ketone concentrations in the reduced sample is approximately equal to the total concentration of products in the solution untreated with triphenylphosphine. These results can be explained by the fact that on interaction of the reagent under discussion with cyclohexane the alkane is oxidized mainly to yield cyclohexyl hydroperoxide. It is known that cyclohexyl hydroperoxide is totally decomposed in the chromatograph to produce cyclohexanol and cyclohexanone in the ratio ~1:1. The peroxide is readily and quantitatively reduced by triphenylphosphine to yield cyclohexanol.[21] Thus, by comparison of the data of chromatographic analysis of the reaction solution before and after reduction by triphenylphosphine, the amounts of cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone present in the solution at a given moment can be estimated. For example, if the chromatogram of a solution before the reduction exhibits two peaks of approximately equal area for cyclohexanol and cyclohexanone and after the reduction only cyclohexanol is determined by GLC, these data testify that only cyclohexyl hydroperoxide is present in the solution.

Fig. 1 demonstrates that the temperature influences not only the rate of cyclohexane oxidation but also the composition of the mixture of products formed (only data obtained after the reduction are shown). At elevated temperatures (40–50 °C) the accumulation of oxidation products terminates after *ca.* 0.5 h. In this case a substantial amount of cyclohexanone is formed (the ratio cyclohexanol:cyclohexanone is ~5:1). However, at room temperature, when the accumulation of products is slow, only negligible quantities of cyclohexanone are detected after 24 h (the ratio cyclohexanol:cyclohexanone is ~25:1). These data may be explained as follows. Only cyclohexyl hydroperoxide is formed in cyclohexane oxidation by the reagent 'H_2O_2·urea–VO_3^-–PCA', but some part of this peroxide is decomposed to produce a mixture of cyclohexanol and cyclohexanone. The higher the temperature the faster the decomposition. The vanadium complex present in the solution apparently accelerates the decomposition (metal complexes are known to catalyse the decomposition of peroxides[22]).

An excess of cyclohexane over hydrogen peroxide was used in experiments shown in Fig. 1. In this case, at room temp., the yield of oxidation products after 24 h is 20% with respect to hydrogen peroxide (if it is assumed that one H_2O_2 molecule is required to produce one alkyl hydroperoxide molecule). The catalyst turnover number equals 100. When concentration of cyclohexane is lower and an excess of adduct H_2O_2·urea is used (Fig. 2) the yield of oxidation products is 37% with respect to cyclohexane (the catalyst turnover number reaches 260).

The dependence of the initial rate of oxidation (determined as concentration of products after 15 min of the reaction) on the concentration of PCA (Fig. 3) exhibits a maximum at ratio [V]:[PCA] = 1:2. However, the composition of the catalyst in all experiments described here was slightly different ([V]:[PCA] = 1:4) in order to minimize the influence of deviations of the PCA concentration in different experiments on the oxidation rate. In the absence of PCA the oxidation rate is negligible.

As shown in Fig. 4, at low catalyst content, the reaction rate is proportional to the catalyst concentration. However, when $[VO_3^-] > 0.1 \times 10^{-3}$ mol dm^{-3}, W_0 is almost independent of $[VO_3^-]$. The shape of the dependence curve of the reaction rate on concentration of cyclohexane is analogous (Fig. 5). The reaction is first order in H_2O_2·urea (Fig. 6).

In addition to cyclohexane, we carried out the oxidation of some linear and branched saturated hydrocarbons and deter-

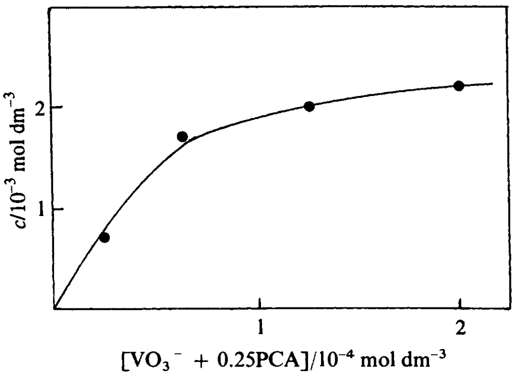


Fig. 4 Plot of initial rate of the reaction W_0 (see caption to Fig. 3) *versus* concentration of the catalyst (VO_3^- + 4PCA). Conditions: $[CyH]_0$ = 0.37 mol dm^{-3}; $[H_2O_2{\cdot}urea]_0$ = 0.07 mol dm^{-3}; 30 °C.

