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Selectivity switch in the aerobic oxygenation of sulfides photocatalysed by visible-light-responsive decavanadate

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Abstract

Nanometre-sized metal oxides are promising species for the development of visible-light-responsive photocatalysts for the selective transformation of organic functional groups. In this article, we report that decavanadate ($[\text{V}_{10}\text{O}_{28}]^{6-}$, **V10**) behaved as an efficient visible-light-responsive photocatalyst in the product-selective oxygenation of sulfides achieved using O_2 (1 atm) as the green oxidant. In particular, we revealed that visible-light-responsive photocatalysis of **V10** showed remarkable activity for the oxygenation of structurally diverse sulfides to form the corresponding sulfones using O_2 in methyl ethyl ketone (MEK). Furthermore, by simply adding water to the reaction mixture, the product selectivity of sulfide oxygenation can be significantly switched toward the production of sulfoxides, without concomitant loss of **V10** photocatalytic activity. Based on experimental evidence, we inferred the following mechanistic steps for this photocatalytic system: the aerobic oxygenation of sulfides to form the corresponding sulfoxides initiated by a visible-light-induced photoredox reaction of **V10**. As for the formation of sulfones, MEK-derived peroxide species as the co-catalysts are probably involved in the oxygenation of sulfoxides to sulfones. The selectivity switch of the **V10**-photocatalysed reaction brought about by water addition is most likely achieved by suppressing the formation of MEK-derived peroxide species.

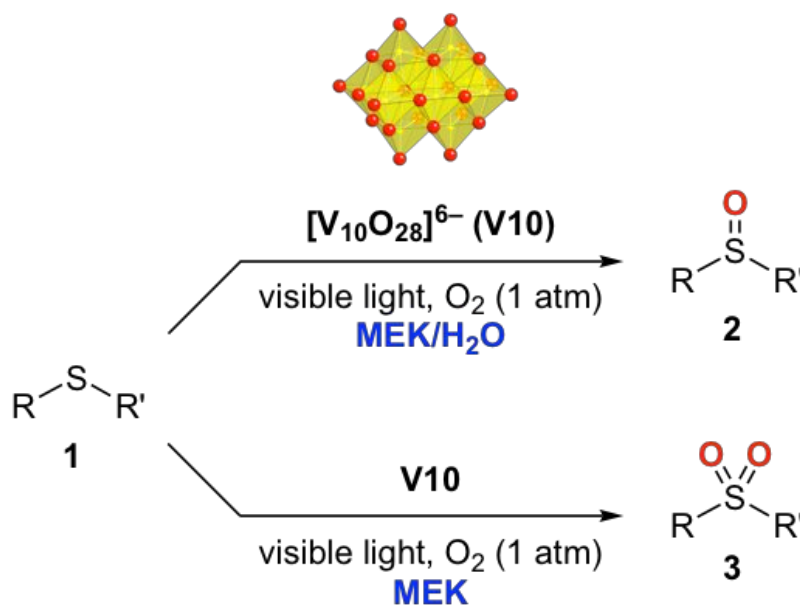
Introduction

Over the past few decades, the importance of photocatalysts assisting the green transformation of functional groups has grown exponentially.¹ A wide variety of chemical, electrical, and optical properties typical of metal oxides render these species attractive in the design of efficient photocatalysts.² Substantial efforts have been directed at developing nanometre-sized metal oxides as part of studies focusing on fundamental catalytic mechanisms (*e.g.*, the determination of the relevant size and quantum effects) and the technological applications of these materials.^{2,3} Polyoxometalates (POMs) have recently emerged as attractive materials in the search for efficient photocatalysts of functional group transformations.^{4,5} POMs are structurally well-defined nanometre-sized metal oxide clusters, and their properties, such as redox potentials and electronic structures, can be finely controlled at molecular level by simply modifying their structures, constituent elements, and oxidation states. Notably, POMs are more thermally and oxidatively stable than commonly utilised molecular photocatalysts, like, for instance, organometallic complexes and organic dyes. Given their molecularity and robustness, POMs have been used as powerful tools in photocatalytic oxidative reactions, including the oxidative degradation of organic pollutants and water oxidation.⁵ POM photocatalysts, *e.g.*, decatungstate ($[W_{10}O_{32}]^{4-}$),⁶ have also proven useful in assisting the oxidative transformation of functional groups as part of the synthesis of fine chemicals. However, photocatalysis with decatungstate required the use of ultraviolet (UV) light to achieve the excitation of oxygen-to-tungsten charge transfers; in fact, the energy gap between these molecular orbitals was quite large. Various strategies have been developed to try to utilise visible light to achieve the mentioned goal.^{5a} Thus far, we have employed HOMO- and LUMO-engineering strategies to successfully develop visible-light-responsive POM photocatalysts able to assist the oxidative transformation of a range of functional groups.⁷

