

Vanadium Catalyst in Micelles: Towards a Greener Aerobic Oxidative Cleavage of Vicinal Diols in Water

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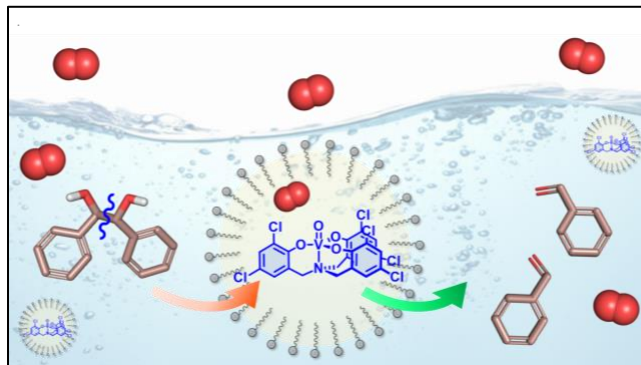
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TOC/Abstract Graphic



Synopsis

The catalytic aerobic oxidative cleavage of vicinal diols can be achieved in water using a vanadium aminotriphenolate complex incorporated in a recyclable micellar medium.

Abstract

Aqueous micellar media offer an alternative to organic solvents for the development of safe and environmentally benign synthesis. A vanadium aminotriphenolate complex, known to be an effective catalyst for the aerobic oxidative C-C cleavage of vicinal diols in organic solvents, was incorporated in zwitterionic dodecyl phosphocholine (DPC) and in mixed TPGS-750-M:DPC micelles. It efficiently performed affording the corresponding carbonyl derivatives with no overoxidation, with catalyst loading down to 0.2 mol% and reaching TONs up to 500. The mixed micelles, which combine the enhanced stability conferred by zwitterionic DPC and the exceptional extraction properties of non-ionic TPGS-750-M, could be recycled and full conversion achieved upon reloading with catalyst and substrate. The study of the correlation between the reactivity of different substrates and their local concentration in the micellar core, derived from DOSY experiments, highlights that, while lipophilicity is important, the ease with which the substrate can access the catalyst, and therefore the location of the catalyst in the micellar phase, must also be considered when trying to rationalize reactivity in micelles.

Introduction

Water is a sustainable, eco-friendly and safe (non-toxic, non-flammable, non-volatile) solvent and interest in using it as a solvent in chemical processes has been growing steadily over the last years. Despite the need to treat industrial wastewater prior to discharge in nature, water can considerably decrease the environmental impact of industrial processes and simultaneously ensure operator safety.¹⁻⁶ Many catalysts and substrates are however not soluble or stable in water and the use of aqueous micellar systems is a simple and yet very effective strategy to transfer organic reactions into water.⁷⁻⁹ Micelles are not only easy to prepare but also easy to handle, are stable for

weeks and can adapt to different experimental conditions.¹⁰ High local concentration is furthermore reported to be a key factor favoring the rate of reactions in micelles.^{11–13}

Various commercially available amphiphilic surfactants (Chart 1) that self-aggregate into micelles have already been used as nanoreactors to transfer a large variety of transition metal catalyzed reactions into water. Early publications include the micellar incorporation of palladium catalysts to perform Heck,¹⁴ Suzuki-Miyaura¹⁵ and Sonogashira¹⁶ coupling reactions in water. The scope of reactions has increased significantly in the last few years with recent reviews discussing the use of Pd, Ru, Cu, Ni, Fe and Au complexes to perform, among others, hydrogenation, phosphonation, amination, amidation, nitro reduction, nucleophilic aromatic substitution, C-H functionalization, and click-chemistry reactions.^{17–22} Micellar conditions are reported to offer advantages in terms of yield, waste generation, operational ease, catalyst loading, and safety over the use of organic solvents. The commercially available designer nonionic surfactants TPGS-750-M and PS-750-M are attracting particular attention as they can be recovered and recycled.^{7,22–28} They have proven to be versatile, in terms of both type of transformation and nature of substrate. Novartis Pharma AG has developed a multi-step industrial kilogram synthesis of an active pharmaceutical ingredient using TPGS-750-M,²⁹ and has more recently reported on a general protocol for a kilogram scale Suzuki–Miyaura cross-coupling using the same medium.^{30,31}