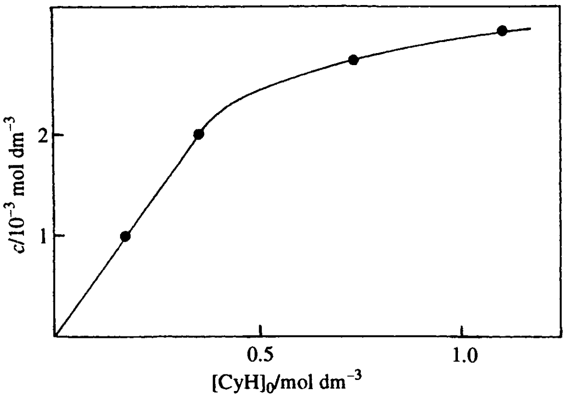


Fig. 5 Plot of initial rate of the reaction W_0 (see caption to Fig. 3) *versus* initial concentration of cyclohexane. Conditions: $[VO_3^-]$ = 0.125 × 10^{-3} mol dm^{-3}; [PCA] = 0.5 × 10^{-3} mol dm^{-3}; $[H_2O_2{\cdot}urea]_0$ = 0.07 mol dm^{-3}; 30 °C.

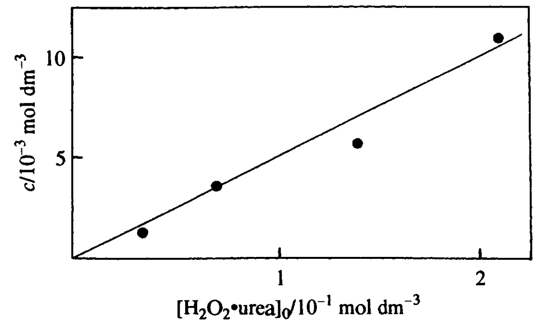
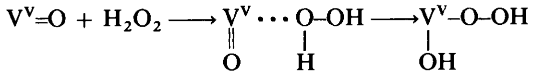


Fig. 6 Plot of initial rate of the reaction W_0 (see caption to Fig. 3) *versus* initial concentration of adduct $H_2O_2{\cdot}urea$. Conditions: $[VO_3^-]$ = 0.125 × 10^{-3} mol dm^{-3}; [PCA] = 0.5 × 10^{-3} mol dm^{-3}; $[CyH]_0$ = 0.56 mol dm^{-3}; 35 °C.

mined the regioselectivities of this reaction. The data are summarized in Table 1. The parameters listed in this Table testify to the low selectivity of the reaction under discussion and are close to those determined for oxygenations of hydrocarbons by hydroxyl radicals. Thus, in the hydroxylation of hexane by hydrogen peroxide in MeCN upon UV irradiation, selectivity parameters C(1):C(2):C(3) = 1:10:7. The selectivities 1°:2°:3° for 2- and 3-methylhexane in this photochemical reaction are 1:6:20 and 1:4:12, respectively.[2] So, it may be assumed that the key role in the transformation of alkanes into alkyl hydroperoxide under the action of the reagent described in this paper is played by O-centred radicals, *i.e.* hydroxyl radicals[4] or vanadium-containing radical-like species. Vanadium hydroperoxide **1** may be formed in the first stage of the reaction [eqn. (1)]:



$$V^V{=}O + H_2O_2 \longrightarrow \underset{O}{\overset{}{\underset{\|}{V^V}}} \cdots \underset{H}{\underset{|}{O}}{-}OH \longrightarrow \underset{OH}{\underset{|}{V^V}}{-}O{-}OH \quad (1)$$

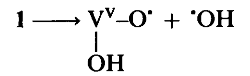
1

Compound **1** then rearranges into radical **2** (see ref. 15*a*) [eqn. (2)]:

$$\mathbf{1} \longrightarrow H_2O \cdots V^{IV}{-}O{-}O^{\bullet} \quad (2)$$

2

or decomposes to produce two radicals [eqn. (3)]:



$$\mathbf{1} \longrightarrow \underset{OH}{\underset{|}{V^V}}{-}O^{\bullet} + {}^{\bullet}OH \quad (3)$$

