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Trace Water-Promoted Oxidation of Benzylic Alcohols with Molecular Oxygen Catalyzed by Vanadyl Sulfate and Sodium Nitrite under Mild Conditions

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Abstract: An inexpensive catalytic system consisting of vanadyl sulfate and sodium nitrite was developed for the oxidation of benzylic alcohols with molecular oxygen under mild conditions. Benzyl alcohols with various substitutions were efficiently converted to their corresponding aldehydes with high conversion and selectivity under 80 °C (e.g., 4-nitrobenzyl alcohol was smoothly oxidized to 4-nitrobenzyl aldehyde with 94% yield under 0.5 MPa of molecular oxygen). Halogen, noble metals, extra base or complicated ligands were avoided. Addition of a trace of water to this system before the reaction was crucial for the high efficiency.

Keywords: benzylic alcohols; molecular oxygen; nitrite; oxidation; vanadium

Oxidation of alcohols to carbonyl compounds is a fundamental transformation in organic chemistry both at the laboratory and industry levels.[1] Furthermore, the oxidative conversion of the hydroxy group has also attracted much attention in biorefinery field recently.[2] Traditionally, such a transformation is performed with stoichiometric oxidants such as CrO_3 and permanganate.[1] Much progress has been made to develop catalytic systems using molecular oxygen as the terminal oxidant.[3] Representative examples are the catalytic systems using transition metal catalysts (Pd,[4] Ru,[5] Au,[6] Cu,[7] Pt,[8] Ni,[9] polyoxometalates,[10] Mo,[11] manganese oxide octahedral molecular sieves,[12] Fe[13], etc.), or stable nitroxyl free radicals (e.g., 2,2,6,6-tetramethylpiperidyl-1-oxyl,TEMPO).[14] However, noble metals, halogen (e.g., bromine), extra base (e.g., NaOAc or K_2CO_3) or complicated ligands are often used. The quest for efficient and inexpensive catalytic systems for the oxidation of alcohols with molecular oxygen remains an important challenge.

Because of their unique redox property, vanadium compounds were widely used for oxidation.[15–17] For example, vanadium phosphorus oxide (VPO) for the oxidation of *n*-butane to maleic anhydride has been employed in industry for decades.[15,16] In the liquid-phase oxidation catalyzed by vanadium species, researchers mainly focused on hydrogen peroxide or organic peroxides as terminal oxidants.[17] Only a few vanadium-based systems for the oxidation of alcohols with molecular oxygen are known. V_2O_5/K_2CO_3, $VO(acac)_2$/MS 3 Å, V-Cu/DABCO, $VOCl_3$ etc, were described.[18] However, in these catalysts systems, extra bases, drying agents or ligands were often indispensable; or the scope of alcohols was quite limited. Efficient example using inexpensive vanadyl sulfate under mild conditions remained to be explored. Here we disclose a novel and efficient, vanadium-based catalytic system for the oxidation of benzylic alcohols with molecular oxygen.

During the synthesis of VPO, benzyl alcohol was usually used as the reductant of V_2O_5.[15] Therefore stoichiometric $[V^{5+}]$ species could oxidize benzyl alcohol. If a catalytic cycle could be established, the keystone is the facile reoxidation of low-valent vanadium species by O_2 under mild conditions. We noticed that in industry cyclohexanone was oxidized to adipic acid with stoichiometric HNO_3 catalyzed by vanadium and assumed that low-valent vanadium species could be oxidized back to $[V^{5+}]$ by nitric compounds.[16,19] Then $NaNO_2$ as a nitric source was introduced to establish the vanadium redox cycle. Initial experiments were carried out using benzyl alcohol as the test substrate (Table 1). Inexpensive $VOSO_4$ was employed as vanadium source. The results clearly indicated that the introduction of $NaNO_2$ greatly improved the conversion of benzyl alcohol (Table 1, entries 1–4). Nearly complete conversion was obtained with the addition of 5 mol% $NaNO_2$ within only 2 h (Table 1, entry 3). $VOSO_4$ alone is a poor catalyst. Trace products were detected within 4 h at 80 °C using 5 mol% $VOSO_4$ (Table 1, entry 1). $NaNO_2$ itself is not active as catalyst either, though 50 μL acetic acid were added to keep the acidic conditions (Table 1, entry 5). Vanadyl sulfate/sodium nitrite was still effective even when the temperature was decreased to 50 °C. High conversion was also obtained at 50 °C when the time was prolonged to 10 h (Table 1, entry 6).

