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New efficient aerobic oxidation of some alcohols with dioxygen catalysed by *N*-hydroxyphtalimide with vanadium co-catalysts

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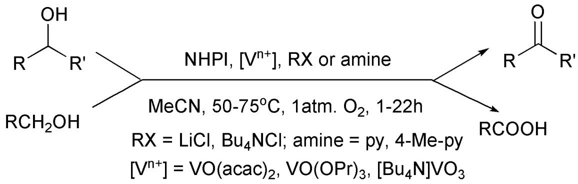
New efficient vanadium co-catalysts have been developed for the oxidation of some alcohols with O_2 catalysed by *N*-hydroxyphthalimide (NHPI). Various alcohols (primary and secondary) were selectively oxidized by O_2 under mild conditions in the presence of a catalytic amount of NHPI as a radical-producing agent combined with small amounts of vanadium complexes with or without the addition of a simple salt (*e.g.* LiCl) or base (*e.g.* pyridine).

Recently a great number of interesting aerobic oxidation reactions of organic compounds have been achieved by using *N*-hydroxyphthalimide (NHPI), which serves as a radical-producing catalyst.[1] The catalytic system is especially attractive because of the mild conditions and high selectivity of the reactions. Among a number of co-catalysts used, complexes of Co and Mn,[1] as well as acetaldehyde,[2] acids, ammonium salts,[3] NO_2,[4] and other species, have shown a positive effect on catalytic activity. During our studies on influence of different transition metal complexes (mainly acetylacetonates) as co-catalysts we have observed interesting effect in the cyclohexanol oxidation reaction in acetonitrile (at 75 °C and 1 atm O_2) catalysed by a system composed of NHPI, $VO(acac)_2$ and some additives (*vide infra*).

$VO(acac)_2$ is well known as a catalyst for oxidation reactions of unsaturated hydrocarbons,[5] hydroquinones,[6] and propargylic alcohols[7] using dioxygen as oxidant. Vanadyl tetradentate Schiff base complexes[8] and $VOCl_3$[9] are also catalysts in aerobic selective oxidation of olefins and α-hydroxycarbonyls, respectively. Nevertheless, under the reaction conditions described above (with purified reagents), $VO(acac)_2$ does not catalyse the cyclohexanol oxidation reaction with dioxygen and shows hardly any influence on the course of reactions with the participation of NHPI, although positive catalytic activity of $VO(acac)_2$ towards the oxidation of adamantane with NHPI has been reported.[10] On the other hand, it is well known that in many solvents $VO(acac)_2$ undergoes rather slow air oxidation to vanadium(V) species.[11] However, this process proceeds rapidly after the addition of H_2O_2 and is accompanied by the appearance of a characteristic heather colour of the solution.[12] Indeed, the addition of stoichiometric amounts of H_2O_2 or *t*-BuOOH to the mixture of well purified components containing $VO(acac)_2$ caused the transient appearance of a heather colour but did not generate a catalytically active form of the vanadium complex. Only just after the addition to the vanadium of stoichiometric amounts of amines, pyridine and its derivatives, tetra-alkylammonium chlorides and/or lithium chloride does the system become highly catalytically active (Table 1). Such a high activity allowed us to decrease the NHPI concentration in further experiments from 10% to 5%. Among a number of tetraalkylammonium halogenides, the best activity was found for tetraethyl- and tetrabutylammonium chloride (entry 1). The addition of 4-methylpyridine (entry 4) was the most effective among the different pyridine derivatives used. A particular effect was observed for lithium chloride (entries 2, 3). Each of these compounds interacts with the vanadium complex $VO(acac)_2$ of a nearly square pyramidal structure in its six-coordinate site to form distorted octahedral complexes. To prove this hypothesis we prepared six-coordinated vanadium complexes, (*e.g.* $VO(acac)_2Cl$, $VO(acac)_2py$), and these compounds were found to be effective co-catalysts without any additional additives (entries 5, 6).

ESR and ^{51}V NMR studies of the reaction mixtures show that V (IV) is rapidly oxidized to V (V). Therefore V (V) complexes should also demonstrate catalytic activity as co-catalysts. This assumption was proved when $VO(OPr)_3$ or $[Bu_4N]VO_3$ (entries 7, 9) were used

Table 1 Aerobic oxidation of alcohols catalysed by NHPI combined with various vanadium (IV, V) co-catalyst[a]