3

All radicals proposed in these schemes are capable in principle of reacting with alkanes, RH, to abstract a hydrogen atom [reactions (4)–(7)]:

$$^{\bullet}OH + RH \longrightarrow H_2O + R^{\bullet} \quad (4)$$

$$V{-}O^{\bullet} + RH \longrightarrow V{-}OH + R^{\bullet} \quad (5)$$

$$V{-}OO^{\bullet} + RH \longrightarrow V{-}OOH + R^{\bullet} \quad (6)$$

Alkyl radicals thus formed react rapidly with an oxygen molecule:[23]

$$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet} \quad (7)$$

The last radical after abstraction of the hydrogen atom or addition of electron and proton is transformed into alkyl hydroperoxide. The same compound may be obtained in the reaction shown in equation (8):

$$V^{IV}{-}OOH + R^{\bullet} \longrightarrow V^{III} + ROOH \quad (8)$$

In this case molecular oxygen does not participate in the process. However, it is reasonable to assume that ROOH is formed predominantly (or exclusively) from atomospheric oxygen. The following examples taken from the literature support this hypothesis. Molecular oxygen seems to participate in the functionalization of saturated hydrocarbons by Gif-type systems (GoAgg^{II}) to produce alkyl hydroperoxides.[24] The oxygen atom of cyclodecanone, formed by oxidation of cyclodecane using $FeCl_3$–H_2O_2 in pyridine–acetic acid, is largely derived from molecular oxygen.[25] Iron(II)-induced generation of hydrogen peroxide from dioxygen has been described recently.[26] We have shown that oxidation of cyclohexane by hydrogen peroxide catalysed by Cr^{VI} complexes,[27] iron porphyrinate[27] in MeCN, and vanadate ion[27] in $MeCO_2H$ as well as palladium peroxo complexes[28] in MeCN affords cyclohexyl hydroperoxide in sufficient amounts. It is noteworthy that, like our case, alkane oxidation by hydrogen peroxide catalysed by iron complexes in pyridine–acetic acid is accelerated in the presence of pyridine-2-carboxylic (picolinic) acid and other related chelating ligands (the GoAgg^{III} system).[29]

At last, the route[15a] leading to alcohol [eqn. (9)] cannot

$$V^{IV}{-}O{-}OH + R^{\bullet} \longrightarrow V^V{=}O + ROH \quad (9)$$

be excluded. Indeed, we were unable to determine directly the quantity of cyclohexanol formed in the reaction solution if this amount is small (unfortunately, the accuracy of hydroperoxide determination by titration is not satisfactory for our purposes;

Table 1 Oxidation of linear and branched alkanes by the reagent 'H_2O_2·urea–VO_3^-–PCA' in MeCN at 22 °C

Alkane	Selectivity[a]
Pentane	C(1):C(2):C(3) = 1.0:6.7:7.2
Hexane[b]	C(1):C(2):C(3) = 1.0:6.8:6.0
2-Methylpentane	1°:2°:3° = 1:9:40
3-Methylpentane	1°:2°:3° = 1:6:39

[a] The relative reactivities of hydrogen atoms at carbon atoms 1, 2 and 3 of linear alkanes and at the primary, secondary and tertiary carbon atoms of branched alkanes are listed, taking into account the number of hydrogen atoms at each of the carbon atoms. [b] In oxidation by 30% aq. hydrogen peroxide selectivities were C(1):C(2):C(3) = 1:8:7 (see ref. 2).

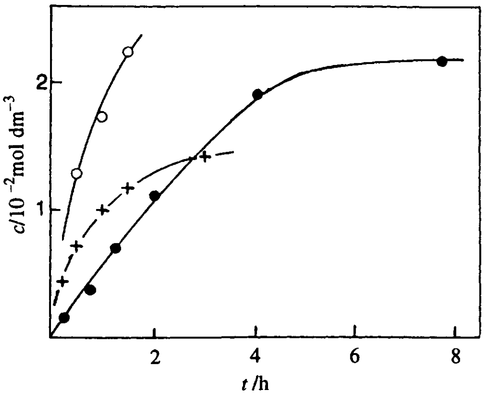


Fig. 7 Accumulation of acetone (●), propanal (○) and phenol (+) in the oxidation of propan-2-ol (0.5 mol dm^{-3}), propan-1-ol (0.5 mol dm^{-3}) and benzene (0.5 mol dm^{-3}), respectively in MeCN. Conditions: $[H_2O_2\text{·urea}]_0$ = 0.14 mol dm^{-3}; $[VO_3^-]$ = 0.125 × 10^{-3} mol dm^{-3}; [PCA] = 0.5 × 10^{-3} mol dm^{-3}; temperature 30 °C for ● and ○, 50 °C for +.

