Aerobic oxidation of alcohols and alkylaromatics with dioxygen catalysed by *N*-hydroxyphthalimide with vanadium co-catalysts

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$[Bu_4N]VO_3$ or a combination of vanadium complexes with chloride salts are attractive co-catalysts for oxidation reactions of organic compounds with dioxygen catalysed by *N*-hydroxyphthalimide. The role of the chloride additive relates to the formation of more labile six-coordinate vanadium complexes. The same effect is also observed with amines. Two catalytic systems based on NHPI/$VO(acac)_2$ with LiCl or $[Bu_4N]Cl$ and NHPI/$[Bu_4N]VO_3$ are most effective in oxidation reactions of primary and secondary alcohols, but oxidation of alkylaromatics proceeds with conversion rates of from 14.4% in the case of toluene to 67.0% in the case of ethylbenzene and with different selectivities, dependent on the structure of the substrate.

1 Introduction

Selective catalytic oxidation using dioxygen is one of the most attractive transformations in organic synthesis.[1–4] In recent years, there has been a noticeable increase of interest in oxidation reactions with nitroxyl radicals used as catalysts. Generally, it is possible to divide these reactions into two groups: those in which the catalysts are persistent nitroxyl radicals, such as 2,2′,6,6′-tetramethylpiperidine-*N*-oxyl derivatives (TEMPO),[3–5] and those with non-persistent radicals, *e.g.* phthalimide-*N*-oxyl (PINO) derivatives,[2,3,6] or saccharin-*N*-oxyl (SINO) derivatives,[7] generated *in situ* from suitable *N*-hydroxy derivatives. The great attraction of above mentioned reactions is application of different co-catalysts, most often transition metal complexes (regarding TEMPO, see, refs. 3 and 8–10 regarding PINO, developed especially by the Ishii group[2,6] and others[10–17]). The catalytic systems are particularly attractive 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 with dioxygen catalysed by *N*-hydroxyphthalimide combined with vanadium co-catalysts.[15]

In this paper, investigations of the oxidation reaction of organic compounds by dioxygen, catalysed by NHPI in combination with vanadium complexes and some additives, are presented.

2 Experimental

2.1 Materials

Acetonitrile (ROTH) was distilled with CaH_2 under a nitrogen atmosphere (MeCN for HPLC from J. T. BAKER was used without additional purification).

Cyclohexanol (POCh) was distilled under a nitrogen atmosphere.

N-Hydroxyphthalimide (Sigma), toluene, ethylbenzene, cumene, *ortho*-, *meta*- and *para*-xylene, (POCh), mesitylene (Koch-light), 2-pentanol (Schuchard), isopropanol (J. T. Baker), 1-hexanol and benzyl alcohol (Reachim), 1-decene, quaternary ammonium salts (Fluka), triethylamine (Ubichem), 4-methyl and 4-cyano-pyridine (Riedel), $VO(O^iPr)_3$ (Aldrich), were used as received. Pyridine (Ubichem) was dried over NaOH.

$VO(acac)_2$[18] was recrystalized from $CHCl_3$, $VO(acac)_2py$,[19] $[Bu_4N]VO_3 \cdot H_2O$,[20] $VO(acac)_2Cl$,[21] and $[Bu_4N]_3H_3V_{10}O_{28}$[22] were prepared according to the published methods.

LiCl was obtained in reaction of Li_2CO_3 (BDH) with a solution of hydrochloric acid (POCh).

2.2 Procedure for catalytic oxidation

The standard conditions for oxidation reactions of organic substrates, were as follows: organic substrate 5 mmol, NHPI 0.25 mmol (0.0408 g), co-catalyst 0.025 mmol, and acetonitrile to top up the volume to 10 cm^3 at atmospheric pressure of O_2. The reactions were carried out at constant volume in a thermostated glass-reactor equipped with a magnetic stirring bar and connected to computer-controlled automatic gas absorption measuring apparatus. The substrate, acetonitrile and NHPI were added to the reactor under an oxygen atmosphere. Next, a fixed amount of the co-catalyst was introduced in one portion, immediately after which stirring was started and the progress of the absorbed dioxygen was measured. The mmole of oxygen that reacted was calculated from the volume, pressure and temperature data using the ideal gas equation.

