

Efficient Vanadium-Catalyzed Aerobic C-C Bond Oxidative Cleavage of Vicinal Diols

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Received: ((will be filled in by the editorial staff))



Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/adsc.201#####>. ((Please delete if not appropriate))

Abstract. The aerobic oxidative C-C bond cleavage of vicinal diols catalyzed by vanadium amino triphenolates is described. Our results show that C-C bond cleavage can be performed in different solvents, under an air or oxygen atmosphere, with a large variety of glycols (cyclic or linear, with aromatic or aliphatic substituents) affording the corresponding carbonyl derivatives with high chemoselectivity.

Reactions can be performed with as little as 10 ppm of catalyst reaching TON up to 81,000 and TOFs of up to 4150 h⁻¹. A reaction mechanism, rationalized by density functional theory calculations, is also proposed.

Keywords: C-C Activation, Vanadium, Homogeneous Catalysis; Aerobic Oxidation, Oxygen

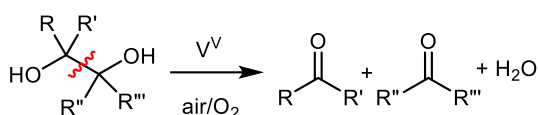
Introduction

Oxidative carbon-carbon bond cleavage of vicinal diols yielding carbonyl compounds is a fundamental reaction in organic synthesis^[1] as well as in lignin-cellulose valorization and the general context of renewable feedstock transformation.^[2]

Since the pioneering work of Malaprade in 1928,^[3] 1,2-diols oxidative cleavage has been generally performed using stoichiometric high-valent inorganic oxidants, mainly periodates,^[4] or lead tetracarboxylates.^[5] Beside the intrinsic problem related to the use of stoichiometric amounts of oxidants, most of these reagents suffer from severe drawbacks in terms of selectivity, toxicity, storage, handling, cost and solubility. More recently, catalytic procedures have been reported using homogeneous iron,^[6] molybdenum,^[7] copper,^[8] manganese,^[9] ruthenium,^[10] cobalt,^[11] palladium,^[12] or polyoxometalate^[13]

complexes. Sacrificial stoichiometric organic or inorganic oxidants are however still required.^[7,8,13b] When O₂ is used as primary oxidant, high pressures^[8,10] or activating sacrificial substrates^[5,9,11] are required or the scope of the substrate is limited to the more reactive tertiary or benzylic glycols.^[7] Therefore, the design of more efficient and environmentally benign catalytic processes for the C-C bond cleavage of diols remains a topic of key importance.

Recently, the use of vanadium complexes, an Earth abundant element, as catalysts for the aerobic oxidative C-C bond cleavage of vicinal diols has been reported (Scheme 1).^[2a,b] Vanadium salts (VO₂⁺,^[14] VO(acac)₂,^[15] VOCl₃, VO(OEt)Cl₂, VOCl₂,^[16] H₅[PMo₁₀V₂O₄₀]^[17]) have been used with cyclic and acyclic *di*-tertiary diols providing the corresponding ketones in high yields. Unfortunately, the efficiency of these catalytic systems dramatically decreases with less substituted glycols.



Scheme 1. Aerobic C-C oxidative cleavage of diols to the corresponding carbonyl derivatives.

Only vanadium-based polyoxometalates or $\text{Pt/C-V}_2\text{O}_5$ with high O_2 pressures and temperature, strong acidic conditions could convert cyclohexane-1,2-diols, 1,2-ethanediol or monosaccharides forming mixtures of the corresponding **carboxylic acids** and over-oxidized products.^[18,19]

More recently Baker, Hanson and Thorn reported that vanadium complexes **V1-V3** (Figure 1) are able to oxidize pinacol under stoichiometric conditions to yield acetone.^[20] Complex **V1**^[21] is effective also under aerobic, catalytic conditions in pyridine or 1-methyl-2-pyrrolidinone. Under the best conditions, 97% yield of acetone was obtained using 5% of catalyst at 100°C at atmospheric pressure.^[20a]

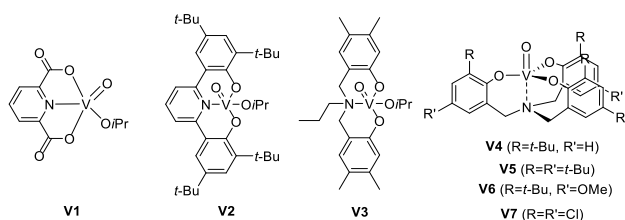


Figure 1. Vanadium complexes **V1-V7** as catalysts for the aerobic oxidative carbon-carbon cleavage of diols.

While the capability of homogeneous vanadium complexes to catalyze the aerobic C-C bond cleavage of glycols has been explored to some detail, the development of an effective and sustainable vanadium-based catalytic process with broad substrate scope is still missing. Herein we report that V(V) amino triphenolate complexes **V4-V7** are efficient catalysts for the oxidative aerobic C-C bond cleavage of glycols, not only tertiary and benzylic diols but also cyclic and linear aliphatic diols, both internal and terminal ones, affording the corresponding carbonyl derivatives with high yields and selectivity, with catalyst loadings down to 0.001%, TONs of up to 81,000 and TOFs of up to 4150 h⁻¹.

