Journal of Catalysis 263 (2009) 167–172

Contents lists available at ScienceDirect

Journal of Catalysis

www.elsevier.com/locate/jcat

Mechanistic investigation of the catalytic system based on *N*-hydroxy-phthalimide with vanadium co-catalysts for aerobic oxidation of alcohols with dioxygen

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ARTICLE INFO

Article history:
Received 6 January 2009
Revised 6 February 2009
Accepted 6 February 2009
Available online 23 February 2009

Dedicated to the memory of Professor Józef Julian Ziółkowski (1935–2008), whose contributions to science were longstanding and far-reaching

Keywords:
Aerobic catalytic oxidation
Nitroxyl radicals
PINO
N-hydroxyphthalimide
NHPI
Vanadium complexes

ABSTRACT

$[n\text{-Bu}_4\text{N}]\text{VO}_3$ or a combination of vanadium complexes with some additives, as chloride salts or amines, are attractive and effective co-catalysts for aerobic oxidation of alcohols with dioxygen catalyzed by *N*-hydroxyphthalimide (NHPI). The role of the additives relates to the formation of more labile six co-ordinate vanadium complexes. A mechanism for the aerobic oxidation of alcohols with dioxygen is proposed and its essential steps are the formation of oxotrialkoxyvanadium(V) complexes and generation of a phthalimide-*N*-oxyl ($\text{PINO}^\bullet$) radical as result of reaction of NHPI with oxovanadium(V) compounds. The oxidation of alcohols concerns to both radical and molecular pathways.

1. Introduction

N-hydroxyphthalimide (NHPI) has attracted interest in the past decade as a new organocatalyst for a wide variety of free radical autoxidations [1]. The great attraction of oxidation reactions catalyzed by NHPI is application of different co-catalysts, most often transition metal complexes because of the mild conditions and high selectivity of the reactions.

In a recent preliminary report, we described new efficient aerobic oxidation of some alcohols and alkyloaromatics with dioxygen catalyzed by *N*-hydroxyphthalimide combined with vanadium co-catalysts [2,3]. As a consequent continuation of these studies, we report here mechanistic investigations of the NHPI–vanadium system for the aerobic oxidation of alcohols with dioxygen.

2. Experimental

The materials, reagents, procedure for catalytic oxidation reactions, apparatus and analytic methods have been described earlier [3].

^{51}V NMR spectra were recorded on a Bruker ARX 300 NMR spectrometer at room temperature. The instrument was operated at 78.943 MHz. ^{51}V NMR spectra were referenced to neat $VOCl_3$ (Aldrich) using the external substitution method.

The ESI-MS measurements were obtained using an ESI-(Q)-TOF Bruker Daltonics instrument model microTOF-Q. The MS peaks were observed <1 min after the injection.

Q-band EPR spectra were measured on a Bruker ESP 300E spectrometer.

UV–vis electronic spectra were obtained by using a Hewlett Packard model 8452A diode array spectrophotometer.

An EMU/0 (Electrochemical Universal Meter) produced by Technical University Wrocław (Poland) was applied to the polarographic measurements.

3. Results and discussion

The catalytic system investigated in this work contains *N*-hydroxypthalimide as a key catalyst and a vanadium derivative with or without additives, as an obligatory co-catalyst. Primary and secondary alcohols were used as substrates and molecular oxygen as an oxidant. The oxidation reaction leads to corresponding products: ketones, aldehydes and/or acids, depending on the alcohol used.

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0021-9517/$ – see front matter
doi:10.1016/j.jcat.2009.02.007

Previously we have demonstrated moderate catalytic activity of NHPI combined with ammonium salts or acids as co-catalysts in oxidation of alcohols and alkylaromatics [4]. Summing up those results, we concluded that these co-catalysts are effective because their interaction with NHPI weakens the O–H bond in NHPI as a result of the hydrogen bonding O–H...X, where X = an electronegative atom or ion with a lone electron pair (halogen ion in ammonium salts, Brønsted acids), or due to donor–acceptor interaction (Lewis acid) [4].

Furthermore, we recently described new efficient aerobic oxidation of some organic compounds with dioxygen catalyzed by NHPI combined with vanadium co-catalysts [2,3]. On the basis of the results obtained [3] it was concluded that active co-catalysts are formed from complexes of vanadium with a labile co-ordinating sphere (such as $VO(OR)_3$ and $[n\text{-}Bu_4N]VO_3$, which do not require any additives) or complexes such as $VO(acac)_2$, which require the addition of chloride salt (LiCl or $[R_4N]Cl$) or amine, weakening the vanadium–acetylacetonate bond.