2.3 Product analysis by chromatography

Product analysis was performed on a Hewlett–Packard HP 5890 II series gas chromatograph equipped with a flame ionization detector and an HP 5971A mass selective detector. An HP-5 25-m-long capillary column (25 × 0.2 × 0.33 mm) was used in both cases. In some experiments an HP 1090 II Liquid Chromatograph with an ODS Hypersil column (10 cm long and 2.1 mm in diameter) and equipped with an HP 1047A RI detector was used.

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3 Results and discussion

$VO(acac)_2$ is well known as a catalyst for oxidation reactions of unsaturated hydrocarbons,[23] hydroquinones,[24] and propargylic alcohols,[25] using dioxygen as oxidant. Vanadyl tetradentate Schiff base complexes[26] and $VOCl_3$[27] are also catalysts in aerobic selective oxidation of olefins and α-hydroxycarbonyls, respectively. Nevertheless, under the reaction conditions described in the experimental part, $VO(acac)_2$ does not catalyse the cyclohexanol oxidation reaction with dioxygen and shows hardly any influence on the course of reactions with the participation of NHPI (Fig. 1), although positive catalytic activity of $VO(acac)_2$ towards the oxidation of adamantane with NHPI has been reported.[28]

We found that $VO(acac)_2$ combined with pyridine hydrochloride and NHPI gives an effective catalytic system for oxidation reactions. This catalytic system is particularly attractive compared with other metal complex co-catalysts, it is characterised by a shortest induction time and the highest rates of the oxidation reactions (Fig. 1).

Fig. 2 shows the influence of some ammonium salts combined with $VO(acac)_2$ on the oxidation reaction of cyclohexanol catalysed by NHPI. It presents a considerable influence of the anion of tetrabutylammonium salts on the rate of the reaction, the induction time and dioxygen uptake. The influence of the quaternary ammonium cation is not as significant as the influence of the anion.

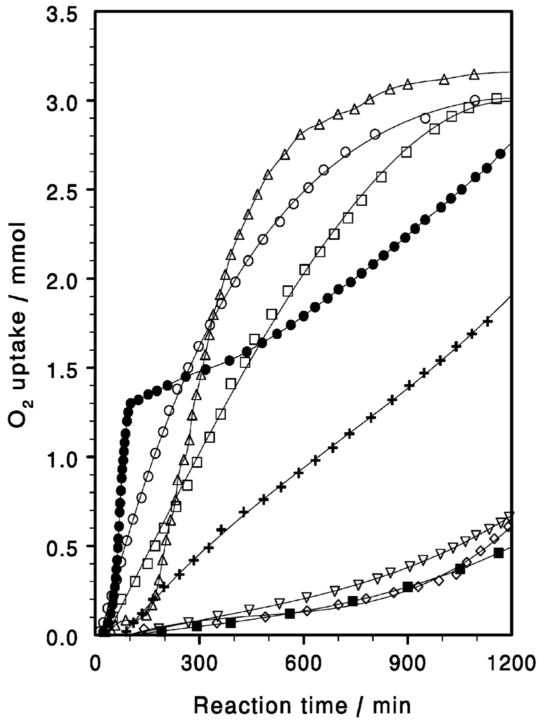


Fig. 1 Aerobic oxidation of cyclohexanol (5 mmol) in MeCN (9.5 ml) at 75 °C, catalysed by NHPI (0.5 mmol) with metal acetylacetonates (0.02 mmol): (◇) none; (●) $VO(acac)_2$ + py·HCl (1 : 1); (▽) $VO(acac)_2$; (○) $TiO(acac)_2$; (△) $Cr(acac)_3$; (□) $Co(acac)_3$; (+) $Al(acac)_3$; (■) $Ni(acac)_2$.