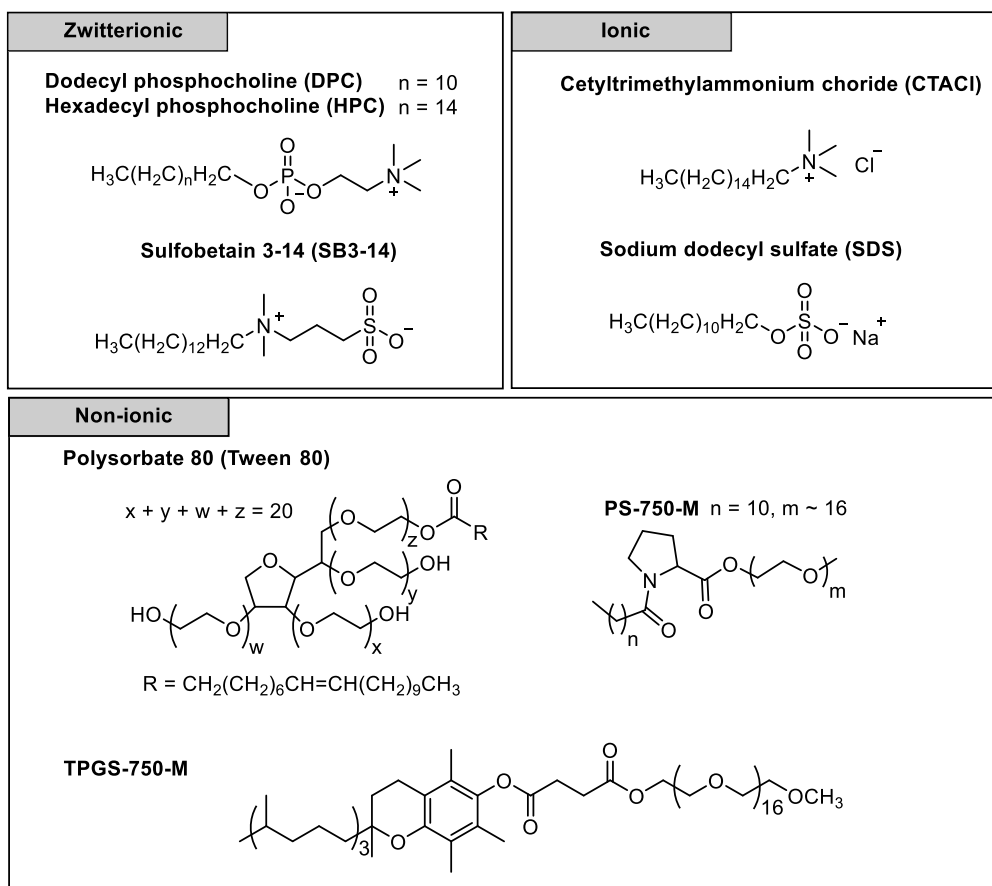
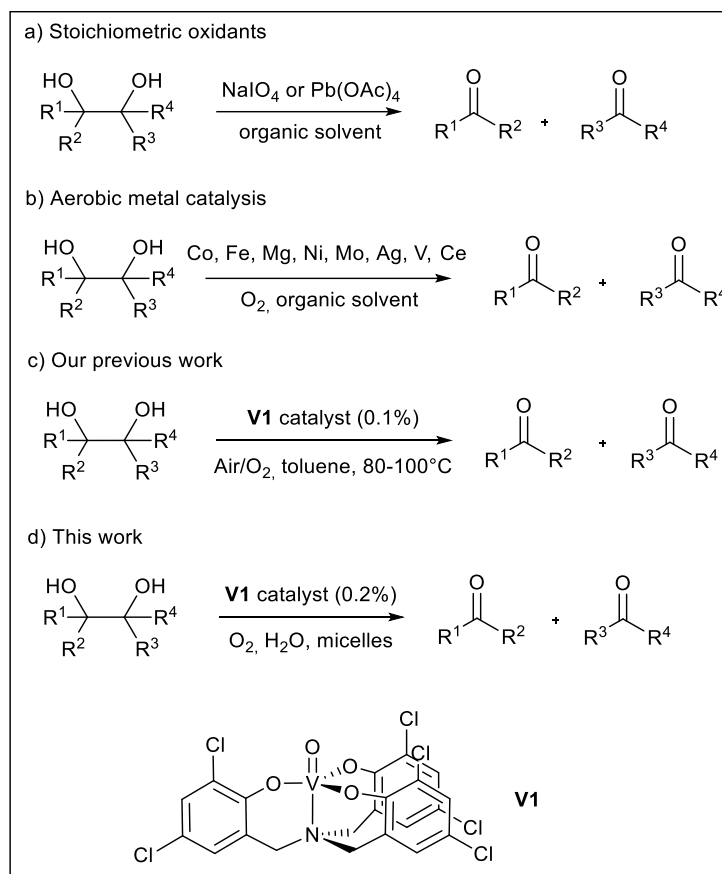


Chart 1. Commercially available surfactants used in this study.

As far as oxidation reactions in micellar media are concerned, most reported protocols use either stoichiometric amounts of transition metals³²⁻³⁴ or primary oxidants such as hydrogen peroxide (H_2O_2), tert-butyl hydroperoxide (TBHP)^{35,36} or sodium hypochlorite (NaOCl)³⁷ to run reactions such as the oxidation of alkenes,³⁸⁻⁴⁰ phenols⁴¹ or organosulfur compounds,⁴²⁻⁴⁴ and Baeyer Villiger oxidations.^{45,46} Aerobic oxidations have interestingly enough not been the object of many studies, despite the fact that air and O_2 are cheap and clean oxidants and exhibit high solubility inside the hydrophobic core of micelles, thus increasing local oxygen concentration.⁴⁷⁻⁵⁰ Reported aerobic reactions are the Cu/TEMPO catalyzed oxidation of benzylic and allylic alcohols,⁵¹⁻⁵⁴ the oxosulfonylation of aryl alkynes under acidic conditions,⁵⁵ and the NaI-catalyzed oxidative sulfonylation of ketones. Gold nanoclusters trapped in the PEG chains of non-ionic cross-linked

micelles have also been used to oxidize α -hydroxy ketones under oxygen to form the corresponding bis-ketone product.⁵⁶