Generally, lability of vanadium complexes determines their catalytic activity and $[n\text{-}Bu_4N]VO_3$ and $VO(OR)_3$ can confirm this hypothesis, because there are very active co-catalysts without any other additives.

3.1. Formation of PINO radical

It is generally accepted that NHPI is called a carbon radical chain promoter (CRCP) [5] because $PINO^\bullet$ radicals, formed from NHPI, can generate $R^\bullet$ radicals from organic substrates, do not undergo termination reactions and they propagate the chain. In the absence of co-catalysts or initiators $PINO^\bullet$ is produced in reaction of NHPI with free radicals (mainly with $ROO^\bullet$) formed in autoxidation process [6].

Formation of the $PINO^\bullet$ radicals in oxidation reactions of organic compounds catalyzed by NHPI has been proposed or documented in many articles. One of the first examples is work by Grochowski et al. on reaction of diethyl azodicarboxylate with ethers and the oxidation of 2-propanol with *m*-chloroperbenzoic acid catalyzed by NHPI [7].

Another is the paper by Masui et al. [8] on electrochemical oxidation of *sec*-alcohols to ketones with NHPI as mediator where it has been shown that $PINO^\bullet$ radicals are formed by an electrochemical oxidation of NHPI.

It should be noted that on a preparative scale $PINO^\bullet$ radicals can be generated by simply treating NHPI with well-known inorganic oxidant $Pb(OAc)_4$ [9,10].

There are many reported co-catalysts which can be grouped into inorganic, organic and organometallic which function as initiators for generating $PINO^\bullet$ radicals. Cerium(IV) ammonium nitrate (CAN) [11], sodium periodate [12], HNO_3 [13], NO [14], and NO_2 [15] belong in the first group.

Examples of organic initiators for generating the $PINO^\bullet$ radicals are acylperoxyl radical generated from acetaldehyde [16], AIBN [17], benzoyl peroxide [18], peracids [19] and anthraqinones [20].

In combination with transition metal co-catalysts, NHPI affords an effective catalytic system for the oxidation of various organic compounds [1,5,21]. Especially effective co-catalysts are complexes of cobalt [22], cobalt with manganese [23], heteropolycompound—$(NH_4)_5[H_6PV_8Mo_4O_{40}]$ [24], CuCl [25] and heterogeneous, Co/SiO_2 [26], Fe/MgO [27].

More recently, it has been shown that NHPI in combination with the enzyme laccase can catalyze the aerobic oxidation of benzylic alcohols to corresponding aldehydes [28]. The function of laccase (multicopper oxidase) would be similar to that of the transition metal co-catalysts [29].

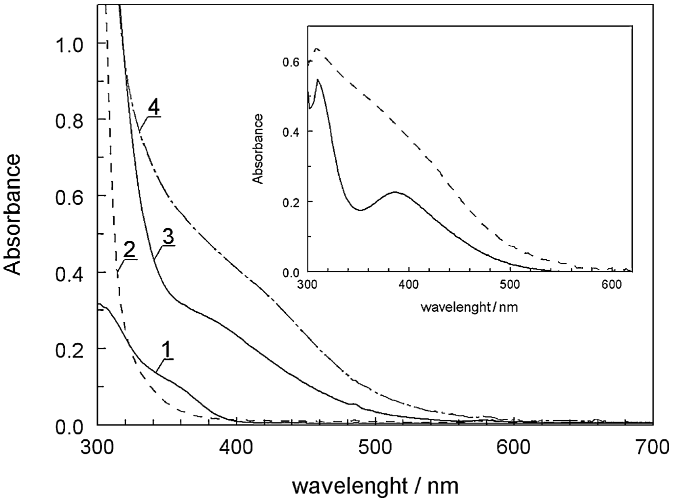


Fig. 1. UV–vis spectra of acetonitrile solutions: (1) 0.35 mM $[n\text{-}Bu_4N]VO_3$, (2) 0.74 mM NHPI, (3) a mixture of 2 ml NHPI (0.83 mM) and 0.25 ml $[n\text{-}Bu_4N]VO_3$ (3.14 mM), (4) a mixture of 2 ml NHPI (1.06 mM) and 0.02 ml $VO(O^iPr)_3$ (30 mM); components were mixed in cuvette and after 1 min the spectrum was taken (r.t.). The inset shows a difference spectrum obtained by subtraction of the spectra of vanadium complexes and NHPI from that of 3 (solid line) or 4 (dashed line); it represents the spectrum of $PINO^\bullet$ radicals.