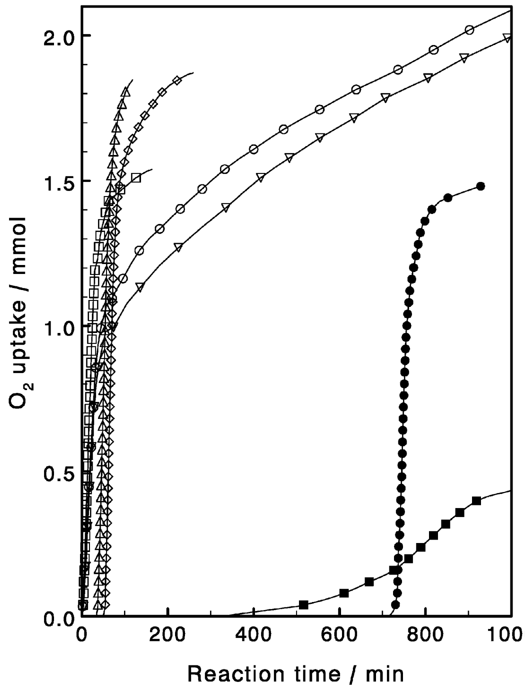


Fig. 2 Aerobic oxidation of cyclohexanol (5 mmol) in MeCN (9.5 ml) at 75 °C, catalysed by NHPI (0.25 mmol) and $VO(acac)_2$ (0.01 mmol) with ammonium salts (0.01 mmol): (▽) $[Me_4N]Cl$; (△) $[Bu_4N]Cl$; (■) $[Bu_4N]HSO_4$; (◇) $[Bu_4N]Br$ (0.03 mmol); (●) $[Bu_4N]I$; (○) $[Et_4N]Cl$; (□) $[Et_3NH]Cl$.

The highest reaction rate was observed for tetrabutylammonium chloride (0.059 mmol O_2 min^{-1}) and the lowest for $[Bu_4N]HSO_4$ (0.0011 mmol O_2 min^{-1}).

For halogen ions, the reaction rate decreases in the order $Cl > Br > I$.

The longest induction time is observed for iodide salt (*ca.* 730 min) and $[Bu_4N]HSO_4$ (516 min). Fast reactions with $[Et_3NH]Cl$, $[Bu_4N]Cl$ and $[Bu_4N]Br$ show lower induction times: 4, 38 and 54 min, respectively.

The above presented results led to the conclusion that the active form of the co-catalyst forms faster in systems where chloride or bromide salts are used. This prompted us to study the influence of other chloride additives combined with $VO(acac)_2$ on the course of the oxidation reaction of cyclohexanol catalysed by NHPI (Table 1).

Table 1 Oxidation of cyclohexanol with O_2 catalysed by the system: NHPI + $VO(acac)_2$ + chloride additive[a]

Entry	Chloride additive	Induction time/min	V_{max} mmol O_2/min	Conversion[b] (%)	Selectivity[b] [%]
1	$[Bu_4N]Cl$	38	0.059	79,5[c]	88.5[c]
2	LiCl	3.7	0.034	93.8	87.2
3	NH_4Cl	6.1	0.036	91.8	66.4
4	HCl	328	0.0004	~10	37.7
5	$VO(acac)_2Cl$[d]	265	0.035	89.2	60.1

[a] *Reagents and conditions*: cyclohexanol (5 mmol), MeCN (9.5 ml), NHPI (0.25 mmol), $VO(acac)_2$ (0.01 mmol) and chloride additive (0.03 mmol), 75 °C, 1 atm. O_2, 18 h. [b] Conversion of cyclohexanol and selectivity to cyclohexanone were calculated from HPLC analysis. [c] Data after 2 h. [d] Without $VO(acac)_2$.

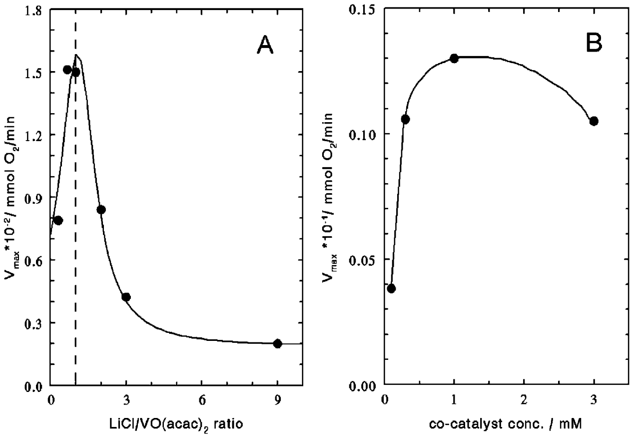


Fig. 3 Effect of the molar ratio of LiCl to $VO(acac)_2$ (A) and the co-catalyst concentration (B) on the oxidation reaction of cyclohexanol catalysed by NHPI.