Results and Discussion

In recent years TPA complexes^[22] have been reported to be effective and tunable Lewis acid catalysts, affording processes with high turnover numbers and frequencies, by us^[23] and other research groups.^[24,25,26] Among the systems investigated, V(V) *tris-t*-butylphenolate complex **V4** (Chart 1) is one of the most active homogeneous catalyst for sulfoxidations and bromoperoxidations using hydrogen peroxide as

oxidant.^[23b,27] More recently **V7** has been successfully used as catalysts for the synthesis of cyclic carbonates via CO_2 /internal epoxide cycloaddition.^[24d] In particular, it has been demonstrated that the tetradentate nature of the complex and the presence of bulky *t*-butyl or chloro groups *ortho* to the phenol play a fundamental role for the catalyst stability and activity under turnover conditions. Furthermore, the nature of the multiple substituents in the *ortho/para* positions of the phenol rings can effectively tune the reactivity of the catalyst.^[23a,b] Therefore, V(V)-amino triphenolate complexes **V4-V7** seemed to us to be good candidates for exploring the aerobic oxidative C-C bond cleavage of vicinal diols.

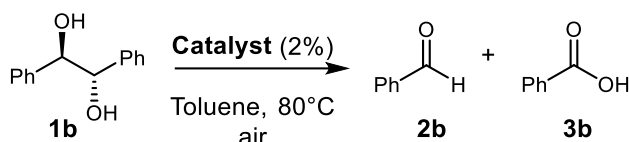
Vanadium complexes **V4-V7** can be easily prepared by mixing the appropriate triphenolamine^[28] with an equimolar amount of $\text{V}(\text{O})(\text{O}i\text{Pr})_3$ in dry CH_2Cl_2 or THF under nitrogen. In all cases, high yields of reddish brown (**V4**), dark-red (**V5**), reddish violet (**V6**) or dark-blue (**V7**) crystalline solids were obtained. For all the complexes, characterizations (¹H, ¹³C and ⁵¹V NMR, FT-IR and ESI-MS) in agreement with literature data were obtained.^[23b,28c]

The effectiveness of our systems as catalysts for the aerobic carbon-carbon cleavage was first tested for the oxidation of pinacol **1a** [0.05M] (Scheme 1, R=R'=R''=R'''=Me), in the presence of 10% **V4** at 80°C under air and in different solvents (toluene, pyridine and NMP). The course of the reaction was monitored via ¹H NMR. We were very pleased to observe that **V4** was effective, as complete conversion of the substrate into acetone occurred in only 2 hours. A more detailed study, undertaken in order to define the performances of **V4-V7** was carried out with *meso*-hydrobenzoin **1b** as model substrate in toluene. The reactions were carried out at 80°C under air with 2% catalyst loading. For comparison, the behavior of other vanadium complexes such as **V1** and commercially available vanadium oxo tri-isopropoxy ($\text{VO}(\text{O}i\text{Pr})_3$) and vanadium oxodiacylacetone ($\text{VO}(\text{acac})_2$) were also tested under the same experimental conditions (Table 1).

The oxidative C-C bond cleavage of **1b** affords two equivalents of benzaldehyde **2b**, which, at longer reaction times, can be over-oxidized to benzoic acid **3b**. The reaction courses were monitored via quantitative HPLC. The results in Table 1 not only show that **V4-V7** can effectively catalyze the process but also that the electron-withdrawing character of the TPA ligand plays a major role: **V7** (R=R'=Cl), bearing the most electron-withdrawing substituents, was significantly more active than the **V4-V6** complexes (reaction fourteen-fold faster with respect to **V6**, bearing the most electro-donating substituents (*t*-Bu/MeO)), as well as the commercially available $\text{VO}(\text{O}i\text{Pr})_3$ and $\text{VO}(\text{acac})_2$ complexes and catalyst **V1** (Table 1, entries 5-7). Furthermore, the acceleration of the reaction was found to have a beneficial effect on the chemoselectivity of the reaction: catalyst **V7** affords exclusively two equivalents of benzaldehyde **2b** (Table 1, entry 4). The uncatalyzed reaction is negligible under the same

reaction conditions with only 2% conversion after 24 h.^[29]

Table 1. Aerobic oxidative cleavage of *meso*-hydrobenzoin **1b** in the presence of complexes **V1**, **V4-V7**, VO(OiPr)₃ or VO(acac)₂ (2%).^a Catalyst screening

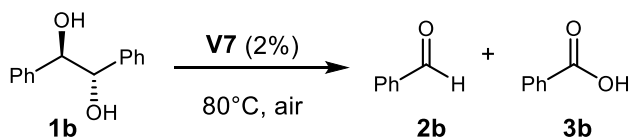


Entry	Cat.	Conv. (%)	Time (h) ^b	2b:3b
1	V4	>99	4	98:2
2	V5	>99	5	97:3
3	V6	>99	10	94:6
4	V7	>99	0.7	>99:1
5	VO(OiPr) ₃	>99	6	98:2
6	V1	>99	6	99:1
7	VO(acac) ₂	>99	9	97:3
8	--	2	24	>99:1

^aReaction conditions: [1b]₀=0.05 M, 2% of V-catalyst, toluene, 80 °C. ^bTime required for complete substrate conversion. ^cDetermined by quantitative HPLC, naphthalene as internal standard.

The effect of other reaction parameters like solvent (Table 2), temperature, atmosphere and catalyst loading (Table 3, Figure 1) were explored using the best performing catalyst **V7**.

Table 2. Aerobic oxidative cleavage of **1b** catalyzed by **V7** (2%).^a Solvent screening.