3.2. Interaction of NHPI with $[n\text{-}Bu_4N]VO_3$ and $VO(O^iPr)_3$

We suppose that in reactions catalyzed by NHPI and vanadium co-catalysts, the $PINO^\bullet$ radicals will be generated in oxidation reactions of the NHPI by vanadium(V) complexes. Indeed, the mixing of acetonitrile solutions of NHPI and $[n\text{-}Bu_4N]VO_3$ or $VO(O^iPr)_3$ results in the appearance of a yellow color; the UV–vis measurements confirmed the formation of the $PINO^\bullet$ radicals (Fig. 1). The spectrum of $PINO^\bullet$ radicals has been obtained according to the procedure described by Espenson et al. [10]. Two electronic transitions at 321 and 386 nm were observed (Fig. 1, inset).

In order to obtain additional evidence on formation of $PINO^\bullet$ radicals, we have performed an electrospray ionization mass spectrometry (ESI-MS) analysis of NHPI solutions in the presence of $[n\text{-}Bu_4N]VO_3$. In our case we directly observed $PINO^\bullet$ radicals (the base peak at $m/z = 162.0$) (Fig. 2). The other significant peak is associated with the formation of the vanadium complex with *o*-phthalate anion, $[V(O)_2(o\text{-}C_6H_4(CO_2)_2(H_2O)]^-$ ($m/z = 265.1$).

Decomposition of NHPI to phthalic derivatives was also observed (Fig. 2, inset).

3.3. Effect of hydroperoxides

When non-purified cyclohexanol was used for oxidation with catalytic system NHPI–$VO(acac)_2$–additives, then a transient red color [30–32] (characteristic for vanadium(V) alkylperoxidic complexes [31–33]) was observed at the beginning of the reaction. The above observation led us to investigate the influence of organic hydroperoxides and H_2O_2 on the oxidation reaction of purified (distilled) cyclohexanol. The $VO(acac)_2$/4-Me-py system, which was efficient catalyst for the oxidation [3], was chosen for this purpose (Fig. 3).

These effects indicate that peroxide compounds have significant influence on the induction period of the oxidation reaction. Additionally, chromatographic analyses (HPLC) revealed that the addition of a small amount of hydrogen peroxide does not effect on both cyclohexanol conversion and cyclohexanone selectivity.

Iodometric titrations of reaction mixtures during cyclohexanol oxidation catalyzed by NHPI combined with vanadium co-catalysts showed the presence of peroxides in the concentration range of

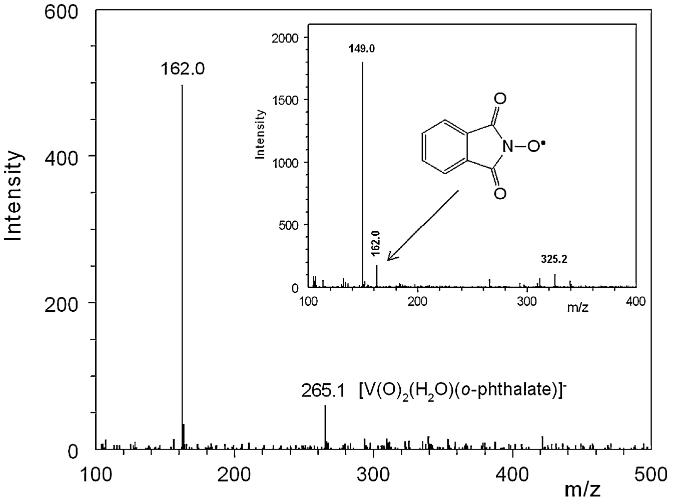


Fig. 2. Mass spectra (ESI, negative) of acetonitrile solutions of NHPI with [*n*-Bu$_4$N]VO$_3$ and NHPI (inset); acetonitrile solutions of 2 ml NHPI (0.83 mM) and 0.25 ml [*n*-Bu$_4$N]VO$_3$ (3.14 mM) were mixed and measured after 1 min.