For $[Bu_4N]Cl$, NH_4Cl and LiCl (entries 1–3) very effective catalytic systems were obtained and the dioxygen absorption curves were almost the same. Unexpectedly, HCl (entry 4), which is on its own an effective co-catalyst in oxidation reactions of alcohols catalysed by NHPI,[29] shows very low absorption of dioxygen in combination with $VO(acac)_2$. This result was attributed to the formation of oxovanadium chlorides, for example $VOCl_2$ and/or $VOCl_3$, which are inactive as co-catalysts in reactions catalysed by NHPI ($VOCl_2$ and $VOCl_3$ were re-examined in separate experiments).

However, complex $VO(acac)_2Cl$ (entry 5) used as a co-catalyst in oxidation reaction of cyclohexanol catalysed by NHPI shows similar activity (except induction time) as in reactions where a combination of $VO(acac)_2$ and chloride salt was used.

The above results indicate that the combination of $VO(acac)_2$ and LiCl is the most active co-catalyst for oxidation of cyclohexanol with dioxygen catalysed by NHPI.

The effect of the LiCl : $VO(acac)_2$ molar ratio and co-catalyst concentration on the oxidation reaction of cyclohexanol catalysed by NHPI is presented in Fig. 3.

The rate of O_2 absorption reaches its maximum at a LiCl : $VO(acac)_2$ molar ratio equal to 1 : 1, as shown in Fig. 3(A). Likewise, the maximum rate of the oxidation reaction of

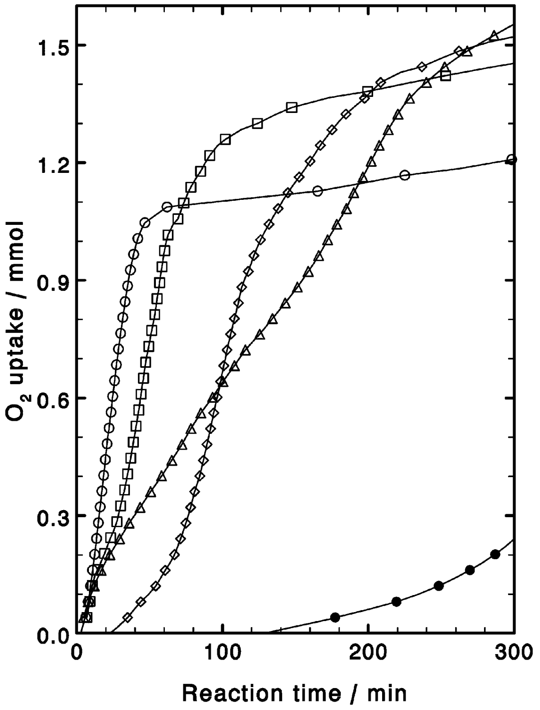


Fig. 4 Aerobic oxidation of cyclohexanol (5 mmol) in MeCN (9.5 ml) at 75 °C, catalysed by NHPI (0.25 mmol) and $VO(acac)_2$ (0.01 mmol) with amines (0.01 mmol): (○) 4-Me-py; (△) Et_3N; (◇) py; (●) 4-CN-py) or $[VO(acac)_2(py)]$ (0.01 mmol) (□).

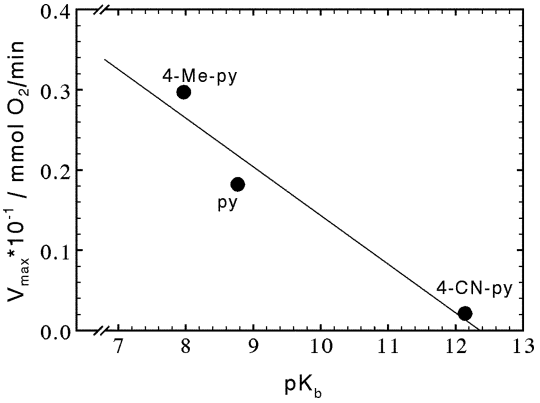


Fig. 5 Effect of basicity of amines in oxidation reaction of cyclohexanol catalysed by NHPI with combination of $VO(acac)_2$ and amine (V_{max} were calculated from Fig. 4 and pK_b values were taken from ref. 18).