our attempts to measure *precisely* the amount of triphenylphosphine oxide formed were also unsuccessful). The stage of abstraction of hydroxy group from iron ion by radical R$^•$ is postulated for the mechanism of alkane oxidation with participation of cytochrome *P*-450 (see, *e.g.*, refs. 7 and 8). The interaction of R$^•$ with V–OOH in a similar manner could produce a product of abstraction of group OOH, as shown in eqn. (8). Earlier we proposed such a stage for the formation of cyclohexyl hydroperoxide in the photochemical oxidation of cyclohexane catalysed by cyclopentadienyl complexes of iron(II).[30] Therefore, the mechanism of the reaction is not fully clear. However, we assume that participation of hydroxyl radicals as key intermediates is the most probable (see also ref. 4).

The reagent under discussion hydroxylates benzene to yield phenol, and oxidizes propan-1-ol and propan-2-ol to afford propanal and acetone, respectively (Fig. 7).

In conclusion, although the reagent 'H_2O_2·urea–VO_3^-–PCA' oxidizes alkanes less efficiently in comparison with a similar reagent based on 30% aq. hydrogen peroxide,[1–4] the selectivity of the process in the first case is noticeably higher (the ratio cyclohexanol:cyclohexanone = 25:1 at room temperature after the reduction with triphenylphosphine; this value is only 12:1 for aq. H_2O_2). So the reagent described in the present paper may be used for the selective transformation of alkanes into the corresponding alcohols.

Experimental

The oxidation experiments were carried out in thermostatted cylindrical vessels equipped with reflux condensers, in air, with intensive stirring. The total volume of the reaction solution was 10 cm^3. Initially, a portion of a stock solution of H_2O_2·urea (Fluka) was added to the solution. The process was monitored by withdrawing aliquots at specific intervals and analysing them by means of GLC (each sample was analysed twice, *i.e.* before and after the addition of triphenylphosphine).

For the analysis a DANI 86.10 gas chromatograph (the column 0.25 mm in diameter with Carbowax) and Chrom Jet integrator (Spectra-Physics) were employed.

Acknowledgements

This work was financially supported in part by the International Science Foundation (grant # MMS000) as well as the Russian Basic Research Foundation (grant # 93-03-5226). One of us (G. B. Sh.) thanks Université de Neuchâtel for the invitation for a sabbatical stay during which a part of this work was carried out. The authors are indebted to Dr S. Claude, Mr A. Béguin and Mr G. Meister for help in experiments.