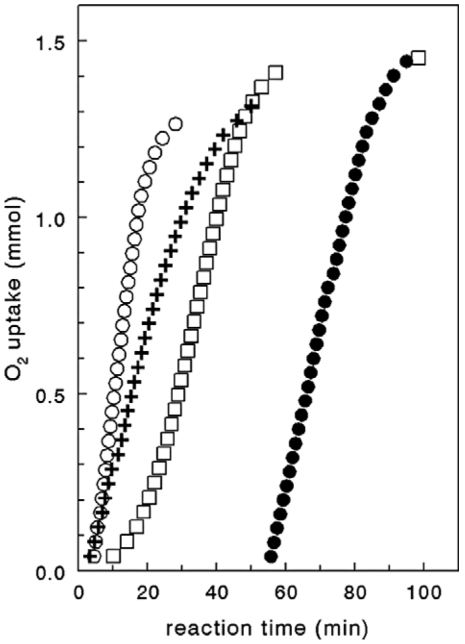


Fig. 3. The effect of organic hydroperoxides and H$_2$O$_2$ on the oxidation reaction of cyclohexanol, catalyzed by NHPI (0.25 mmol), VO(acac)$_2$ (0,01 mmol) and 4-methylpyridine (0.01 mmol) in MeCN at 75 °C (peroxides (1 mmol): (○) H$_2$O$_2$; (+) *tert*-butyl hydroperoxide; (□) cumyl hydroperoxide; (●) none).

about 2–4 mM. We have observed, that after introduction of additional amounts of hydrogen peroxide (to a concentration of 20 mM) during the oxidation reaction, the concentration of peroxides returns to the previous level.

3.4. *Intermediate vanadium complexes*

In order to obtain additional insight into the mechanism of alcohols oxidation catalyzed by the system NHPI–vanadium complexes, we have applied ^{51}V NMR spectroscopy to study transformations of various vanadium precursors during the oxidation reaction.

Two catalytic systems which were the most effective in oxidation of alcohols, (1) NHPI/VO(acac)$_2$ with LiCl or [*n*-Bu$_4$N]Cl and (2) NHPI/[*n*-Bu$_4$N]VO$_3$, were objects of spectroscopic studies.

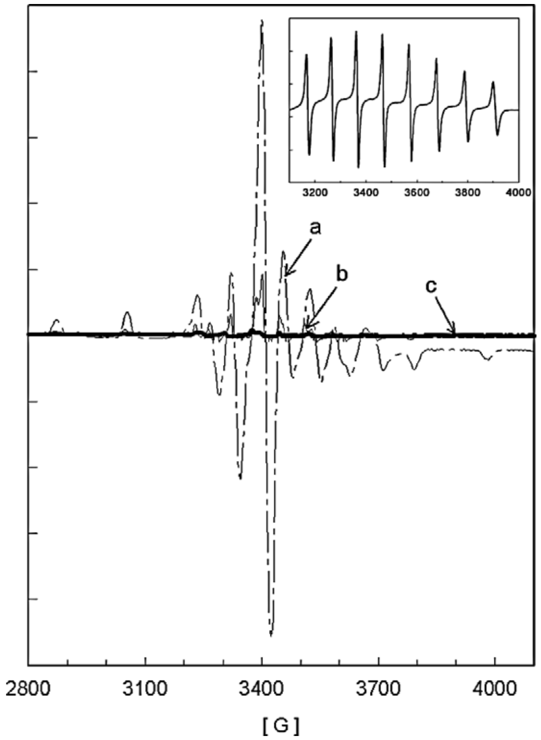


Fig. 4. Q-band EPR spectra of a samples taken in time from aerobic oxidation of cyclohexanol in MeCN, catalyzed with NHPI–VO(acac)$_2$ and LiCl (after: 5 min—dashed line (a), 1 h—full thin line (b) and 20 h—full bold line (c)). Inset: EPR spectrum of VO(acac)$_2$ in MeCN at r.t. ($g = 1.97$ and $a_N = 10.5$ mT are the same as in Ref. [34]).

Table 1
^{51}V NMR spectra of VO(OR)$_3$ complexes.

Compound	δ_V (ppm)	
	Exp.	Lit.
VO(O-*i*-Pr)$_3$	−628	−629 [37]
VO(O-2-C$_5$H$_{11}$)$_3$[a]	−625	–
VO(O-*c*−C$_6$H$_{11}$)$_3$	−619	−616 ÷ −620 [36][b]
VO(O-*n*-C$_6$H$_{13}$)$_3$	−598	−603 [37][c]

[a] O-2-C$_5$H$_{11}$ = CH$_3$CH(O$^{(-)}$)CH$_2$CH$_2$CH$_3$.
[b] Position of signal depends on the solvent used.
[c] Value for VO(O-*n*-Oct)$_3$.