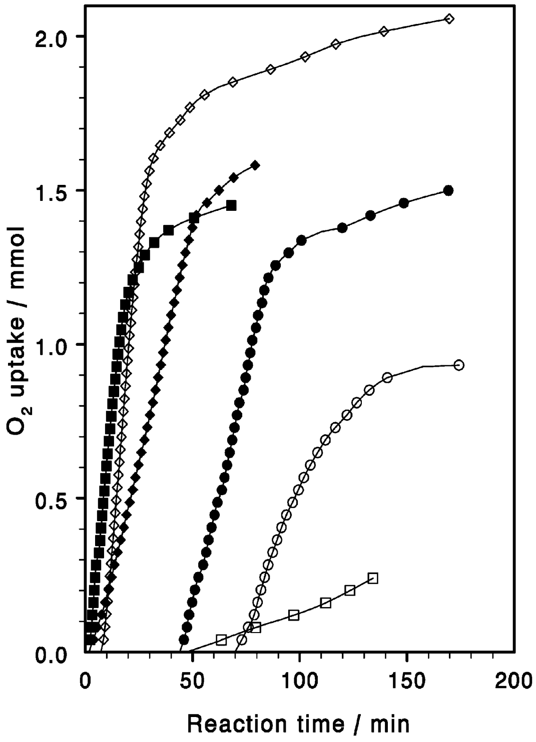


Fig. 6 Aerobic oxidation of cyclohexanol (5 mmol) in MeCN (9.5 ml) at 75 °C, catalysed by NHPI (0.25 mmol) and vanadium complexes (0.01 mmol) without any additive (open symbols) and with LiCl (0.01 mmol) (solid symbols): (●, ○) $[Bu_4N]_3H_3V_{10}O_{28}$; (◆, ◇) $Bu_4NVO_3 \cdot H_2O$; (■, □) $VO(O^iPr)_3$.

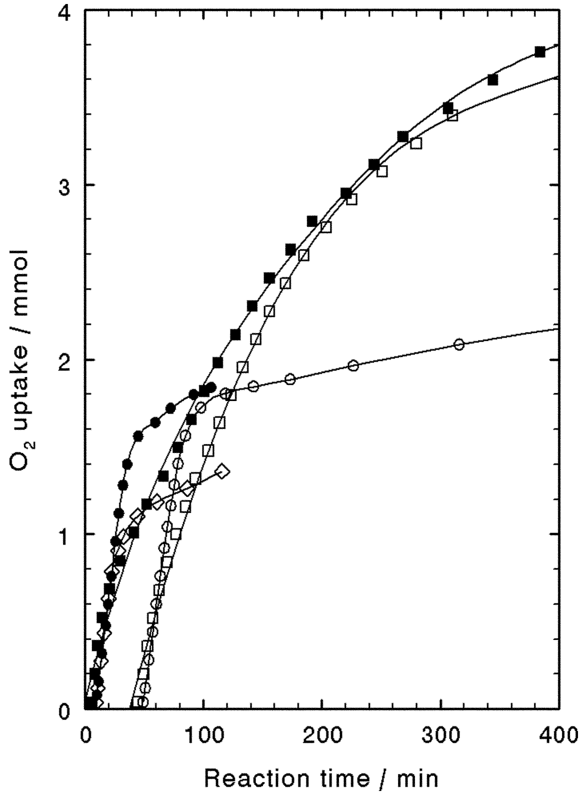


Fig. 7 Aerobic oxidation of alcohols (5 mmol) in MeCN at 75 °C, catalysed by NHPI (0.25 mmol) with $VO(acac)_2$ with LiCl (each 0.01 mmol) (open symbols) or with $[Bu_4N]VO_3$ (0.01 mmol) (solid symbols): (■, □) 1-hexanol; (●, ○) 2-pentanol; (◇) 2-propanol.