Entry	Solvent	Conv. (%)	Time (h) ^b	2b:3b ^c
1	EtOH	50	2	>99:1
2	Pyridine	>99	6	99:1
3	DMSO	>99	4.5	99:1
4	DCE ^d	>99	4	85:15
5	CH ₃ CN	>99	3	99:1
6	AcOEt	>99	0.7	99:1
7	Toluene	>99	0.7	>99:1

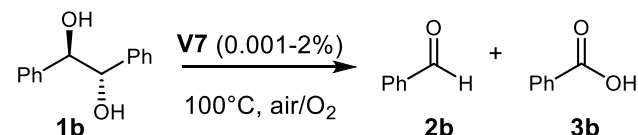
^aReaction conditions: [1b]₀=0.05 M, **V7** (2%), 80 °C. ^bTime required for complete substrate conversion. ^cDetermined by quantitative HPLC, naphthalene as internal standard. ^dDCE = 1,2-dichloroethane

As far as the solvent is concerned, besides ethanol, all solvents examined gave complete conversions with 2% catalyst loading (1 mM). Best solvents are toluene and ethyl acetate: in both cases fast and exclusive formation of benzaldehyde was obtained in only 40 min (Table 2, entries 6 and 7). As far as temperature is concerned, increasing reaction temperature to 100°C

accelerates the reaction (conversion into products in 20 min instead of 40 min, Table 2, entry 7 vs Table 3, entry 1) without affecting catalyst stability and the selectivity of the reaction.

Under the same conditions catalyst loading could be decreased down to 0,1% (Table 3, entry 2). However, at higher substrate concentrations ([1b]₀=0.5M) at 0.2% catalyst loading only 56% conversion of the substrate was observed (Figure 2A ▲).

Table 3. Oxidative cleavage of mesohydrobenzoin (**1b**) (0.5 M) catalyzed by **V7** (2-0.001%) in toluene at 100°C in air or O₂. Catalyst loading.



#	V7 (%)	Time (h) ^b	Conv. (%) ^{b,c}	2b:3b	TONs	TOFs, (h ⁻¹)
Air, (1 atm, balloon) [1b]₀=0.05 M						
1	2	0.3	>99	>99:1	50	200
2	0.1	2.5	>99	99:1	1000	650

^aTime required for complete substrate conversion. ^bDetermined by quantitative HPLC, naphthalene as internal standard. ^cChemical yields (2b+3b) > 99%.

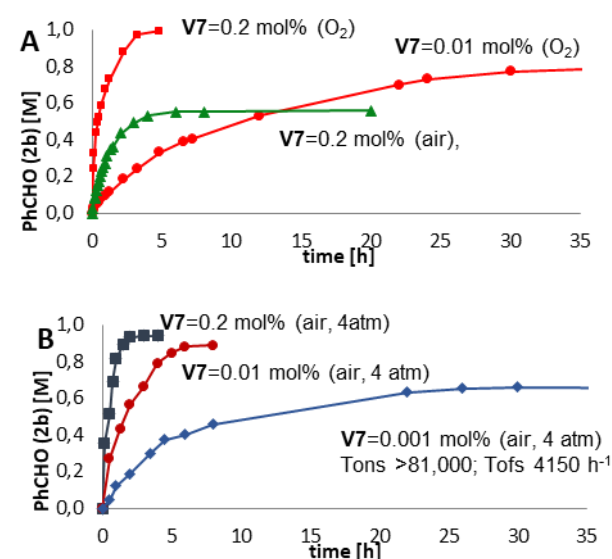


Figure 2. Reaction profiles for benzaldehyde **2b** formation for the oxidation of [1b]₀ = 0.5M in toluene, 100°C catalyzed by **V7**: **A**: reaction in air: ▲, **V7**=0.2 mol%; (TONs 280, Tofs 60 h⁻¹) reaction in O₂ (balloon) ■, **V7**=0.2 mol%; reaction in O₂ (balloon) ●, **V7**=0.01 mol%; **B**: reaction in air (4 atm), semi-continuous reactor: ■, **V7**=0.2 mol%, ●, **V7**=0.01 mol%, ◆, **V7**=0.001 mol%. Uncatalyzed process gave negligible substrate conversions (<6% after 48 h).

In order to improve the performance of the systems and determine if the lower conversion observed at high substrate concentration could originate from rapid oxygen depletion in the reaction mixture, the reactions were carried out under an oxygen atmosphere. Under

these new conditions the reaction with 0.2 % loading was complete in 5 hours, affording exclusively and quantitatively benzaldehyde. (Figure 2A ■). With 0.01% loading (Figure 2A ●) selective 82% conversion of **2b** into benzaldehyde could be still obtained. A further improvement in catalytic performance was obtained when working under higher pressure. As oxygen/toluene mixtures are potentially explosive at high pressure,^[30] the reactions were carried out under air using a semi-continuous stirred glass autoclave reactor at an operating air pressure of 4 atm with a flow rate of 150 mL/min.¹⁹ The reactions have been carried out in a 100 mL on a 25 mmol scale, using 0.2, 0.01 and 0.001% catalyst loading (Figure 2B). All the reactions gave a much faster and complete substrate conversions. Under these conditions some over-oxidation to benzoic acid **3b** was observed (5-18%). The reaction at 0.01 % catalyst loading gave, in only 8 h, complete reagent conversion with TOFs of up to 1660 h⁻¹ and TONs >9,700 (Figure 2B ●). Even in the presence of 10 ppm of catalyst (Figure 2B ◆) **1b** was completely converted in 26 h yielding benzaldehyde/benzoic acid (**2b**:**3b**=83:17) in 81% yields with TOFs= 4150 h⁻¹ and TONS> 81,000.^[31] In all reaction conditions the uncatalyzed reaction is negligible.