The spectroscopic investigations of reactionary mixtures with V^{4+} complexes have shown that in the beginning of the reaction the initial vanadium ions are rapidly oxidized to V^{5+}. For the reactions where VO(acac)$_2$ with LiCl or [*n*-Bu$_4$N]Cl were used as co-catalysts changes of EPR spectrum of V^{4+}(d^1) and disappearance of EPR signal were observed (Fig. 4); subsequently the appearance of the signal (V^{5+}) in spectra ^{51}V NMR was observed.

The role of the chloride additive is probably important for the formation of a more labile six co-ordinate complex which can be easily oxidized to V^{5+} (the same effect has been observed for amine additive [3]; Atherton et al. [35] called attention to the air-sensitivity of VO(acac)$_2$ solutions). The ^{51}VNMR studies of the reaction mixtures revealed that in the initial stage of cyklohexanol oxidation, independent of co-catalyst used ([*n*-Bu$_4$N]VO$_3$, VO(O-*i*-Pr)$_3$, VO(acac)$_2$ with LiCl or [*n*-Bu$_4$N]Cl), one single signal was observed ($\delta_V = -619$ ppm, $\omega_{1/2} = 90$ Hz; Fig. 5A). Following the literature [36], this signal was attributed to the VO(O-*c*-C$_6$H$_{11}$)$_3$ complex. In case of oxidation of other alcohols we have also observed in the initial stage single signals in ^{51}V NMR, characteristic for complexes of type VO(OR)$_3$. Their position depended on the substrate used (see Table 1).

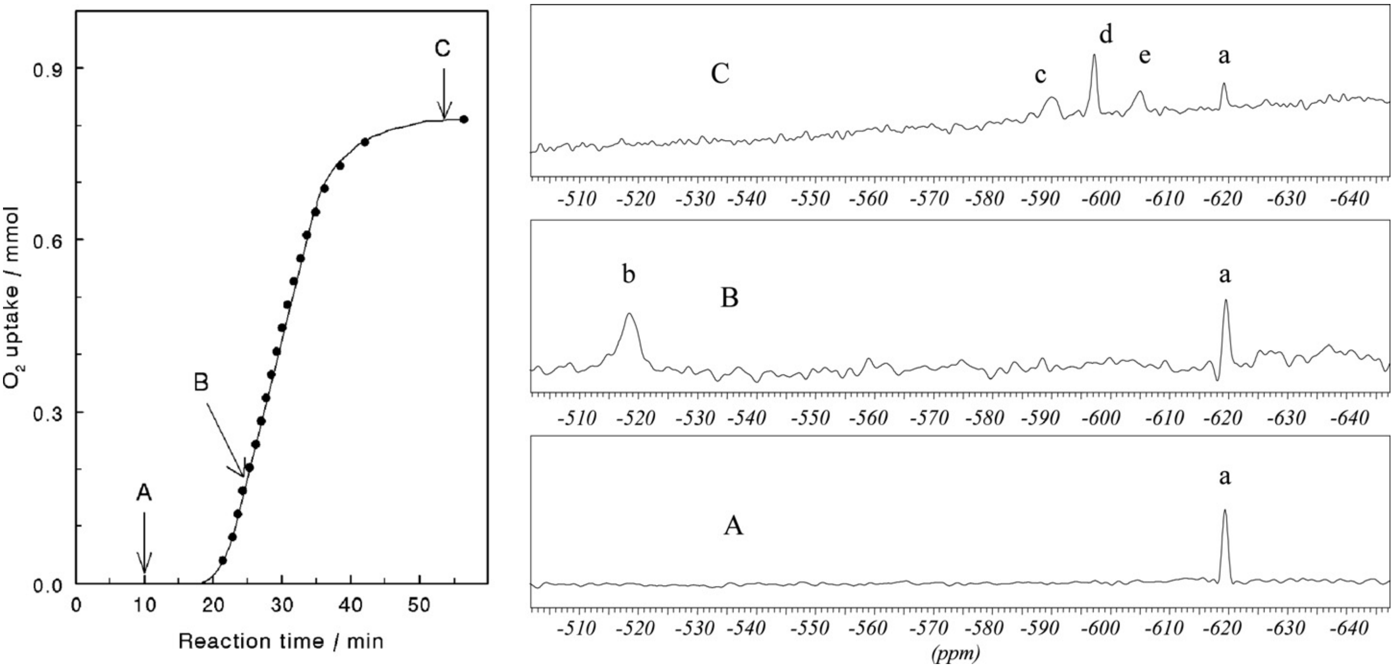


Fig. 5. Aerobic oxidation of cyclohexanol (5 mmol) in MeCN at 75 °C, catalyzed by NHPI (0.25 mmol) and $[n\text{-}Bu_4N]VO_3$ (0.03 mmol) (left) and ^{51}V NMR spectra of samples taken from reaction mixture (right: (A) before absorption of O_2, (B) after 5 ml O_2 uptake, (C) after 20 ml O_2 uptake).