This work focuses on the aerobic oxidative cleavage of vicinal diols in micellar media. This important synthetic transformation has historically been performed in organic solvents with stoichiometric amounts of oxidants such as periodates⁵⁷ or lead tetra-acetate (Scheme 1a).⁵⁸ Transition metal catalyzed aerobic oxidations (Scheme 1b) have also been reported using cobalt,^{59,60} iron,^{61,62} manganese,^{63–65} nickel,⁶⁶ molybdenum,⁶⁷ silver,^{68,69} cerium⁷⁰ or vanadium complexes.^{71–73} Very recently, the aerobic oxidative C-C bond cleavage of vicinal diols in CTABr micellar medium has been reported, using a heterogeneous graphitic carbon nitride photocatalyst.⁷⁴ Herein, we report the use of a vanadium aminotriphenolate complex (**V1**) incorporated in micelles to cleave vicinal diols in water under aerobic conditions (Scheme 1d). Vanadium aminotriphenolate complexes have already been used in organic solvents for the aerobic carbon-carbon bond cleavage of a broad scope of vicinal diols (cyclic or linear glycols with aromatic or aliphatic substituents) affording water as sole by-product (Scheme 1c).^{71,75,76} These complexes are highly modular and the best performances were obtained with **V1**, which bears six electron withdrawing chloro groups on the ortho and para-position of the phenolates.⁷⁵



Scheme 1. Oxidative C-C bond cleavage of vicinal diols (a) using stoichiometric oxidants in organic solvents (b) metal catalyzed under aerobic conditions in organic solvents (c) vanadium catalyzed under aerobic conditions in toluene (d) this work: vanadium catalyzed under aerobic conditions in aqueous environment, and structure of vanadium aminotriphenolate complex (**V1**)

Results and discussion

Selection of surfactant and optimization of the reaction conditions

Catalyst **V1** is not soluble in water and its transfer into an aqueous environment was tested with micelles prepared from a series of different commercially available surfactants (see Chart 1 for structure and full name of surfactants). Quantitative incorporation ($[\text{V1}] = 1 \text{ mM}$) was observed with neutral and zwitterionic DPC (20 mM), HPC (20 mM), SB3-14 (20 mM), Tween 80 (20 mM), TPGS-750-M (2 wt%) and PS-750-M (3 wt%). The solutions exhibited the deep blue color characteristic of the complex in solution and 2D DOSY NMR experiments confirmed inclusion of

the catalyst in these micelles as the surfactant and the catalyst exhibit the same diffusion coefficients (SI-5).⁷⁷ In contrast, in anionic SDS micelles (20 mM), fast and complete demetallation occurred (loss of color), and in cationic CTACl micelles (50 mM) **V1** was poorly soluble. No changes were observed over time in the UV-Vis spectra of the catalyst incorporated in DPC and TPGS-750-M micelles, confirming the stability of the catalyst under these conditions (SI-6).

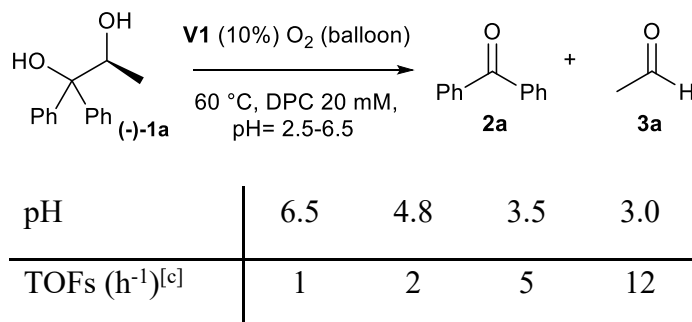
Using 1,1-diphenyl-1,2-propanediol (**1a**, 3.5 mM) as a benchmark substrate, the catalytic activity of catalyst **V1** (0.35 mM) was first tested in DPC solutions (20 mM in H₂O) at 60 °C under an O₂ atmosphere (balloon) (SI-7). Solutions were homogeneous and the reactions were monitored by quantitative HPLC (SI-8). At pH 6.5 complete conversion into benzophenone (**2a**) and acetaldehyde (**3a**) was observed in 9 hours, with no by-product formation (also confirmed by ¹H NMR - SI-9), while in the absence of catalyst or the absence of micelles (blank reactions) no reactivity was observed.