Entry	Alcohol	Co-catalyst	Conversion[b] (%)	Time/h	Selectivity[b] (%)
1	Cyclohexanol	$VO(acac)_2 + Bu_4NCl$	90.3	18	66.4
2	Cyclohexanol	$VO(acac)_2$ + LiCl	81.7	2	100
3	Cyclohexanol[c]	$VO(acac)_2$ + LiCl	87.4	21	100
4	Cyclohexanol	$VO(acac)_2$ + 4-Me–py	84.7	1.5	73.9
5	Cyclohexanol	$VO(acac)_2Cl$	89.2	18	60.1
6	Cyclohexanol	$VO(acac)_2py$	82.7	18	80.2
7	Cyclohexanol	$VO(OPr)_3$	11.2	2	> 99
8	Cyclohexanol	$VO(OPr)_3$ + LiCl	80.1	1	89.0
9	Cyclohexanol	$[Bu_4N]VO_3$	72.5	1.5	89.0
10	Cyclohexanol	$[Bu_4N]VO_3$ + LiCl	74.4	1.5	85.8
11	1-Hexanol	$VO(acac)_2$ + LiCl	100	22	96.6[d]
12	2-Pentanol	$[Bu_4N]VO_3$	73.6	2	100
13	2-Pentanol	$VO(acac)_2$+LiCl	96.4	20	> 99

[a] Substrate (5 mmol) was reacting with O_2 in the presence of NHPI (0.25 mmol, 5 mol %) and vanadium co-catalyst (0.01 mmol, 0.2 mol %) at 75 °C. [b] Conversion of alcohols and reaction selectivity to ketones were calculated from HPLC analysis. [c] At 50 °C. [d] Selectivity to hexanoic acid.

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as co-catalysts, although for $VO(OPr)_3$ the addition of LiCl was necessary (entry 8). Among a number of catalytic systems based on NHPI and vanadium complexes, the most attractive was that composed of $VO(acac)_2$–LiCl and $[Bu_4N]VO_3$ (*i.e.* entries 8 and 9). For these two catalysts the oxidation of other alcohols (1-hexanol and 2-pentanol) was studied (entries 11–13). Recently, a new highly active and selective catalytic system for alcohol oxidation with dioxygen, based on NHPI (10 mol %), $Co(OAc)_2$ (0.5 mol %) and *meta*-chlorobenzoic acid (MCBA) (5 mol %), has been reported.[13,14] Ishii *et al.*[13] reported oxidation of different alcohols at room temperature with high conversions (from 75 to $>99\%$) and yields (47–98%) after 15–20 hours. Minisci *et al.*[14] demonstrated unusual selectivity of that system in the oxidation of benzyl alcohols to benzaldehydes with a selectivity of from 91 to 99% (at alcohol conversions of from 75 to 100%) at room temperature after 1–4 hours. We compared our catalytic system (with carefully purified reactants, however) at reaction conditions similar to those reported in papers[13] and[14] except for temperature, which in our case was 30 °C. We studied the oxidation reaction of cyclohexanol (3 mmol) in EtOAc (5 ml) and benzyl alcohol (3 mmol) in MeCN (15 ml) catalysed by NHPI (10 mol %) with $[Bu_4N]VO_3$ (0.3 mol %) and additionally NHPI (10 mol %) with $Co(OAc)_2 \cdot 4H_2O$ (0.5 mol %) and MCBA (5 mol %). The results presented in Fig. 1 are completely different from those reported in.[13 and 14] Generally, for the oxidation of cyclohexanol, a catalytic system based on NHPI–$Co(OAc)_2$–MCBA shows a lower conversion of alcohol than one based on our NHPI–$[Bu_4N]VO_3$ system. In the case of benzyl alcohol oxidation reaction, quite long induction times were observed for both catalytic reactions (165 and 172 min for cobalt- and vanadium-based systems, respectively). It is worth noting that for the cobalt-based system very rapid oxidation to benzoic acid is observed after *ca.* 1086 min. Such a reaction course may suggests that during the first stage of the reaction, when slower absorption is observed (1.26×10^{-3} mmol O_2/min), only alcohol-to-aldehyde oxidation occurs whereas after *ca.* 1100 min very fast oxidation of aldehyde to benzoic acid takes place (0.15 mmol O_2/min). This reaction was confirmed in an additional experiment in which benzaldehyde oxidation was carried out at the same reaction conditions and found to be very fast (0.11 mmol O_2/min) (Fig. 1). However, in a sample taken from the reaction mixture after 991 min of benzyl alcohol oxidation the following amounts were found: benzyl alcohol (0.54 mmol), benzaldehyde (1.82 mmol), benzoic acid (0.65 mmol). These results may suggest simultaneous oxidation of both the substrate and the intermediate product — benzaldehyde.

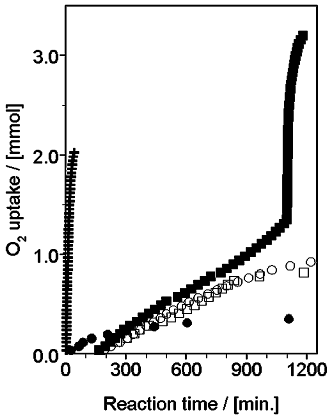

Fig. 1 Aerobic oxidation of benzyl alcohol in MeCN (□,■), cyclohexanol in EtOAc (○,●) catalysed by NHPI–$Co(OAc)_2$–MCBA (solid symbols) and NHPI–Bu_4NVO_3 system (open symbols), respectively, and benzaldehyde in MeCN (+) catalysed by NHPI–$Co(OAc)_2$–MCBA at 30 °C (see text for reagent concentrations).

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