



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

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ABSTRACT

[*n*-Bu₄N]VO₃ 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 (PINO[•]) radical as result of reaction of NHPI with oxovanadium(V) compounds. The oxidation of alcohols concerns to both radical and molecular pathways.

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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].

⁵¹V NMR spectra were recorded on a Bruker ARX 300 NMR spectrometer at room temperature. The instrument was operated at 78.943 MHz. ⁵¹V NMR spectra were referenced to neat VOCl₃ (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*-hydroxyphthalimide 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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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 $\text{VO}(\text{OR})_3$ and $[n\text{-Bu}_4\text{N}]\text{VO}_3$, which do not require any additives) or complexes such as $\text{VO}(\text{acac})_2$, which require the addition of chloride salt (LiCl or $[\text{R}_4\text{N}]\text{Cl}$) or amine, weakening the vanadium–acetylacetonate bond.

Generally, lability of vanadium complexes determines their catalytic activity and $[n\text{-Bu}_4\text{N}]\text{VO}_3$ and $\text{VO}(\text{OR})_3$ 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• radicals, formed from NHPI, can generate R• radicals from organic substrates, do not undergo termination reactions and they propagate the chain. In the absence of co-catalysts or initiators PINO• is produced in reaction of NHPI with free radicals (mainly with ROO^\bullet) formed in autoxidation process [6].

Formation of the PINO• 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• radicals are formed by an electrochemical oxidation of NHPI.

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

There are many reported co-catalysts which can be grouped into inorganic, organic and organometallic which function as initiators for generating PINO• 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• radicals are acylperoxy radical generated from acetaldehyde [16], AIBN [17], benzoyl peroxide [18], peracids [19] and anthraquinones [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– $(\text{NH}_4)_5[\text{H}_6\text{PV}_8\text{Mo}_4\text{O}_{40}]$ [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].

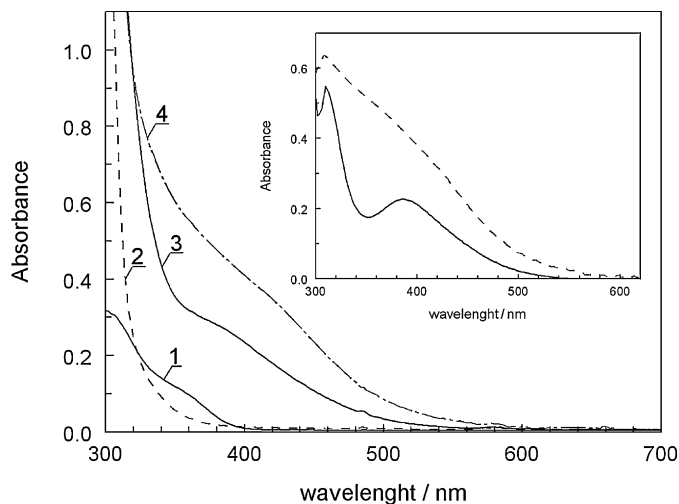


Fig. 1. UV-vis spectra of acetonitrile solutions: (1) 0.35 mM $[n\text{-Bu}_4\text{N}]\text{VO}_3$, (2) 0.74 mM NHPI, (3) a mixture of 2 ml NHPI (0.83 mM) and 0.25 ml $[n\text{-Bu}_4\text{N}]\text{VO}_3$ (3.14 mM), (4) a mixture of 2 ml NHPI (1.06 mM) and 0.02 ml $\text{VO}(\text{O}^i\text{Pr})_3$ (30 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• radicals.

3.2. Interaction of NHPI with $[n\text{-Bu}_4\text{N}]\text{VO}_3$ and $\text{VO}(\text{O}^i\text{Pr})_3$

We suppose that in reactions catalyzed by NHPI and vanadium co-catalysts, the PINO• radicals will be generated in oxidation reactions of the NHPI by vanadium(V) complexes. Indeed, the mixing of acetonitrile solutions of NHPI and $[n\text{-Bu}_4\text{N}]\text{VO}_3$ or $\text{VO}(\text{O}^i\text{Pr})_3$ results in the appearance of a yellow color; the UV-vis measurements confirmed the formation of the PINO• radicals (Fig. 1). The spectrum of PINO• 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• radicals, we have performed an electrospray ionization mass spectrometry (ESI-MS) analysis of NHPI solutions in the presence of $[n\text{-Bu}_4\text{N}]\text{VO}_3$. In our case we directly observed PINO• 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, $[\text{V}(\text{O})_2(\text{o-C}_6\text{H}_4(\text{CO}_2)_2(\text{H}_2\text{O}))]^-$ ($m/z = 265.1$).

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– $\text{VO}(\text{acac})_2$ –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 $\text{VO}(\text{acac})_2/4\text{-Me-py}$ 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

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