Confinement and high local concentrations are reported to be key factors favoring the rate of reaction in micelles.^{9,11–13} Contrary to the catalyst, which is fully incorporated with, on average, one molecule of **V1** per micelle (SI-5), the substrate partitions between the micellar core and the aqueous phase. Full conversion is nevertheless achieved as the micelles are “reloaded” when the substrate is consumed. The local concentration of the substrate in the core of a micelle could be derived quantitatively by DOSY NMR: when a species partitions between two environments (the aqueous and the micellar phases in this case), the measured diffusion coefficient is a weighted average of its diffusion coefficient in the two environments.⁷⁸ The diffusion coefficient of **1a** was determined in water and in the DPC solution at 60 °C and the fraction of **1a** incorporated in the micelles was determined to be 66 ± 6%, which corresponds to a local concentration of 475 ± 43 mM (SI-10). DPC forms small homogeneous micelles and using the Stokes-Einstein equation,⁷⁹

the hydrodynamic radius of the loaded micelles was derived and observed not to be significantly different from the hydrodynamic radius of the empty micelles (SI-10). With other types of surfactants, PS-750-M in particular, swelling has been observed by Dynamic Light Scattering (DLS) measurements following substrate loading.²⁴⁻²⁶ DLS however cannot not yield quantitative information on the local concentration in the micellar environment.

The reaction was also performed at different initial pH levels and a significant acceleration of the reaction course was observed with decreasing pH, obtaining complete conversions and quantitative yields in the products with no by-product formation (Table 1); the TOF (at 20% conversion) increased from 1 h⁻¹ (pH 6.5) to 13 h⁻¹ (pH 2.5) (SI-8). This is consistent with the reported proposed mechanism where proton transfer processes are involved in the coordination of the substrate to the vanadium metal center.⁷⁵ At 100 °C and pH 3 complete conversion was observed in 0.5 h, compared to 1.1 h at 60 °C (Table 2). Notably, despite the harsh conditions (high temperatures and low pH), the catalyst did not degrade over the course of the experiment. Its UV-vis spectrum in DPC did not change over time at pH 3 (SI-6). The stability of the catalyst under harsh conditions in organic solvents has also already been reported.⁸⁰⁻⁸²

Table 1. Effect of pH on reaction rates of aerobic oxidative C-C cleavage of substrate **1a** catalyzed by **V1** (10%) in DPC micelles.^{[a] [b]}



[a] Conditions: [**1a**]₀=3.5 mM, 10% **V1**, 20 mM DPC at 60 °C. Solutions acidified with 1M HCl.

[b] Conversion determined by quantitative HPLC, biphenyl as external standard. [c] determined at 20% conversion (5% error).

Scope of the C-C oxidative cleavage in DPC micelles

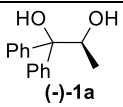

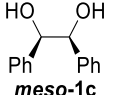

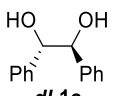
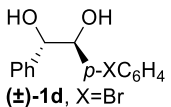
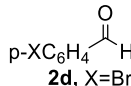
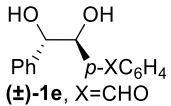
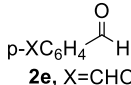
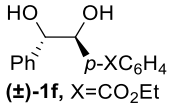
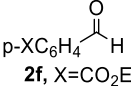
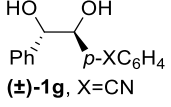
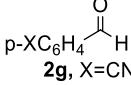
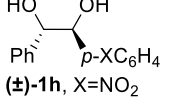
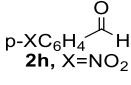
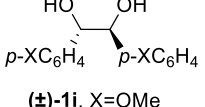
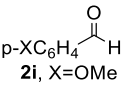
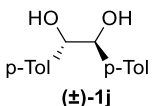
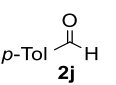
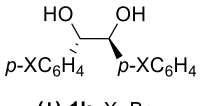
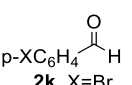
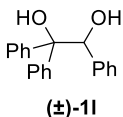
The substrate scope was explored at 100 °C and pH = 3 with a series of representative aryl 1,2-diols (Table 2). Quantitative conversions and yields, with no by-product formation, were observed with all the substrates containing at least two aromatic substituents (**1a-m**). Times required for complete conversion ranged considerably, with the shortest time (0.15 h) observed with the tri-1,1,2-phenylethane-1,2-diol **1l** and the longest with the tetra-1,1,2,2-phenyl-1,2-ethanediol **1m** (24 h). The reactions under micellar conditions were in all cases slower than in toluene, but to be noted so are the reactions in other organic solvents such as DMSO or ACN.⁷⁵ Similar reactivity trends are however observed in toluene and the micellar medium (SI-11), with **1m** (tetra-1,1,2,2-Ph) less reactive than **1b/1c** (di-1,2-Ph) and **1l** (tri-1,1,2-Ph).⁷⁵