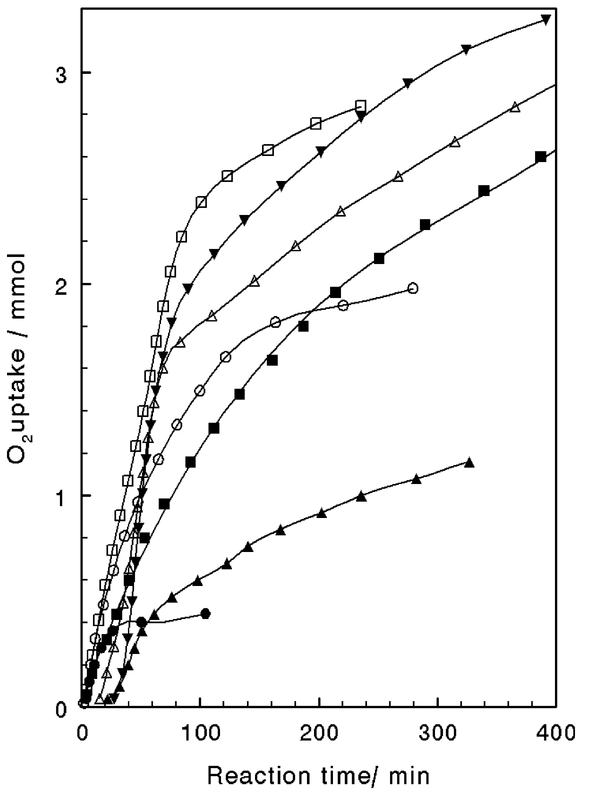


Fig. 8 Aerobic oxidation of alkylaromatics (5 mmol) in MeCN at 75 °C, catalysed by NHPI (0.25 mmol) with $VO(acac)_2$ with LiCl (each 0.01 mmol) (open symbols) or with $[Bu_4N]VO_3$ (0.01 mmol) (solid symbols): (●, ○) cumene; (■, □) ethylbenzene; (▲) *m*-xylene; (▼) *o*-xylene; (△) *p*-xylene.

cyclohexanol (V_{max} = 0.02 mmol O_2 min^{-1}) was observed for the molar ratio $[Bu_4N]Cl : VO(acac)_2 = 1 : 1$.

Fig. 3(B) presents the maximum rates of dioxygen absorption for various concentrations of the co-catalyst, at a ratio of LiCl to $VO(acac)_2$ equal to 1 : 1. The optimum concentration of the co-catalyst is between 0.7 and 2 mmol dm^{-3}.

The role of the chloride additive probably is important for the formation a more labile six-coordinate complex $VO(acac)_2Cl$. The same effect should also be observed with amines because $[VO(acac)_2A]$, where A—amines, are well known vanadium complexes.[30] Fig. 4 presents the course of oxidation reaction of cyclohexanol catalysed with NHPI and a combination of vanadyl acetylacetonate with some amines.

It should be noted that amines in combination with NHPI (without $VO(acac)_2$) show an inhibiting effect. This can explain the lower catalytic activity of the system based on NHPI + $VO(acac)_2$ + py, compared to NHPI and the complex $[VO(acac)_2(py)]$. Generally, the activity of the catalytic system depends on the basicity of the amines (Fig. 5); the more basic the amine, the more labile the vanadium complex and the more effective the co-catalyst (for example, for the $V–O_a$ bond between the vanadyl ion and the acetylacetonate ligand, the corresponding $V–O_a$ stretching force constant was estimated at 2.88 and 0.51 N cm^{-1} for $VO(acac)_2$ and $VO(acac)_2(py)$, respectively).[31]

It is possible to explain the lack of effect of vanadyl complexes with Schiff bases in aerobic oxidation of cyclohexanol catalysed by NHPI; however, such complexes are known as catalysts of oxidation reactions.[26,32]

Using above discussed results we decided to check influence of other, more labile vanadium complexes on the catalytic activity of NHPI (Fig. 6).