Table 1. Oxidation of benzyl alcohol with molecular oxygen catalyzed by vanadyl sulfate/sodium nitrite.[a]

Entry	Sodium nitrite [mol%]	Time [h]	Conversion [%]
1	0	4	trace
2	2.5	2	61.1
3	5.0	2	99.5
4	7.5	2	100
5[b]	5.0	2	trace
6[c]	5.0	10	99.8

[a] *Reaction conditions:* 5 mmol benzyl alcohol, 5 mol% $VOSO_4$, 80 °C, 5 mL CH_3CN, 25 μL H_2O, 0.5 MPa O_2. Conversion was based on GC analysis, selectivity for benzaldehyde $>$ 98% in all cases.

[b] Without $VOSO_4$; additional 50 μL CH_3COOH were added.

[c] Reaction was performed at 50 °C.

As water was formed as a by-product during the oxidation of alcohols, the effect of water was often ignored. Addition of a trace of water before the reaction was crucial to the efficiency of this catalytic system (Figure 1). Without additional water before reaction, a long induction time was observed and only 11.3% conversion was obtained in 2 h. Addition of about 25 μL water was appropriate to keep the high efficiency (5 mmol benzyl alcohol as substrate, 5 mL CH_3CN as solvent, and 0.09 g H_2O would be generated gradually if 100% benzyl alcohol was converted). However, addition of too much water resulted in a decrease of activity. When the amount of water reached 250 μL, the conversion of benzyl alcohol remarkably decreased to only 33.2% under the same conditions. Furthermore, only 5.6% conversion was obtained even within 10 h when pure water was used as solvent. The phenomena will be discussed in the following section.

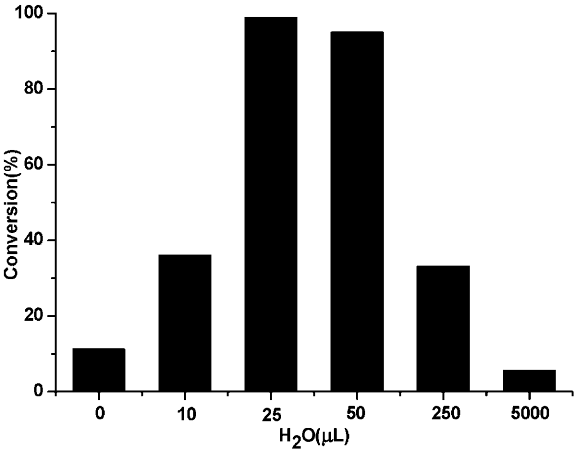


Figure 1. Effect of water on $VOSO_4/NaNO_2$-catalyzed oxidation of benzyl alcohol. *Reaction conditions:* 5 mmol benzyl alcohol, 0.25 mmol $VOSO_4$, 0.25 mmol $NaNO_2$, 80 °C, 5 mL CH_3CN, 0.5 MPa O_2, 2 h. Entry 5000: 100% H_2O as solvent and reaction time = 10 h.

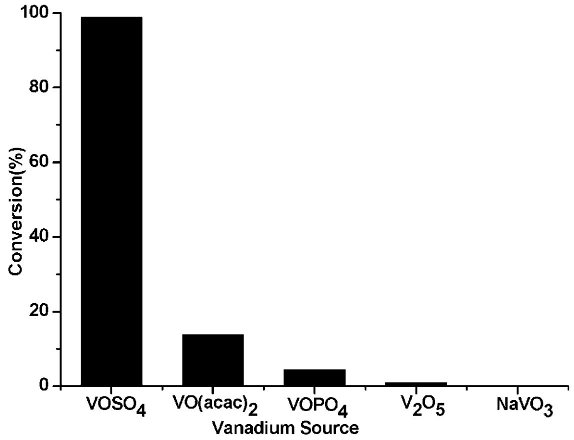


Figure 2. Catalytic oxidation of benzyl alcohol with molecular oxygen using $NaNO_2$ and different vanadium compounds. *Reaction conditions:* 5 mmol benzyl alcohol, 0.25 mmol [V], 0.25 mmol $NaNO_2$, 5 mL CH_3CN, 25 μL H_2O, 80 °C, 0.5 MPa O_2, 2 h.

Some other vanadium compounds were also tested (Figure 2). Among them, $VOSO_4$ showed the highest efficiency. It was interesting that $VO(acac)_2$, which was widely used in oxidation, exhibited a lower activity here.[17] V_2O_5 was reported to be effective for the catalytic oxidation of alcohols at 100 °C in the presence of K_2CO_3.[18e] However, here at 80 °C without bases, the conversion of benzyl alcohol was less than 1%. $NaVO_3$ was completely inactive.