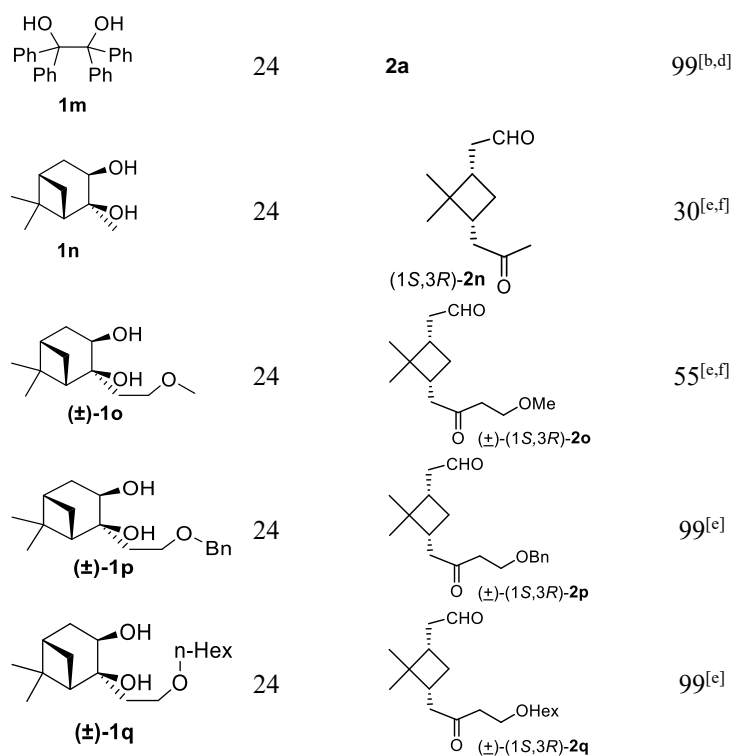
The 1,2-diphenyl-1,2-ethanediols bearing substituents (**1d-k**) reacted faster in the micellar medium than the unsubstituted dihydrobenzoin **1b** and **1c**, as was also observed with the reactions carried on in toluene.⁷⁵ The mono-Br **1d** and di-Br **1k** were the slowest to reach full conversion (3.25 and 5 h respectively), followed by the substrates with electron-donating (ED) groups (3 h for di-methyl **1i** and 1.25 h for di-methoxy **1j**). Reaction times for the substrates with the electron-withdrawing (EW) groups (**1e-h**) ranged between 0.25 and 1.25 h. No obvious correlation exists between the reactivity and nature of the substituents on the phenyl rings.

As far as unsubstituted dihydrobenzoin *meso*-**1b** and *dl*-**1c** are concerned, slightly slower reactivity was observed for the *meso* compared to *dl* diastereoisomer (5.5 h vs 5 h). This was also observed in toluene and is consistent with the reaction mechanism previously proposed on the basis of experimental evidence and DFT calculations:⁷⁵ the occurrence of a pre-equilibrium with coordination of the substrate to the vanadium center, formation of a substrate-metal chelate which affords the C-C bond cleavage with the synchronous formation of the carbonyl derivatives and the reduction of the V(V) to a V(III) species, which is then oxidized back to V(V) by O₂ with release

of water. In the chelate the vicinal phenyl substituents of the ethane group are partially eclipsed which results in an increased steric hindrance in the *meso*-**1b** where the phenyl groups are *cis*.

Table 2. Oxidative cleavage of vicinal diols using **V1** in DPC micelles at 100 °C^[a]

Substrate	Time (h)	Products	Yield 2 (a-q) (%)
 (-)-1a	0.5	 2a	99 ^[b,c]
 <i>meso</i> - 1c	5.5	 2b	99 ^[b]
 <i>dl</i> - 1c	5.0	2b	99 ^[b]
 (±)-1d , X=Br	3.25	2b +  2d , X=Br	99 ^[b]
 (±)-1e , X=CHO	0.25	2b +  2e , X=CHO	99 ^[b]
 (±)-1f , X=CO ₂ Et	0.5	2b +  2f , X=CO ₂ Et	99 ^[b]
 (±)-1g , X=CN	0.25	2b +  2g , X=CN	99 ^[b]
 (±)-1h , X=NO ₂	1.25	2b +  2h , X=NO ₂	99 ^[b]
 (±)-1i , X=OMe	1.25	 2i , X=OMe	99 ^[b]
 (±)-1j	3	 2j	99 ^[b]
 (±)-1k , X=Br	5	 2k , X=Br	99 ^[b,d]
 (±)-1l	0.15	2a + 2b	99 ^[b,d]



^[a] Conditions: 3.5 mM substrate, 10% **V1**, 20 mM DPC under O₂ atmosphere at pH 3 and 100 °C. Solutions acidified with 1M HCl; ^[b] conversions and chemical yields were determined by quantitative HPLC with biphenyl as external standard. ^[c] No conversion observed in the absence of **V1**. ^[d] Substrate partially soluble; colloidal solution; ^[e] conversion and chemical yields determined by ¹H NMR on the crude of the reaction; ^[f] conversion after 24h.