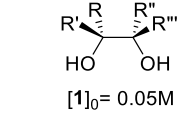
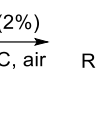
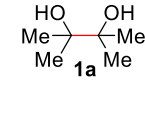
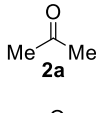
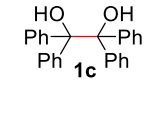
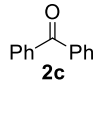
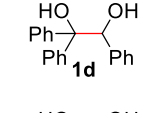
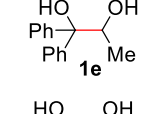
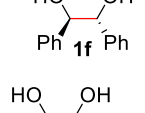
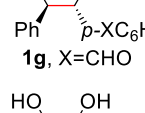
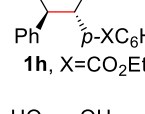
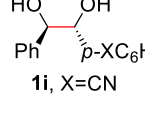
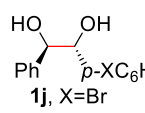
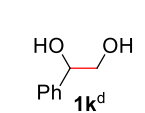
The scope of the substrate was explored with a series of glycols: benzylic and aliphatic, cyclic and linear, with tertiary, secondary and even primary alcoholic functions (Tables 4-6 and Table 2S in SI). The most reactive diols (**1a-k**) could be efficiently transformed at low concentrations (0.05M) under air at 80°C with 2% of **V7** (Table 4), while the less reactive ones (cyclic, aliphatic secondary and primary ones) require harsher reaction conditions (oxygen atmosphere, 100°C and higher catalyst loadings) (Tables 5 and 6).

The reactions were carried out on 0.5-0.25 mmol scale (10 ml), monitored by quantitative methods (HPLC or ¹H NMR), and the products were isolated via chromatography/distillation. The best results for each substrate are reported in Tables 4-6. With tertiary diols **1a**, **1c-f** (2% catalyst, 80°C), quantitative transformation into the corresponding ketones (acetone or benzophenone) was obtained (Table 4). Due to their volatility, acetone and acetaldehyde were not isolated. Secondary benzyl derivatives, **1b**, **1f-k**, gave the corresponding aromatic aldehydes quantitatively as the only products. Interestingly, non-symmetric *p*-substituted *dl*-hydrobenzoin derivatives **1f-j** gave, in a 1:1 ratio, benzaldehyde and respectively the *p*-substituted benzaldehydes, without any further over-oxidation/decomposition. For **1b** the reaction has been also carried out on larger scale (2.5 mmol) and **2b** was isolated in 85% yield. 1-Phenyl-1,2-ethandiol (**1k**), bearing a primary alcoholic function, was converted quantitatively into **2b**.

The catalytic system was also effective with more challenging, less reactive secondary aliphatic cyclic diols **1m** and **1n** (Table 5). *Trans* and *cis*-cyclopentan-1,2-diols (**1m** and **1n**) afforded quantitatively glutaraldehyde at 100°C using 10 mol% of **V7**. *trans*-

1m requires 2h for reaction completeness while *cis*-**1n** was converted quantitatively in only 40 min.

Table 4. Oxidative cleavage of linear diols **1a-k** (0.05M) catalyzed by **V7** (2%), toluene, air at 80°C. Scope of the substrate.

Substrate	Time (h)	Products	Yields (%) ^{a,b,c}
	1		98 ^b
	0.7		>99 ^a (90)
	4.0		98 ^a (82)
	0.3	2b + 2c	99 ^a (2b =72, 2c =88)
	0.6	2c	99 ^a (96)
	0.5	2b	>99 ^a (92)
	0.3	2b + <i>p</i> -XC ₆ H ₄ CHO 2g , X=CHO	99 ^a (2b =81, 2g =87)
	0.3	2b + <i>p</i> -XC ₆ H ₄ CHO 2h , X=CO ₂ Et	99 ^a (2b =87, 2h =90)
	0.3	2b + <i>p</i> -XC ₆ H ₄ CHO 2i , X=CN	99 ^a (2b =75, 2i =84)
	0.3	2b + <i>p</i> -XC ₆ H ₄ CHO 2j , X=Br	99 ^a (2b =76, 2j =85)
	4.0	2b	>99 ^a (85)

^a)Yield determined by HPLC using naphthalene as internal standard; ^b)Yield determined by ¹H NMR using 1,3,5-trimethoxybenzene as internal standard. ^c)Yields of isolated products in parenthesis. ^d)Reaction carried at 100°C and with O₂

Under more concentrated conditions, (0.25 M, O₂, **V7** (2%)) only the more reactive *cis*-**1n** could be transformed quantitatively and selectively into product, while **1m** gave less than 20% conversion (Table 2S). Bicyclic, more strained, *cis*-derivatives **1o** and **1p** gave, in less than one hour, complete and clean conversion into the corresponding cyclic products: (1*R**,3*S**)-1,2,2-trimethylcyclopentane-1,3-dicarbaldehyde (**2o**) and [(1*S*,3*S*)-3-acetyl-2,2-dimethylcyclobutyl]-acetaldehyde (**2p**) (table 5).

Table 5. Oxidative cleavage of cyclic diols **1l-1p** (0.05-0.25M) catalyzed by **V7** in toluene, air/O₂. Scope of the substrate.

1 ^a	[1] ₀ (air/O ₂)	V7 (%)	Time (h)	2	Yields (%) ^{b,c}
	0.05M (air)	10	4.0		50 (46)
	0.05M (air)	10	2.0		98 (72)
	0.05M (air)	10	0.7		95 (70)
	0.25M (O ₂)	2	0.7		95 (70)
	0.25M (O ₂)	2	0.5		99 (46)
	0.25M (O ₂)	2	1.5		98 (72)

^aReaction carried out at 80°C ^bYield determined by ¹H NMR using 1,3,5-trimethoxybenzene as internal standard. ^cYields of isolated products (in parenthesis).