References

1 For parts 1–3 see refs. 2–4, respectively. A brief preliminary account of previous parts of this series has also been published (see ref. 5).
2 G. B. Shul'pin, D. Attanasio and L. Suber, *Russ. Chem. Bull.*, 1993, **42**, 64.
3 G. B. Shul'pin, A. N. Druzhinina and G. V. Nizova, *Russ. Chem. Bull.*, 1993, **42**, 1394.
4 G. V. Nizova and G. B. Shul'pin, *Russ. Chem. Bull.*, 1994, **43**, 1146.
5 G. B. Shul'pin, D. Attanasio and L. Suber, *J. Catal.*, 1993, **142**, 147.
6 R. A. Sheldon and J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981.
7 G. B. Shul'pin, *Organic Reactions Catalysed by Metal Complexes*, Nauka, Moscow, 1988.
8 (*a*) *Activation and Functionalization of Alkanes*, ed. C. L. Hill, Wiley-Interscience, New York, 1989; (*b*) A. E. Shilov and G. B. Shul'pin, *Russ. Chem. Rev.*, 1987, **56**, 442; 1990, **59**, 853.
9 *Catalytic Selective Oxidation*, ed. S. T. Oyama and J. W. Hightower, American Chemical Society, Washington, 1993; R. S. Drago, *Coord. Chem. Rev.*, 1992, **117**, 185.
10 C. A. Tolman, J. D. Druliner, M. J. Nappa and H. Herron, in ref. 8*a*, p. 303.
11 See, for example, reviews in: *Catalytic Oxidations with H_2O_2 as Oxidant*, ed. G. Strukul, Kluwer, Dordrecht, 1992; A. Sobkowiak, H.-C. Tung and D. T. Sawyer, *Prog. Inorg. Chem.*, 1992, **40**, 291; *The Activation of Dioxygen and Homogeneous Catalytic Oxidation*, ed. D. H. R. Barton, A. E. Martell and D. T. Sawyer, Plenum, New York, 1993, and references therein.
12 N. A. Milas, *J. Am. Chem. Soc.*, 1937, **59**, 2342.
13 V. Conte, F. Di Furia and G. Modena, *J. Org. Chem.*, 1988, **53**, 1665; M. Bonchio, V. Conte, F. Di Furia and G. Modena, *J. Org. Chem.*, 1989, **54**, 4368; M. Bianchi, M. Bonchio, V. Conte, F. Coppa, F. Di Furia, G. Modena, S. Moro and S. Standen, *J. Mol. Catal.*, 1993, **83**, 107; I. I. Moiseev, A. E. Gekhman and D. I. Shishkin, *New J. Chem.*, 1989, **13**, 683; A. E. Gekhman, N. I. Moiseeva and I. I. Moiseev, *Koord. Khim.*, 1992, **18**, 3; P. R. H. P. Rao and A. V. Ramaswamy, *J. Chem. Soc., Chem. Commun.*, 1992, 1245; see also M. Bonchio, V. Conte, F. Di Furia, G. Modena, S. Moro, T. Carofiglio, F. Magno and P. Pastore, *Inorg. Chem.*, 1993, **32**, 5797; M. S. Rigutto and H. van Bekkum, *J. Mol. Catal.*, 1993, **81**, 77; R. Neumann, M. Chava and M. Levin, *J. Chem. Soc., Chem. Commun.*, 1993, 1685; M. Bonchio, V. Conte, F. Di Furia, G. Modena and S. Moro, *J. Org. Chem.*, 1994, **59**, 6262.
14 E. P. Talsi, V. D. Chinakov, V. P. Babenko and K. I. Zamaraev, *J. Mol. Catal.*, 1993, **81**, 235.
15 (*a*) H. Mimoun, L. Saussine, E. Daire, M. Postel, J. Fischer and R. Weiss, *J. Am. Chem. Soc.*, 1983, **105**, 3101; (*b*) D. Attanasio, L. Suber and G. B. Shul'pin, *Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 1502; M. Bhattacharjee, S. K. Chettri, M. K. Chaudhuri, N. S. Islam and S. R. Barman, *J. Mol. Catal.*, 1993, **78**, 143; E. P. Talsi and K. V. Shalyaev, *J. Mol. Catal.*, 1994, **92**, 245.
16 K. Nakayama, M. Hamamoto, Y. Hishiyama and Y. Ishii, *Chem. Lett.*, 1993, 1699; A. Atlamsani, J.-M. Brégeault and M. Ziyad, *J. Org. Chem.*, 1993, **58**, 5663.
17 N. D. Charsteen, *Vanadium in Biological Systems*, Kluwer

Academic, Dordrecht, 1990; A. Butler and C. J. Carrano, *Coord. Chem. Rev.*, 1991, **109**, 61; X. Shi and N. S. Dalal, *Arch. Biochem. Biophys.*, 1991, **289**, 355; A. Shaver, J. B. Ng, D. A. Hall, B. S. Lum and B. I. Posner, *Inorg. Chem.*, 1993, **32**, 3109; S. Dutta, P. Basu and A. Chakravorty, *Inorg. Chem.*, 1993, **32**, 5343; C. A. Root, J. D. Hoeschele, C. R. Cornman, J. W. Kamf and V. L. Pecoraro, *Inorg. Chem.*, 1993, **32**, 3855; G. J. Colpas, B. J. Hamstra, J. W. Kamf and V. L. Pecoraro, *J. A. Chem. Soc.*, 1994, **116**, 3627; A. Butler and J. Walker, *Chem. Rev.*, 1993, **93**, 1937; A. Butler, M. J. Clague and G. E. Meister, *Chem. Rev.*, 1994, **94**, 625; V. Conte, F. Di Furia and S. Moro, *Tetrahedron Lett.*, 1994, **35**, 7429; C. J. Carrano, M. Mohan, S. H. Holms, R. de la Rosa, A. Butler, J. M. Charnock and C. D. Garner, *Inorg. Chem.*, 1994, **33**, 646.