Preliminary reactivity studies in DPC micelles were also performed with substrates which are less reactive in toluene but are less hydrophobic than **1m** (ratio of carbon atoms to hydroxy groups, C/OH, of 13). Both with 1-phenyl-1,2-diol **1r** and with *cis*-1,2,3,4-tetrahydronaphatale-1,2-diol (C/OH ratios <5), no conversion was observed in the micellar medium even at long reaction times (24 h). In order to understand if the lack of observed reactivity could be due to the combination of an intrinsic low reactivity and the lack of availability of the substrate in the micellar core, a series of bicyclic camphane diol based-derivatives (**1o-1q**) with alkyl groups of increasing length (R=Me, Bn and n-Hex) were tested. The bicyclic aliphatic substrates **1o-1q** and camphane diol **1n** all afforded, with complete selectivity, the C-C bond cleavage products (**2n-2q**) but longer reaction times, compared to the linear derivatives **1a-1l** were however required (Table 2). Very

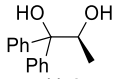
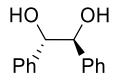
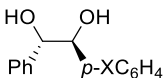
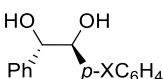
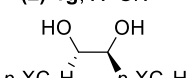
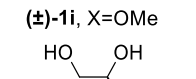
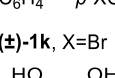
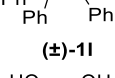
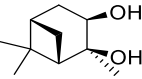
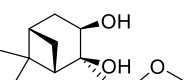
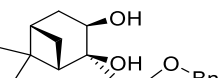
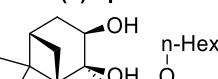
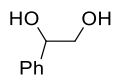
interestingly, the extension of the side arm of the ether function (**1o-1q**) significantly affected the conversion: derivatives **1p** and **1q**, bearing a benzyl and n-hexyl groups, gave quantitative conversions into the product while with **1o** (R=Me) and the camphane diol **1n**, only 55% and 30% conversion were respectively achieved. A clear reactivity trend based on the lipophilicity of the substrate is observed.

To be more quantitative, the concentration of the different substrates in the micellar core was derived from DOSY NMR experiments (SI-10). They are given in Table 3 where the reaction times are also reported. For the aliphatic cyclic diols, **1n** to **1q**, which have the same reactive group and only differ by the length of an aliphatic chain, a clear correlation exists between the reactivity and the degree of lipophilicity (higher local concentration) of the substrate. No correlation can however be made for substrates **1a** to **1m**. For example, **1a** and **1c**, which despite not having the same reactive group exhibit the same reactivity in toluene (SI-11), have very different times for complete conversion in micelles (0.5 h and 5 h respectively) but similar local concentrations.

The predicted LogP values for the substrates for which local concentrations were determined are also reported in Table 3. They have their limitations. While a trend is observed between the LogP and the local concentration for substrates with $\text{LogP} < 4$, the correlation ceases with the further increase in LogP, certainly due to the difficulty for these very hydrophobic compounds to transit via the aqueous phase to be incorporated in the micellar core.

Results suggest that, while lipophilicity is important for the reaction in micellar media, the ease with which the substrate can access the catalyst, and therefore the precise location of the substrate molecules and the catalyst in the micellar phase, must certainly also be considered when trying to rationalize reactivity. This has already been emphasized in the literature.^{9,11-13}

Table 3. Local concentration of substrates in DPC 20 mM and LogP vs reaction time to completion

Time (h)	Time to completion (h)	Local concentration (mM) ^[a]	LogP ^[b]
 (-)-1a	0.5	475 ± 43	2.85
 (-)-1c	5.0	440 ± 22	2.64
 (±)-1d, X=Br	3.25	688 ± 47	3.46
 (±)-1g, X=CN	0.25	410 ± 43	2.67
 (±)-1i, X=OMe	1.25	418 ± 29	2.83
 (±)-1k, X=Br	5	490 ± 30	4.29
 (±)-1l	0.15	103 ± 5	4.25
 1m	24	< 5	5.86
 1n	30% in 24h	187 ± 87	1.15
 (±)-1o	55% in 24h	267 ± 23	0.76
 (±)-1p	24	627 ± 36	2.5
 (±)-1q	24	Co-micelle ^[c]	2.84
 (±)-1r	No conversion	101 ± 36	0.20

^[a] Based on DOSY experiments performed at 60 °C. ^[b] Predictions by ChemDraw Pro 15. ^[c] This substrate was observed to form mixed-micelles with DPC surfactants.

Catalyst loading

The decrease of the catalyst loading for the reaction at pH = 3, both at 60 °C and 100 °C, was studied. The catalyst concentration was kept constant ($[V1]_0 = 0.35$ mM) and the concentration of substrate **1a** was increased from 3.5 up to 175 mM, reaching 0.2 mol% catalyst loading (Table 4). Under the more concentrated condition a colloidal solution was obtained due to substrate and product solubility issues (entries 2 and 5, Table 4). This however did not affect the course of the reaction and full conversion was observed in 12 h for the highest substrate concentration at 100 °C, corresponding to a TON of 500. As discussed in the introduction, aerobic C-C bond cleavage with homogeneous metal catalysts have been reported in the literature but all methods require high catalyst loadings (5-10%). Only the **V1** catalyzed process in toluene is known to work with much lower catalyst loadings (down to 0.01%).⁷⁵ It is thus rather remarkable that also in micellar medium complete conversions can be obtained using 0.2% catalyst loadings reaching 500 TONs. The reaction at 60 °C proceeds also to full conversion and quantitative yields at 20h. Product **2a** could be recovered in high yields (96%) by extraction with an organic solvent (EtOAc) after addition of brine to break the micelles.