Noticeably, catalyst **V7** was effective in the carbon-carbon cleavage of both internal and terminal linear aliphatic diols (Table 6). With linear, aliphatic diols **1q-1s** the catalytic oxidation gave an unprecedented and effective C-C bond cleavage, affording the corresponding linear aldehydes in yields up to 99% with catalyst loading down to 2%. At low catalyst loadings quantitative transformation of the substrate into products was hampered by the concomitant *in-situ* formation of acetals **4-7**, deriving from the condensation of the starting diols and the aldehyde

products. Taking this into account, the overall yield in aldehydes **2q-s** is given considering also the amount of aldehyde that has been transformed into the acetals **4-7** (Table 6, last column).^[32] The *in situ* acetal formation, observed also by others for similar reactions,^{13a,18} is favored by higher substrate concentrations (Table 6, entries 3, 6, 9) and longer reaction times (Table 6, entries 2, 5, 8).

Internal diol **1q**, (Table 6, entries 1, 2) gave hexanal **2q**, acetaldehyde and the corresponding acetals: 4-methyl-2,5-dipentyl-1,3-dioxolane (**4**) and 2,4-dimethyl-5-pentyl-1,3-dioxolane (**5**). Reaction carried out with 10% of **V7** (Table 6, entry 1) gave complete substrate consumption in 3 h with a 92% yield in **2q**, 80% after purification.

Table 6. Oxidative cleavage of diols **1q-1s** (0.05-0.25M) catalyzed by **V7** in toluene, air/O₂. Scope of the substrate.

#	[1] ₀ (M)	V7 (mol%)	Time (h)	Prod. ^a	Yield, (%) ^{b,c}
1q					
2q: 4: 5					
1	0.05	Air	10	3	91:5:4 92(80)
2	0.25	O ₂	2	7	60:29:11 72
1r					
2r:6a:6b					
3	0.05	O ₂	10	0.5	96:4:0 96(86)
4	0.25	O ₂	2	8	70:26:4 77
1s					
2s:7a:7b					
5	0.05	O ₂	10	0.5	99:1:0 99(96)
6	0.25	O ₂	2	8	60:33:7 71

^aDetermined via ¹H NMR/quantitative GC analysis of the reaction crude, 1,3,5-trimethoxybenzene as internal standard. ^b Yields considering aldehyde **2** + acetals.

^cYields of isolated products (in parenthesis).

At lower catalyst loadings (2%) the reaction gave 72% yield in **2q** together with the formation of acetals **4** and **5** (30%). (Table 5, entry 1,2). The reaction proceeds even more effectively with terminal diols. Reaction of hexan-1,2-diol (**1r**) and dedecanal-1,2-diol (**1s**) (Table 6, entries 3 and 5 respectively), under O₂ atmosphere, gave the longer chain aldehydes, pentanal (**2r**) and undecanal (**2s**), in yields of up to 99% in only 30 min (86 and 96%, respectively, after chromatography). The formation of acetals **6** and **7**, as a mixture of *cis/trans* diastereoisomers, was also observed, especially when 2% of catalyst and higher substrate concentration were used (Table 5, entries 4 and 6). In the reaction mixture we detected only the acetals deriving from the condensation of the longer chain aldehydes (**2r**, **2s**) with the reacting diols, no acetals originating from formaldehyde were observed. The catalytic activity of commercially available **VO(acac)₂**

was also tested, using the optimized reaction conditions ($[\text{sub}]_0 = 0.25 \text{ M}$, 2 mol% catalyst, toluene, O_2 (balloon), 100°C) with three aliphatic 1,2-diols: *cis*-1,2-cyclopentane (**1n**), *exo,exo*-2,3-camphanediol (**1o**) and hexan-1,2-diol (**1r**) (Table 2S, SI). In all cases no significant substrate conversion was observed for **1n** and **1o** (1 h) and for **1r** (8 h) (see for comparison Tables 4 and 5). Only after 24 h some substrate conversion was detected (10-60%, Table 2S, SI), but complex reaction mixtures with only traces of the desired products were obtained.

The chemoselectivity of the reaction was also explored. When looking at the scope of substrate we highlighted the inertness of functional groups like formyl, bromo, cyano, or ethyl-ester (**1g**, **h**, **i**, **j**). We also performed a series of reactions with different substrates like benzylic alcohol, thioanisole, dioctyl and diisopropylamine, styrene and cycloctene [$[\text{substrate}] = 0.05 \text{ M}$, toluene, 100°C , **V7** (10 mol %)]. In all cases neither substrate conversion nor the formation of oxidation products after 48 h was detected. Noticeably, no catalyst degradation was observed during the reaction time.

The stability of catalyst **V7** under turn-over conditions has been monitored by NMR (Figure 3 and Figure 1S, SI) and ESI-MS experiments (Figure 4 and Figures 2S and 3S, SI).

Vanadium complexes with tripodal ligands like amino triphenolates are known to undergo temperature dependent structural trigonal-bipyramidal/octahedral equilibria in solution upon coordination of monodentate Lewis bases (*e.g.* H_2O , sulfoxides).^[28c,33] Therefore, the experiment was carried out in acetonitrile, a coordinating solvent, in order to have a single species in solution and thus a single set of ^1H and ^{51}V NMR signals for **V7**. The reaction was performed directly in a NMR tube ($[\text{V7}]_0 = 5.0 \times 10^{-3} \text{ M}$, $[\text{1b}]_0 = 0.05 \text{ M}$; 80°C , air, CD_3CN). The course of the reaction was also monitored during time by ESI-MS. Complete conversion of **1b** into benzaldehyde was obtained in 60 min. No variation of the dark blue color of the solution was observed during the overall

process. The presence of catalyst **V7** could be clearly detected at the beginning and at the end of the reaction via all analytical techniques. In Figure 3 ^{51}V NMR spectra are reported where a singlet at -429.6 ppm can be detected at the beginning and at the end of the reaction (spectra A and C).