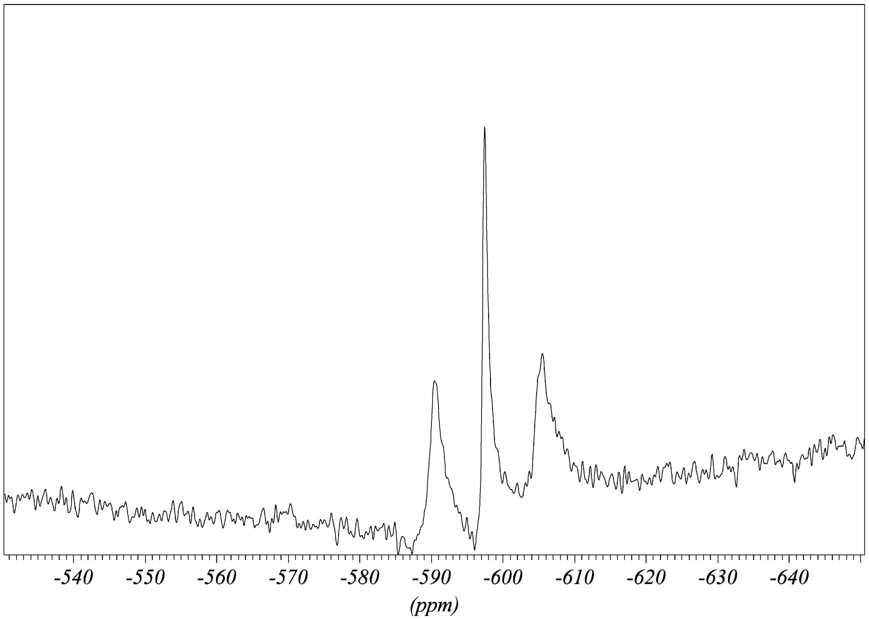


Fig. 6. ^{51}V NMR spectrum of solution $[n\text{-}Bu_4N]VO_3$ (1 mg) with *ortho*-phthalic acid (0.5 mg) in acetonitrile (0.8 ml).

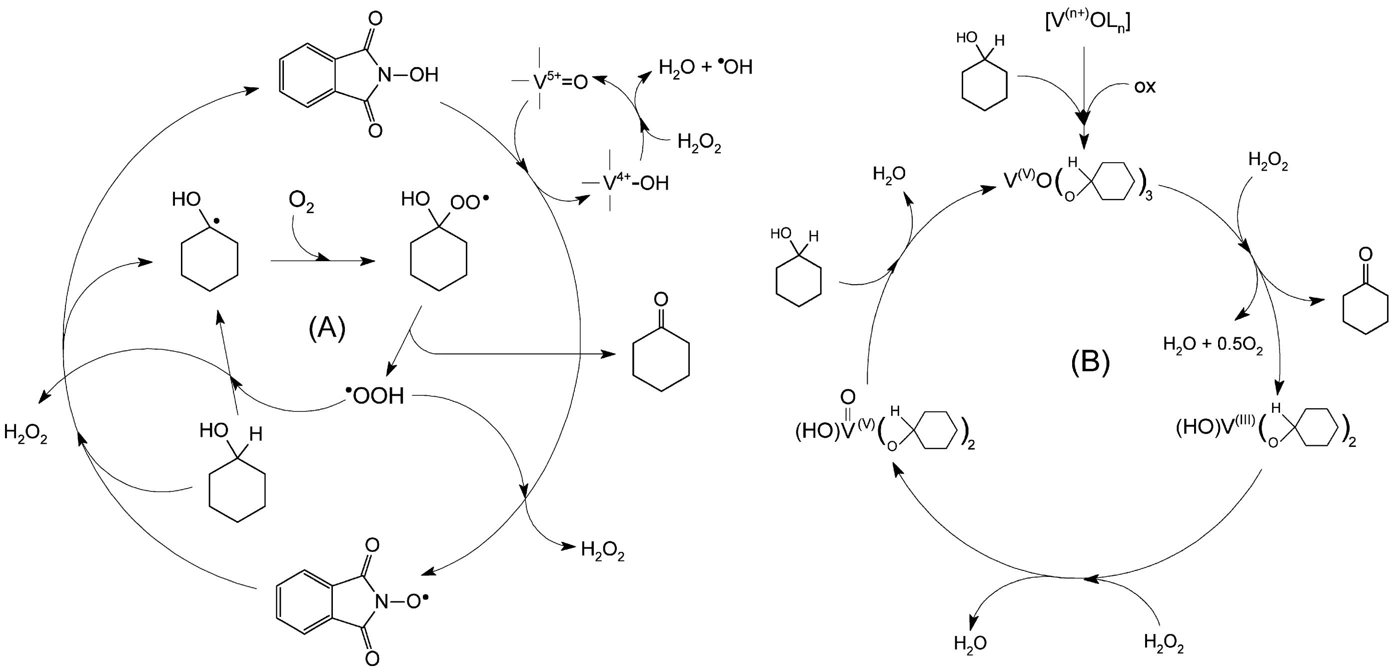
The intensity of these signals of $VO(OR)_3$ complexes decreased in time. Subsequently new signals were observed in ^{51}V NMR spectra (Figs. 5B and 5C).