Table 4. Scale up of the cleavage of vicinal diols with substrate **1a** using **V1** in micelles^[a]

[1a] (mM)	V1 (%)	T (°C)	Time (h)	Yield 2a (%) ^[b]	Isolated yield 2a (%) ^[c]
3.5	10	100	0.5	99	-
175	0.2	100	12	99	96
3.5	10	60	1.1	99	-
35	1	60	7	99	95
175	0.2	60	20	99	96

^[a]conditions: 20 mM DPC and pH 3 at 60 and 100 °C. Solutions acidified with 1M HCl.
^[b]chemical yields determined by quantitative HPLC with biphenyl as external standard. ^[c]isolated yield of **2a** after column chromatography.

As DPC micelles must be destroyed in order to recover the products (dilution below the cmc), recycling of the system was evaluated using TPGS-750-M micelles (2 wt%). The C-C bond oxidative cleavage of **1a** catalyzed by **V1** was attempted at pH 3 (3.5 mM substrate, 10% catalyst loading). Little or no conversion was observed at 30 °C (4%) and at 60 °C (0%). Contrary to what was observed in DPC, catalyst **V1** degraded very quickly, as confirmed by UV-Vis spectroscopy (SI-6), suggesting that TPGS-750-M does not sufficiently protect the catalyst under these conditions. The measured hydrodynamic radius for the TPGS-750-M micelles (18 nm, SI-5) is significantly larger than what would be expected for a single micelle. This is consistent with the theoretical predictions and the DLS and Cryo-TEM data reported in the literature, which describes TPGS-750-M as forming compartmentalized nanoparticles composed of 30-40 aggregated small micelles with a considerable amount of water in the PEG region.^{7,11} The catalyst is most probably located in the hydrated region, exposing it to undesirable interactions with water or HCl.⁸³ The use of TPGS-750-M was also hampered by the systems instability at high temperatures: a sharp increase in viscosity is observed at 45 °C (the gel point, GP) and phase separation occurs at 61.5 °C (the cloud point, CP) (SI-12).

The possibility to form mixed micelles of non-ionic TPGS-750-M and zwitterionic DPC was explored to combine the positive properties of both surfactants. It is known that the addition of suitable co-surfactants to non-ionic micelles can raise the CP by decreasing the hydrophobic interactions that drive phase separation.⁸⁴ In order to optimize the experimental conditions, TPGS-750-M:DPC micelles of different ratios were prepared and studied via DLS and UV-Vis experiments at varying temperatures (SI-12). With 80:20 TPGS-750-M:DPC the CP raised to 81 °C and the GP was completely suppressed.⁸⁵

The stability of the catalyst over time in 80:20 TPGS-750-M:DPC at pH 3 and 60 °C was confirmed by UV-Vis spectroscopy (SI-5). Reactions were consequently carried out under these

conditions with 175 mM substrate **1a** and **V1** (0.2 mol%). Full conversion and quantitative product formation were reached in 24 h (TLC and HPLC monitoring). The reaction products, which accumulate in the form of an oil at the bottom of the reaction vessel (Figure 1), were extracted with an organic solvent (diethyl ether or ethyl acetate). The organic solvent also extracts the catalyst, which can be removed by column chromatography on silica gel. Before the next cycle, the recycled micellar phase was heated at 70 °C for 5 minutes to evaporate the solvent. In the latter procedure we noted a better performance with diethyl ether which could be more easily removed from the aqueous media. Fresh catalyst was added together with the new load of substrate. The reaction was stopped after 24 h, extracted and the micellar phase recycled for a second time. Conversions and isolated yields (column chromatography) were found to be comparable over the three cycles (Figure 2). Extraction of the product out of the mixed micelles was found to be almost quantitative. These results prove that mixed 80:20 TPGS-750-M:DPC is a suitable reaction medium for the aerobic oxidative C-C-bond cleavage of vicinal diols and allows the successful recycling of the micellar phase “as is”.

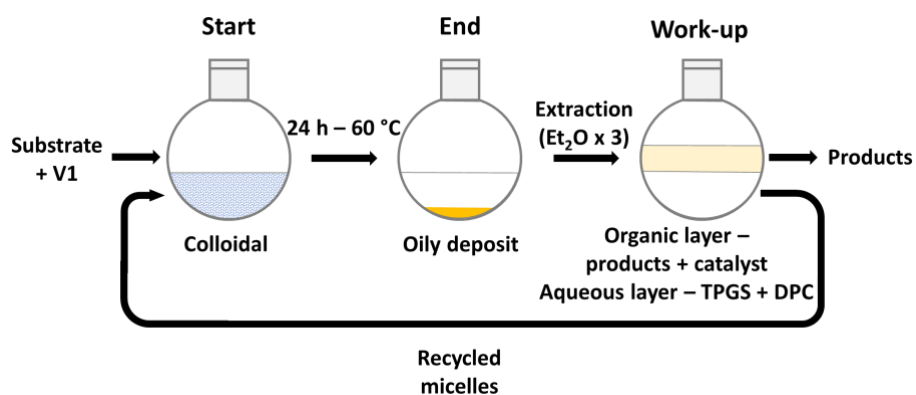


Figure 1. Procedure for the recycling of mixed micelles (SI-13).