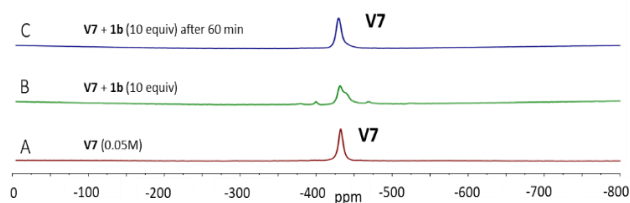


Figure 3. ^{51}V NMR spectra for the monitoring of the aerobic oxidative cleavage of **1b** catalyzed by **V7** (10%) in CD_3CN at 80°C under air (1 atm):. $[\text{V7}] = 5.0 \times 10^{-3} \text{ M}$, rt (A).; after **1b** addition: $[\text{V7}] = 5.0 \times 10^{-3} \text{ M} + 10 \text{ equiv. 1b}$, rt, (B); after 60 min at 80°C , (C).

As far as the ESI-MS analysis is concerned, the presence of complex **V7** as a chloride ($[\text{4d}\cdot\text{Cl}^-]$ $m/z = 637.8$) or a formate adduct ($[\text{4d}\cdot\text{HCO}_2^-]$, $m/z = 647.8$) at the beginning and at the end of the reaction was also clearly detected in negative mode (Figure 2S and 3S, SI).^[34] Noticeably, after **1b** addition (10 equiv) a peak assignable to the **V7**-deprotonated **1b** adduct is observable (Figure 4, $m/z = 817.9$, see also SI). The coordination of the diol to the vanadium complex is considered to be the initial step for the vanadium catalyzed C-C bond cleavage mechanism.^{20a} This substrate/catalyst adduct, after C-C bond cleavage of the diol, will produce a vanadium reduced species that is then re-oxidized back to **V7** by dioxygen. Therefore, we can conclude that in the presence of oxygen **V7** is an active catalyst for the oxidative C-C-bond cleavage of glycols affording, with very high chemoselectivity, the corresponding carbonyl derivatives can be easily regenerated.

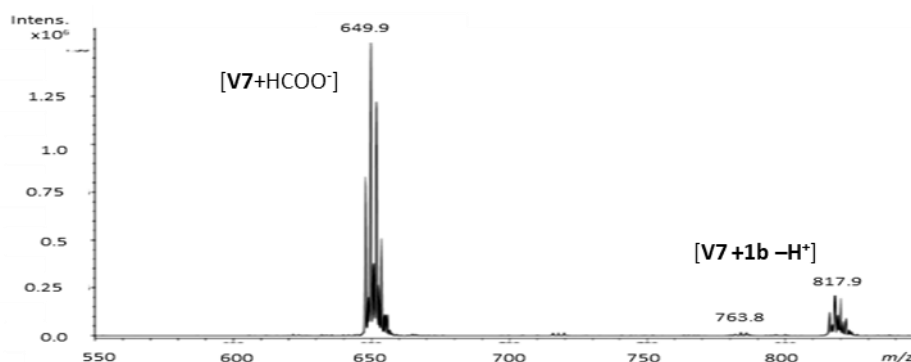


Figure 4. ESI-MS spectrum (negative mode) for **V7** ($5.0 \times 10^{-3} \text{ M}$) in CD_3CN after addition of $[\text{1b}] = 10 \text{ equiv.}$

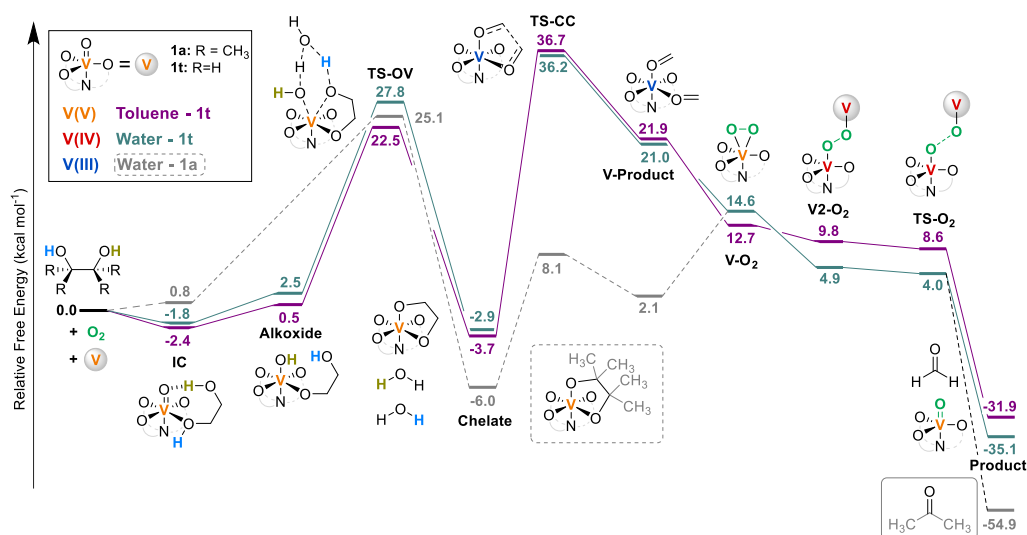


Figure 5. Gibbs free-energy profile ($\text{kcal}\cdot\text{mol}^{-1}$) of the oxidative carbon-carbon (C-C) cleavage of ethylene glycol (**1t**) in water (green line) and in toluene (purple line) and of pinacol (**1a**) in water (grey line), catalyzed by **V7** using molecular oxygen as oxidant.