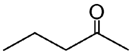
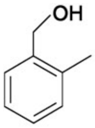
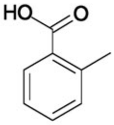
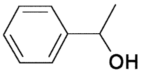
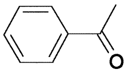
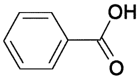
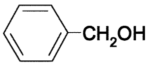
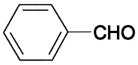
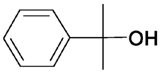
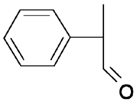
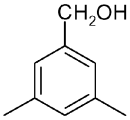
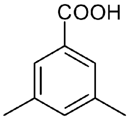
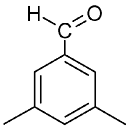
As can be seen from Fig. 6, oxidation reactions of cyclohexanol, catalysed by NHPI and vanadium complexes (without chloride salt or amine additives), proceed in most cases rather ineffectively, like reactions in which the co-catalyst is only $VO(acac)_2$. $[Bu_4N]VO_3$ is an exception: it is a very active co-catalyst without any other additives.

Among catalytic systems in which LiCl was used in addition to NHPI and a vanadium complex, the highest activity was observed for the $VO(O^iPr)_3$ complex (Fig. 6). Other vanadium complexes were also examined, mainly with ligands such as Schiff bases; however, they were ineffective as co-catalysts (also with the addition of LiCl or $[Bu_4N]Cl$) in the oxidation reaction of cyclohexanol, although some of these complexes are known as catalysts of the oxidation reaction.[26,32]

Two catalytic systems based on NHPI/$VO(acac)_2$ with LiCl or $[Bu_4N]Cl$ and NHPI/$[Bu_4N]VO_3$ were chosen for further studies. The results of the investigation of the catalytic activity of these catalytic systems in oxidation reactions of alcohols and alkylaromatics are presented in Fig. 7 and 8 and in Table 2.

It can be seen that both catalytic systems are very effective in oxidation reactions of primary and secondary alcohols, and the observed dissimilarities concern the induction times, which

Table 2 Oxidation of some organic compounds with O_2 catalysed by NHPI/VO(acac)$_2$/LiCl or by NHPI/VO(acac)$_2$/[Bu$_4$N]Cl (values in parenthesis)[a]

Substrate	O_2 uptake/mmol	Substrate conversion (%)	Products, selectivity[b] (%)
1-Hexanol	5.80 (5.20)	100 (100)	 96.6 (>99)
2-Pentanol	2.41 (2.48)	96.4 (97.2)	 >99 (>99)
o-Xylene	(3.39)	(44.4)	 (5.2)  (94.8)
Ethylbenzene	2.84 (3.35)	56.2 (67)	 12.9  79.5 (>99)  7.6
Toluene	1.03	14.4	 6.8  93.2
Cumene	1.98	46.8	 69.1  30.9
Mesitylene	0.89	18.2	 26.3  22.2  51.5

[a] *Reagents and conditions*: substrate (5 mmol), MeCN (9.5 ml), NHPI (0.25 mmol), VO(acac)$_2$ (0.01 mmol) and chloride additive (0.03 mmol), 75 °C, 1 atm. O_2, 20 h. [b] Conversion of substrates and selectivity to determined products were calculated based on GC analysis.

are longer for catalytic systems with vanadyl acetylacetonate (Fig. 7).

Larger differences in the catalytic activity of both catalytic systems can be noticed in oxidation reactions of alkylaromatics, in which tetrabutylammonium vanadate ([Bu$_4$N]VO$_3$) is a low-activity co-catalyst (Fig. 8).

The results presented in Table 2 confirm that these catalytic systems are most effective in oxidation reactions of primary and secondary alcohols, whereas oxidation of alkylaromatics proceeds with conversion rates ranging from 14.4% for toluene to 67.0% for ethylbenzene and with different selectivities, dependent on the structure of the substrate.

It is possible, on the basis of the obtained results, to draw the conclusion that active co-catalysts are complexes of vanadium with a labile coordinating sphere (such as VO(OR)$_3$ and [Bu$_4$N]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$_4$N]Cl) or amine, weakening the vanadium–acetylacetonate bond.

Results of spectroscopic studies of NHPI–vanadium compounds catalytic system are under preparation and will be published.

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