In the oxidation of cyclohexanol (Fig. 5), after absorption of 5 ml of O_2, beside signal at −619 ppm, the second signal appears at $\delta_V = -518$ (b). After absorption of further 15 ml of O_2 signal (b) disappeared and new signals were observed at values of δ_V: −585 (c), −597 (d), and −602 (e).

Similar ^{51}V NMR spectra were recorded in the oxidation reaction of 2-pentanol, catalyzed by NHPI and $[n\text{-}Bu_4N]VO_3$. In the initial stage the single signal at $\delta_V = -625$ ppm was observed due to the $VO(O\text{-}2\text{-}C_5H_{11})_3$ complex formation. After absorption of 5 ml of O_2 a second signal appeared ($\delta_V = -522$ ppm) and after next absorption of 17 ml of O_2 this signal disappeared and three new signals, at −585, −597 and −602 ppm were observed. The signals at $\delta_V = -518$ and −522 ppm observed in oxidation reactions of cyclohexanol and 2-pentanol respectively, probably come from complexes of the type $[n\text{-}Bu_4N][V(O)_2(OR)_2]$ [38] or $[VO(OH)(OR)_2]$ (Scheme 1, cycle B).

The signals in ^{51}V NMR spectra for final stage of oxidation reactions (the signals c, d, and e in Fig. 5C) might be attributed to vanadium(V) complexes with *ortho*-phthalic acid (the product of NHPI decomposition [1,39]), that were confirmed in a separate experiment (Fig. 6).

The position of three signals (in the range −585 to −605 ppm) and the relation of their intensity (about 1.0:1.45:0.96) does not



Scheme 1.

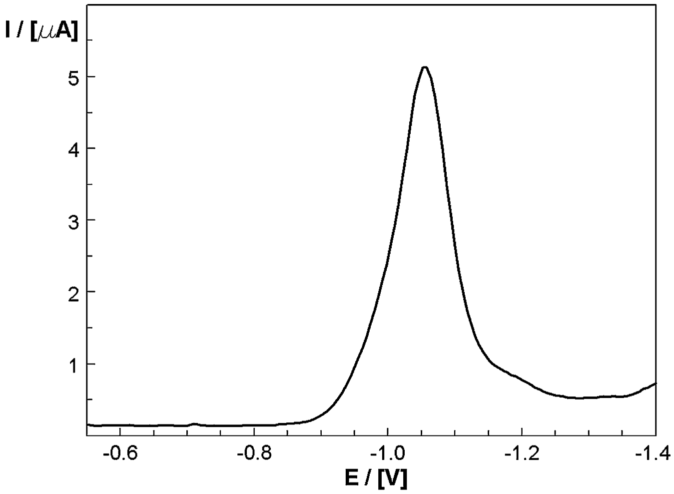


Fig. 7. Polarogram of post-reaction mixture from aerobic oxidation reaction of alcohols catalyzed by NHPI–vanadium co-catalyst.

vary for different molar ratios of *ortho*-phthalic acid to vanadium(V) complex (from 1:1, 2:1 to 4:1) and it is similar to that on spectrum C, Fig. 5.