V7 robustness for effective catalyst recovery and reuse will be exploited in the future by using biphasic systems (*i.e.* ionic liquids/organic solvent) or anchoring the catalyst to a solid support after ligand modifications. Both approaches are currently under investigation in our laboratories.

In order to gain some information concerning the reaction mechanism, a computational study using Density Functional Theory (DFT) of the oxidative carbon-carbon (C-C) cleavage of ethylene glycol (**1t**) catalyzed by **V7** in water and toluene was carried out. The reaction mechanism can be divided into three main steps: first, diol deprotonation and water formation; second, C-C bond cleavage and reduction of V^{V} to V^{III} ; and finally, recovery of the catalytic active species by O_2 mediated oxidation of V^{III} to V^{V} . The complete mechanism is shown in Figure 5 for ethylene glycol (**1t**) and pinacol (**1a**). The initial coordination of **1t** to the **V7** complex was studied in detail by exploring the different interaction modes of the acidic protons of **1t** with the oxygen atoms of the catalytic complex (in ligand and the *axial oxo* site). The most stable situation presents a hydrogen bond between one of the alcoholic protons of **1t** (yellow in Figure 5) and the oxo atom. The initial coordination intermediate (**IC**) presents a relative Gibbs free-energy of $-1.8 \text{ kcal}\cdot\text{mol}^{-1}$ in water ($-2.4 \text{ kcal}\cdot\text{mol}^{-1}$ in toluene). This first deprotonation step leads to an **Alkoxide** intermediate and formation of a hydroxo-group in the *axial* position of the catalyst.^[35]

After the **Alkoxide** formation, the second proton of the diol substrate (labeled blue in Figure 5) is transferred to the hydroxide group through **TS-OV** leading to the **Chelate** non-oxo intermediate ($-2.9/-3.7 \text{ kcal}\cdot\text{mol}^{-1}$) and realizing a water molecule. The relative Gibbs free-energy barrier of this process, computed from **IC** as the most stable intermediate

previous to **TS-OV**, is $27.8 \text{ kcal}\cdot\text{mol}^{-1}$ in water, and $24.9 \text{ kcal}\cdot\text{mol}^{-1}$ in toluene. Non-oxido V^{V} complexes are rare but the natural product Amavidine^[36] is an example and other examples, especially for systems bearing multidentate ligands, have been reported in the literature.^[37]

The C-C bond cleavage takes place in a two-fold, one-electron reduction step, and the metal complex V^{V} gets formally reduced to V^{III} with the oxidation of the two alkoxide groups to carbonyl moieties, thus breaking the C-C bond. The **TS-CC** is a V^{III} complex (triplet state) and presents an associated relative Gibbs free energy of 36.2 (water) or 36.7 (toluene) $\text{kcal}\cdot\text{mol}^{-1}$, constituting a relative barrier of 39.1 (water) or 40.4 (toluene) $\text{kcal}\cdot\text{mol}^{-1}$. The obtained intermediate (**V-Product**) is less energetically stable than the intermediates presented previously (21.0 (water) 21.9 (toluene) $\text{kcal}\cdot\text{mol}^{-1}$), which indicates that the reaction proceeds rapidly to the reoxidation of the catalyst to V^{V} just after the C-C cleavage step.^[38]

The reoxidation from V^{III} to V^{V} takes place through the reaction of one dioxygen molecule with two **V-Product** intermediates. This two-step process occurs through a peroxy intermediate (**V-O₂**), which is a singlet state species and is located energetically between **V-Product** and **V₂-O₂** intermediates. The singlet state of **V-O₂** complex is best described as a V^{V} -peroxy species, while its triplet state (lying $15 \text{ kcal}\cdot\text{mol}^{-1}$ above) is a V^{IV} -superoxo. After this peroxovanadate is formed an extra V^{III} entity is required to break the O-O bond via a bimetallic intermediate (**V₂-O₂**) formed by assembling one **V-O₂** complex and one V^{III} , which is much more stable than the previous intermediates ($4.9 \text{ kcal}\cdot\text{mol}^{-1}$). The transition state (**TS-O₂**) is slightly more stable in free energy than the intermediate because of entropy loss. It is worth mentioning that **V₂-O₂** and **TS-O₂** display

triplet state character. The corresponding singlet configuration of the transition state **TS-O₂** is less stable than the triplet by only 3.5 kcal·mol⁻¹. Therefore, the reoxidation of the vanadium complex and recovery of the catalyst, although spin-forbidden, is a very fast process that leads to the initial catalyst **V7**.

The rapid and spontaneous O₂ oxidation of V^{III} aminotriphenolates (R=R'=Me, *t*-Bu), prepared from VCl₃(THF)₃ to the corresponding V^V oxo-derivatives, was reported by Kol et al.^[28c] In the case of the hexachloro derivative, the V^{III} complex isolated was only partially characterized and the re-oxidation after exposition to O₂ did not afford **V7** but a blue paramagnetic blue species what was no characterized more in detail.

The computed Gibbs free-energy of the complete reaction is -35.1 (water) or -31.9 kcal·mol⁻¹ (toluene) therefore the studied reaction is an exergonic process. The global Gibbs free-energy barrier is high, but taking into account that the reaction is carried out at 80°-100°C, and that the aliphatic diols such as **1r** and **1s** are the least reactive diols, the proposed reaction mechanism is feasible. However, when we considered a more reactive substrate like pinacol **1a**, the more stable **Chelate** (-6 kcal mol⁻¹) can be transformed into the **V-product** via a **TS-CC** with a much lower relative Gibbs free energy (8.1 kcal·mol⁻¹), for a global relative barrier of only 25.1 kcal·mol⁻¹. The computed Gibbs free-energy of the reaction for **1a** oxidation is -54.9 kcal·mol⁻¹, almost double the free-energy determined for the reaction with **1t**.