18 J. Muzart, A. N'Ait Ajjou, G. V. Nizova and G. B. Shul'pin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 1294.

19 A. Goosen, C. W. McCleland, D. H. Morgan, J. S. O'Connell and A. Ramplin, *J. Chem. Soc., Perkin Trans. 1*, 1993, 401; P. H. Dussault and M. R. Hayden, *Tetrahedron Lett.*, 1992, **33**, 443; R. K. Haynes and S. C. Vonwiller, *J. Chem. Soc., Chem. Commun.*, 1990, 1102; J. L. Courtneidge, *J. Chem. Soc., Chem. Commun.*, 1992, 1270; A. J. Bloodworth, C. J. Cooksey and D. Korkodilos, *J. Chem. Soc., Chem. Commun.*, 1992, 926; D. E. Patton and R. S. Drago, *J. Chem. Soc., Perkin Trans. 1*, 1993, 1611; P. H. Dussault and I. Q. Lee, *J. Am. Chem. Soc.*, 1993, **115**, 6458; C. W. Jefford, *Chem. Soc. Rev.*, 1993, **22**, 59.

20 A. Sotomatsu, M. Nakano and S. Hirai, *Arch. Biochem. Biophys.*, 1990, **283**, 334; B. Frei, T. M. Forte, B. N. Ames and C. E. Cross, *Biochem. J.*, 1991, **227**, 133; F. Biasi, E. Albano, E. Chiarpotto, F. P. Corongiu, M. A. Pronzato, U. M. Marinari, M. Parola, M. U. Dianzani and G. Poli, *Cell Biol. Funct.*, 1991, **9**, 111; A. N. Grechkin, R. A. Kuramshin, S. K. Latypov, Y. Y. Safonova, T. E. Gafarova and A. V. Ilyasov, *Eur. J. Biochem.*, 1991, **199**, 451; W. D. Lehmann and G. Fürstenberger, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1027; V. W. Bowry and R. Stocker, *J. Am. Chem. Soc.*, 1993, **115**, 6029; M. H. Glickman, J. S. Wiseman and J. P. Klinman, *J. Am. Chem. Soc.*, 1994, **116**, 793; C.-C. Hwang and C. B. Grissom, *J. Am. Chem. Soc.*, 1994, **116**, 795.

21 L. G. Galimova, S. I. Maslennikov and A. I. Nikolaev, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1980, **29**, 1432.

22 C. A. Tolman, J. D. Druliner, P. J. Krusic, M. J. Nappa, W. C. Seidel, I. D. Williams and S. D. Ittel, *J. Mol. Catal.*, 1988, **48**, 129; C. B. Hansen, G. J. Hoogers and W. Drenth, *J. Mol. Catal.*, 1993, **79**, 153.

23 O. Dobis and S. W. Benson, *J. Am. Chem. Soc.*, 1993, **115**, 8798.

24 D. H. R. Barton and D. Doller, *Pure Appl. Chem.*, 1991, **63**, 1567; *Acc. Chem. Res.*, 1992, **25**, 504; D. H. R. Barton, E. Csuhai, D. Doller and G. Balavoine, *J. Chem. Soc., Chem. Commun.*, 1990, 1787; D. H. R. Barton, S. D. Bévière, W. Chavasiri, E. Chuhai, D. Doller and W.-G. Liu, *J. Am. Chem. Soc.*, 1992, **114**, 2147.

25 C. Knight and M. J. Perkins, *J. Chem. Soc., Chem. Commun.*, 1991, 925.

26 C. Kang, A. Sobkowiak and D. T. Sawyer, *Inorg. Chem.*, 1994, **33**, 79.

27 G. B. Shul'pin and G. V. Nizova, *React. Kinet. Catal. Lett.*, 1992, **48**, 333.

28 J. Muzart, G. V. Nizova, A. Riahi and G. B. Shul'pin, *J. Gen. Chem. (Russia)*, 1992, **62**, 964.

29 E. About-Jaudet, D. H. R. Barton, E. Csuhai and N. Ozbalik, *Tetrahedron Lett.*, 1990, **31**, 1657; G. Balavoine, D. H. R. Barton, J. Boivin and A. Gref, *Tetrahedron Lett.*, 1990, **31**, 659.

30 G. B. Shul'pin, A. N. Druzhinina and L. S. Shul'pina, *Neftekhimiya*, 1993, **33**, 335.

Paper 4/07294D
Received 29*th November* 1994
Accepted 21*st January* 1995