To further probe the potential of the $VOSO_4/NaNO_2$ catalytic system, the oxidation of other alcohols was studied (Table 2). All primary benzyl alcohols were smoothly converted into their corresponding aldehydes with high conversions from 82.5% to 100% (Table 2, entries 1–7). To our delight, the selectivities for the corresponding aldehydes were also quite high under optimal conditions (>99%). No ad-

Table 2. Oxidation of alcohols with molecular oxygen catalyzed by $VOSO_4/NaNO_2$.[a]

Entry	Substrate	Product	Time [h]	Conversion [%]	Selectivity [%]
1	Benzyl alcohol	Benzaldehyde	2	99.5 (93)	99.0
2	4-Methylbenzyl alcohol	4-Methylbenzaldehyde	2	100 (88)	99.5
3	2-Methylbenzyl alcohol	2-Methylbenzaldehyde	2	96.8	99.7
4	3-Chlorobenzyl alcohol	3-Chlorobenzaldehyde	2	99.1 (91)	99.5
5	2-Chlorobenzyl alcohol	2-Chlorobenzaldehyde	8	82.5	99.6
6	3-Methoxybenzyl alcohol	3-Methoxybenzaldehyde	1.5	95.2	~100
7	4-Nitrobenzyl alcohol	4-Nitrobenzaldhyde	1.5	99.3 (94)	~100
8	Cyclopentanol	Cyclopentanone	5	4.8	~100
9	Octan-2-ol	Octan-2-one	20	18.2	79.7
10	Hexanol	Hexanal	5	7.6	32.3
11[b]	4-Nitrobenzyl alcohol	4-Nitrobenzaldhyde	4	98.6	~100
	Octan-2-ol	Octan-2-one		13	96.1
12[b]	4-Nitrobenzyl alcohol	4-Nitrobenzaldhyde	3	98.5	~100
	Hexanol	Hexanal		7.2	59.7

[a] *Reaction conditions:* 5 mmol alcohol, 0.25 mmol $VOSO_4$, 0.25 mmol $NaNO_2$, 5 mL CH_3CN, 25 μL H_2O, 0.5 MPa O_2. Conversions and selectivities were based on GC. Values in parenthesis are the isolated yields of the pure products.

[b] 4-Nitrobenzyl alcohol: 2.5 mmol, the other alcohol: 2.5 mmol.

ditive such as bases was required to keep the high selectivity, and this is quite different from the V_2O_5 system.[18e] Nitration products on the phenyl group were not detected. Electron-donating or electron-withdrawing substitutions on the benzyl alcohols did not apparently affect the efficiency of the oxidation in terms of the conversion (Table 2, entries 2 and 7). 4-Nitrobenzyl alcohol was often difficultly oxidized in some other systems; here it underwent facile oxidation with a high selectivity for 4-nitrobenzaldhyde (Table 2, entry 7). Methoxy and halide substitutions on the phenyl group could survive the reaction conditions, which showed good functional group tolerance (Table 2, entries 4–6). Methyl substitutions on the *o*- or *p*-positions all served as good substrates, which indicated that a steric effect of the substitution is not remarkable (Table 2, entries 2 and 3). However, aliphatic alcohols were difficult to oxidize under the same conditions (Table 2, entries 8, 9 and 10). But no by-products of ring cleavage were found for cyclopentanol (Table 2, entry 8). Prolonging the reaction time resulted in the formation of ether as by-product for octan-2-ol (Table 2, entry 9).

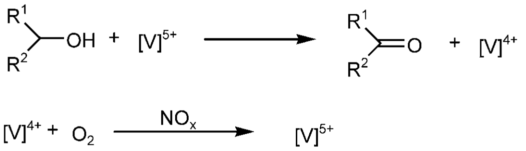
In competition experiments, an equimolar mixture of 4-nitrobenzyl alcohol and an aliphatic alcohol (primary or secondary) was subjected to oxidation. When a mixture of 4-nitrobenzyl alcohol and octan-2-ol was used, 98.6% of the 4-nitrobenzyl alcohol was converted within 4 h, whereas only 13% of the octan-2-ol was oxidized (Table 2, entry 11). For a mixture of 4-nitrobenzyl alcohol and hexanol, 98.6% and 7.2% conversions were obtained after 3 h respectively (Table 2, entry 12). These results proved that this system was quite useful for the chemoselective oxidation of benzyl alcohols with strong electron-withdrawing substitutions in the presence of aliphatic alcohols.