Surprisingly, no ^{51}V NMR signal was observed for post-reaction mixtures.

The EPR spectroscopy of the post-reaction mixtures revealed the absence of a signal due to the vanadium(IV) (however it cannot be excluded that "the EPR-silent" complexes of vanadium(IV) exist [40]). It is known that the ion of V^{3+} ($3d^2$) is the non-Cramer's ion and, due to the short relaxation time of the spin-net, does not give an EPR signal. By additional polarographic experiments we have confirmed that in post-reaction mixtures complexes of vanadium(III) are present (Fig. 7).

3.5. Mechanism for cyclohexanol oxidation

On the basis of the results of our studies and spectroscopic investigations (UV–vis, EPR, ^{51}V NMR), and available published literature data, a plausible mechanism for the oxidation reaction of alcohols with dioxygen catalyzed by NHPI with a vanadium co-catalyst was proposed (Scheme 1). The scheme shows the oxidation reactions of cyclohexanol to cyclohexanone on radical and molecular pathways (cycles A and B, respectively). The essential initial stage of the process being the facile formation of the PINO• radical in the reaction of NHPI with oxovanadium(V) complex (Scheme 1, cycle A). The PINO• radical can in turn abstract the hydrogen atom from the cyclohexanol to produce the α-hydroxy-cyclohexyloxy radical (HCR) and regenerate the NHPI. The resulting carbon-centered radical (HCR) reacts with O_2 to form a peroxyl radical (ROO•), which is further converted to cyclohexanone and a hydroperoxyl radical (HOO•) [41]. HOO• radical can abstract hydrogen from either NHPI or a molecule of cyclohexanol to form hydrogen peroxide and PINO• or HCR, respectively. It should be noted that we have observed constant level of hydroperoxides during reaction and Ishii et al. [21,42] has shown formation of hydrogen peroxide during oxidation of alcohols catalyzed by NHPI.

Crucial to the catalysis is the fact that PINO• radicals do not terminate with each other or with peroxyl radicals [43]. Thereby, PINO• radicals are much more efficient carriers then peroxyl radicals, enhancing the radical chain length.

The further course of the reaction is probably related to oxometal pathway [44], where H_2O_2 plays a role as oxidant (Scheme 1, cycle B, where from $VO(OR)_3$ and H_2O_2[1] are formed cyclohexanone and the hydroxyvanadium(III) complex which is further oxidized to oxovanadium(V)). On the other hand, H_2O_2 reoxidizes V^{4+}–OH to V^{5+}=O, closing the cycle for generating PINO• radicals (cycle A).

It should be also noted that oxovanadium(V) complexes in the presence of hydrogen peroxide can be transformed to peroxo species. G.B. Shul'pin et al. [31] reported the formation of vanadium monoperoxo complex from [n-Bu_4N]VO_3 and H_2O_2 in MeCN. Vanadium(V) peroxo complexes are known catalysts for the oxidation of primary and secondary alcohols by H_2O_2 to aldehydes and

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[1] According to suggestion of reviewer to study the stoichiometric reaction of $VO(OR)_3$ with H_2O_2, to support the second step in mechanism B. In the reaction of $VO(O^iPr)_3$ with H_2O_2 or urea hydrogen peroxide, in both cases we have observed formation of acetone by GC-MS or ^{1}H NMR.

ketones, respectively [45]. The reaction shows an oscillatory behavior, i.e. the concentration of H_2O_2 oscillates between subsequent production and decomposition processes [45].

From the other side, vanadium monoperoxo complex can function as a "catalytic pump" for the generation of hydroxyl radicals [38]. These are very reactive and strong oxidants species and promote other radical chains, e.g. by abstracting an H atom from an organic substrate.

3.6. Conclusion

In summary, a mechanism for the aerobic oxidation of alcohols with dioxygen catalyzed by NHPI and vanadium complexes is proposed. Its essential steps are the formation of oxotrialkoxyvanadium(V) complexes and generation of a phthalimide-*N*-oxyl (PINO$^\bullet$) radicals as result of reaction of NHPI with oxovanadium(V) compounds. The oxidation of alcohols concerns both radical and molecular pathways.

Acknowledgments

This work was supported by the Polish State Committee for Scientific Research (KBN), Grant PBZ-KBN-118/T09/2004. We thank Dr. Maria Kowalska for her expert assistance with the ^{51}V NMR measurements and Mr. Marek Jon for ESI-MS experiments.

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