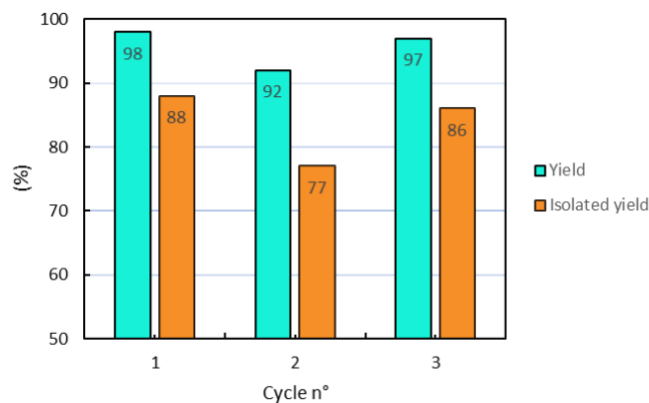


Figure 2. Recycling experiments for the aerobic oxidative C-C bond cleavage of **1a** (175 mM) catalyzed by **V1** (0.2 mol%) in 80:20 TPGS-750-M:DPC under O₂ at pH 3 and 60 °C. Chemical and isolated yields (after column chromatography) obtained for each cycle after 24 h of reaction.

Comparison of the **V1** aerobic oxidative cleavage in micelles, with the reaction using traditional stoichiometric reagents, such as NaIO₄, and organic solvents, underlines the sustainability aspects of the method. The reaction can be carried out in non-toxic and safer water instead of dichloromethane or aromatic solvents, forming water as the only by-product. The catalyst **V1** cannot be recycled, like for most homogeneous catalysts, but it can be used at very low loading (0.2%). Furthermore, the use of mixed TPGS-750-M:DPC allows the recovery of the surfactant. The combination of these advantages can be summarized in the two major metrics: the atom economy (AE, MW of the desired product/MW of all reactants) and the E-factor (ratio of amount of waste formed by unit of product) values.⁸⁶ Calculations on the standard procedure for the C-C bond cleavage of **1a** affords AE= 86.9%, in line with those obtained for aerobic catalytic procedures.⁸⁶ The simple E factor (sEF), recommended as a metric for early stage development processes, was also derived for the scaled-up process undertaken in DPC micelles (175 mM **1a**), taking into consideration that the surfactant and catalyst are not recovered but neglecting acetaldehyde as product (too volatile to be recovered in our procedure) (SI-14). The value of 14.8 is the range of the ones that are usually obtained in industrial processes for the synthesis of fine chemicals (E-factor 5-50).⁸⁶

Conclusions

In this study, we have shown that the vanadium aminotriphenolate complex **V1** is an effective catalyst for the aerobic oxidative C-C bond cleavage of vicinal diols in aqueous micellar systems. The hydrophobic catalyst was successfully incorporated and was stable and active, even at low pH and high temperatures, in zwitterionic DPC micelles and in mixed micelles formed from non-ionic TPGS-750-M and DPC.

In DPC micelles, at 100 °C **V1** is effective with a wide range of diols, with different electronic and steric characteristics. Catalyst loadings could be decreased down to 0.2 mol% reaching TONs up to 500. Furthermore the micellar medium could be recycled using a mixed DPC:TPGS-750-M (20:80) micellar medium. The micellar system was successfully recycled over 3 cycles, with 97-98% conversion maintained along the cycles after reloading of the catalyst and substrate. This successful recycling strategy is a partial answer to the issue of wastewater treatment.

The difference in reactivity for the different substrates was investigated but we could not fully rationalize the obtained results as the reactivity is a complex function of several parameters including steric consideration at the level of the catalyst-substrate complex. However, the reactivity observed in organic solvents is maintained and the catalytic system is effective and completely selective with a wide range of 1,2-diols, provided that the substrates are sufficiently lipophilic to partition into the micellar phase.

This work is a noteworthy contribution to the field of sustainable chemistry micellar catalysis as not only are the experiments run in water using oxygen as oxidant under much safer conditions, but the medium can be recycled, thus avoiding the generation of organic and aqueous waste. This work is also a contribution to a better understanding of the physico-chemical aspects of catalysis in surfactant-based aqueous micellar media.

Supporting Information

General procedures (instruments, samples preparation, monitoring protocols), ¹H characterization and synthesis protocols of **V1** and non-commercially available substrates, DOSY spectra, ¹H NMR spectra and UV-Vis spectra of micellar systems and further characterization of these systems; calculations of green metrics. This information is available free of charge.

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Author Contributions

KB and GL initiated the project. Experiments were undertaken by RC, WD, DC and FSA. Results were discussed among all authors. All authors contributed to the written work and have given their approval for the final version of the manuscript. ‡These authors contributed equally.

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