Conclusion

In summary, we have reported that V(V) amino triphenolate complexes **V4-7** are effective aerobic catalysts for the oxidative C-C bond of vicinal diols. The most active catalyst **V7**, bearing six electron-withdrawing chloro substituents on the phenolate ligand units, works under relatively mild conditions (air/O₂, 80-100°C) in different solvents and is effective with a large variety of diols, including aliphatic, linear and cyclic ones, affording the corresponding aldehydes with very little over-oxidation to the corresponding acids and tolerate the presence of different functional groups. With more reactive substrates it can be used with loadings down to 0.001% reaching TONs of up to 81,000 and TOFs of up to 4150 h⁻¹. The high TONs and TOFs of the system and its ability to transform aliphatic internal and terminal glycols, means that it can be considered to be the most general and effective homogeneous catalytic system reported to date for the aerobic oxidative carbon-carbon cleavage of diols. Computational studies and preliminary experiments suggest a pre-association of the substrate to the metal center followed by a two-electron oxidation mechanism, yielding a reduced V^{III} metal complex and the carbonyl derivatives. Fast re-oxidation by O₂ regenerates **V7** closing the catalytic cycle.

The reactivity of **V4-V7** with α -hydroxy ethers (lignin models) and lignin samples is under investigation, as well as further studies for the elucidation of the reaction mechanism and the characterization of the species involved in the process.

Experimental Section

Catalytic aerobic oxidation of meso-hydrobenzoin (1b) for catalyst, solvents, catalyst loading and solvent screening, (Tables 1-3). In a 2 ml volumetric flask, *meso*-hydrobenzoin **1b** (1.0-0.1 mmol), vanadium catalyst and naphthalene as internal standard were added in a 1 ml solution of the solvent of choice. The solution was made up to a 2.0 ml volume and transferred into a 20 mL reactor equipped with a stirring bar, condenser, in air or oxygen atmosphere (balloon). The reactor was heated (silicon oil bath with a temperature control) under magnetic stirring to the desired temperature (80° or 100°C). The reaction course was monitored *via* quantitative HPLC analysis. All compounds were identified by comparison of their retention time with pure standards. **WARNING: oxygen-toluene mixture flammability range should be taken into account when performing the reactions at high pressure.**

Aerobic oxidative carbon-carbon bond cleavage of diols 1a-s. Scope of the reaction (Figure 3). In a 10 ml volumetric flask, substrate (**1a-s**) (0.5 or 2.5 mmol), **V7** (2 or 10 mol %) were added in 5 ml of toluene. The solution was made up to 10 ml volume and transferred into a 20 mL reactor, equipped with a stirring bar, condenser under air or oxygen atmosphere (balloon). After heating under stirring to 80°C or 100°C, the reaction course was monitored by ¹H NMR analysis or TLC. After complete substrate conversion, the reaction mixtures were purified over a silica gel column to remove the catalyst and impurities. More volatile products were separated by distillation. The results obtained under different reaction conditions are reported in Tables 4, 5, 6 and 2S (see SI for details).

Computational studies. All geometries were fully optimized and later characterized by vibrational frequencies using a DFT method by employing the ADF program (Scientific Computing and Modelling ADF-2016, <http://www.scm.com>). The Perdew-Burke-Ernzerhof gradient-corrected exchange and correlation functionals (PBE),^[39] including the Grimme (PBE-D3) dispersion parameters,^[40] were used in the calculations. The ZORA scalar relativistic Hamiltonian was employed,^[41] with a TZ2P basis set for all atoms.^[42] The geometry optimizations and vibrational frequencies were performed using the *VeryGood* numerical integration (BeckeGrid)^[43] and density fitting (ZlmFit) as implemented in ADF. The COSMO solvation model implemented in ADF has been used in all calculation using water and toluene as solvents.^[44] All open-shell structures have been computed in the different combinations of multiplicity in order to determine the most stable configuration. A data set collection of computational results is available in the ioChem-BD repository,^[45] and can be accessed via <https://doi.org/10.19061/iochem-bd-1-53>.

Experimental Details

Acknowledgements

This research was supported by the Università di Padova (CPDA153122, BIRD 2016, GRIC1410VJ, E. A. fellowship, and Progetto Attrezzature Scientifiche Finalizzate alla Ricerca 2014) and MIUR (Progetto Competitivo CMPT148505). We thank Fondazione CARIPARO, Progetto Dottorato Studenti Stranieri (W. D. fellowship). The authors acknowledge the Spanish Ministerio de Economía y Competitividad (MINECO) through

project CTQ2014-52824-R and the Severo Ochoa Excellence Accreditation 2014–2018 (SEV-2013-0319), and the AGAUR of Generalitat de Catalunya through project 2014-SGR-409, and through the CERCA Programme for financial support. GL also thanks the ULB (Chaire internationale) and the FNRS-Belgium (Missions scientifiques 2017–2018) for funds made available for a sabbatical leave. The project has been carried out in the frame of COST Actions CM1205 CARISMA, Catalytic Routines for Small Molecules Activation, and FP1306 Valorization of Lignocellulose biomass side streams for sustainable production of chemicals, materials & fuels using low environmental impact technologies (W.D. STSM).

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Adv. Synth. Catal. **Year**, *Volume*, Page – Page

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