To the best of our knowledge, this is the first report of vanadyl sulfate and sodium nitrite for the oxidation of benzylic alcohols with dioxygen. Noble metals, halogen and additional base were not used. Side reactions like halogenation and the Cannizzaro reaction were avoided. As the catalysts were simple inorganic salts, they could be easily removed by filtration and washing. This would be quite practical and useful. It would seem to be economic and efficient oxidation process with promising chemoselectivity.

To explain these findings, preliminary investigations of the mechanistic aspects were made. The oxidation of benzyl alcohol in the presence of a radical inhibitor (2,6-di-*tert*-butyl-*p*-cresol or *p*-hydroquinone) was examined. Addition of 5 mol% inhibitor affected the reaction rate greatly. The conversion was reduced from 99.5% to only about 1% within 2 h. This result showed that a radical pathway was probably involved in the main reaction course. It was quite different from Uemura's or Kirihara's system.[18a,c] The radical inhibitor did not influence their systems at all. NO_x is a free radical and was proposed to be responsible for the high selectivity of aromatic alcohols. In a controlled parallel experiment, 65% benzaldehyde was converted to benzoic acid using 2 mol% $VOSO_4$ alone within 2 h, but when additional 5 mol% $NaNO_2$ was present, 87% benzaldehyde remained intact under an oxygen atmosphere at 80 °C in 2 h.

It was reported that NO in aqueous solution containing O_2 was oxidized primarily to NO_2^- anion with little or no formation of NO_3^-.[20] So the trace of water was crucial to the redox cycle between NO and O_2 and the formation of HNO_2 in the beginning. But $VOSO_4$ reacted with hot water to form polyanions of vanadium;[21] this might account for the decreasing conversion when too much water was added. Stoichiometric reactions under N_2 were also studied. When the oxidation of benzyl alcohol using a stoichiometric amount of $VOSO_4$ at 80 °C was performed, a trace of benzaldehyde was detected within 3 h. On the other hand, 54% benzaldehyde was obtained when $VOCl_3$ was used instead of $VOSO_4$ (24% benzyl chloride was detected as by-product). Therefore, $VOSO_4$ was not the active species for the direct oxidation of benzyl alcohol.

Based the experiments above, an overall redox cycle was proposed (Scheme 1). The oxidation of benzyl alcohols by oxygen was divided into several steps. In our system, alcohols might be oxidized by $[V^{5+}]$ species. $NaNO_2$ resulted in the formation of HNO_2 in the presence of a trace of water under acidic conditions. The transformation of $[V^{4+}]$ to $[V^{5+}]$ runs smoothly with assistance of HNO_2.[19] NO_x played the role of a mediator to bridge the gap between oxygen and vanadium. The reoxidation of NO to NO_2 could be easily performed with O_2.



Scheme 1. Proposed vanadium redox cycle.

In conclusion, an economical and efficient catalytic system composed of vanadyl sulfate and sodium nitrite was developed for oxidation of benzylic alcohols with dioxygen. A wide range of benzylic alcohols were efficiently converted to their corresponding aldehydes with high conversion and selectivity at below 80 °C. Addition of a trace of water in the beginning had great promotive effect. This work may be helpful to the further development of vanadium-based oxidation. Investigations of the detailed mechanism are under way.

Experimental Section

General Procedure for Catalytic Oxidation

A typical procedure for the oxidation of benzyl alcohol was as follows: vanadyl sulfate (42.90 mg, 0.25 mmol), sodium nitrite (17.25 mg, 0.25 mmol) and benzyl alcohol (540 mg, 5 mmol) were charged into the autoclave followed by 5 mL acetonitrile, then 25 μL H_2O were added using a 50-μL injection sampler. After the autoclave was closed, oxygen was charged to 0.5M Pa. It was heated to 80 °C within 20 min. After 2 h (heating period is not included), the autoclave was cooled to room temperature and carefully depressurized to normal pressure. A sample was taken from products mixture; The conversion and selectivity were determined by GC without any purification. (All products were determined on GC-MS).

Typical Separation Procedure for Aldehydes

Taking the oxidation of 4-nitrobenzyl alcohol (0.7656 g) as an example, if GC showed that the conversion of 4-nitrobenzyl alcohol was >99%, CH_3CN was removed on a rotary evaporator after filtration. Then solid were washed with saturated $NaHCO_3$ and extracted with CH_2Cl_2, The combined CH_2Cl_2 layer was dried over anhydrous $MgSO_4$, then evaporated to afford a yellow solid; yield: 0.7063 g (94%). The NMR spectrum was recorded using the isolated product directly.

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