This study aims to develop a system that is able to carry out the efficient green photocatalytic oxygenation of sulfides using O_2 as the terminal oxidant. In particular, we focused on achieving the selective generation of sulfoxides and sulfones, which are very important compounds characterised by a wide range of applications in organic synthesis,⁸ including in the preparation of pharmaceuticals⁹ and polymeric materials.¹⁰ Traditionally, (super)stoichiometric amounts of oxidants, such as *meta*-chloroperoxybenzoic acid, dioxirane, hydrogen peroxide, $NaIO_4$, CrO_3 , and $KMnO_4$, have been frequently used to drive the selective oxygenation of sulfides.¹¹ Notably, although from the standpoint of environmental sustainability, the development of a green synthetic approach relying on O_2 as the

terminal oxidant (instead of the aforementioned stoichiometric oxidants) is highly desirable, only a few systems for the selective, dioxygen-driven sulfide oxygenation into both sulfoxides and sulfones have been developed.¹² Furthermore, most of the reported such systems require harsh reaction conditions, like, for instance, high O₂ pressure, high temperature, or use of a highly toxic radioactive uranyl acetate photocatalyst.¹²

In this study, decavanadate ($[\text{V}_{10}\text{O}_{28}]^{6-}$, **V10**) was revealed to be an efficient visible-light-responsive photocatalyst for the selective oxygenation of sulfides achieved using O₂ (1 atm) as an oxidant. Polyoxovanadates like decavanadate are composed of earth-abundant vanadium atoms with mainly +5 oxidation state. They are important compounds in biological processes¹³ and are utilised for a wide range of applications, including in medicine,¹⁴ supramolecular assemblies,¹⁵ and redox flow batteries.¹⁶ Although polyoxovanadates have been known to exhibit strong visible light absorption, their application in photocatalytic transformation of organic functional groups has not been studied. For example, Streb and coworkers have developed photocatalytic systems comprising metal-substituted polyoxovanadates, but their systems are limited to the oxidative degradation of organic dyes.¹⁷ In this study, we found that various kinds of structurally diverse sulfones could be synthesised *via* visible-light-triggered photocatalysis by **V10** under homogeneous conditions. The choice of the solvent was very significant, with the highest synthetic efficiency observed in methyl ethyl ketone (MEK). MEK-peroxide species were likely formed by MEK and O₂ through photocatalysis of decavanadate and acted as the “co-catalysts” (not “stoichiometric” oxidants) for the oxidation. Notably, water played an important role in directing the product selectivity toward sulfoxides over sulfones; in particular, water proved to have minimal influence on the photocatalytic oxygenation of sulfides, but it strongly inhibited the oxygenation of sulfoxides to sulfones, thereby effecting the selective production of sulfoxides (Scheme 1).



Scheme 1 Selective oxygenation of sulfides to sulfoxides and sulfones photocatalysed by visible-light-responsive decavanadate. MEK: methyl ethyl ketone.

Results and discussion

Synthesis of decavanadate photocatalysts

We synthesised a decavanadate catalyst in an aqueous acidic medium and isolated it as a tetraphenylphosphonium (TPP) salt (TPPV10). Single crystals of TPPV10 that were suitable for X-ray crystallographic analysis were successfully obtained by recrystallizing the compound from a mixture of acetonitrile and MEK or from acetonitrile and ethyl acetate. Based on the results of X-ray crystallographic analysis, elemental analysis, cold-spray ionization (CSI) mass spectroscopy, and NMR analysis, the formula of TPPV10 was determined to be $\text{TPP}_4\text{H}_2[\text{V}_{10}\text{O}_{28}]$ (Table S1, Fig. S1–S5). A tetra-*n*-butyl ammonium (TBA) salt of V10 (TBAV10, $\text{TBA}_3\text{H}_3[\text{V}_{10}\text{O}_{28}]$) was also synthesised by employing a similar procedure. The UV-Vis spectra of TPPV10 and TBAV10 were characterised by a visible light absorption that showed more intense absorbance than those of $\text{TBA}_4\text{H}[\gamma\text{-PV}_2\text{W}_{10}\text{O}_{40}]$, $\text{VO}(\text{acac})_2$, and other vanadium-containing POMs, such as $\text{TBA}_4[\alpha\text{-PV}_1\text{W}_{11}\text{O}_{40}]$ and $\text{TBA}_4\text{H}_2[\gamma\text{-SiV}_2\text{W}_{10}\text{O}_{40}]$, still, $\text{TBA}_6[\alpha\text{-PV}_3\text{W}_9\text{O}_{40}]$ showed stronger absorbance than V10 (Fig. 1a and S6). Notably, V10 showed prominent absorbance at the longer wavelength (to *ca.* 580 nm) than other vanadium-containing POMs. Furthermore, according to density functional theory (DFT) calculations, the HOMO and LUMO of V10 consisted of the O2p and V3d orbitals, respectively, and the intense absorption band in the visible light region was likely to be assignable to an O2p-to-V3d charge transfer (Fig. 1b).

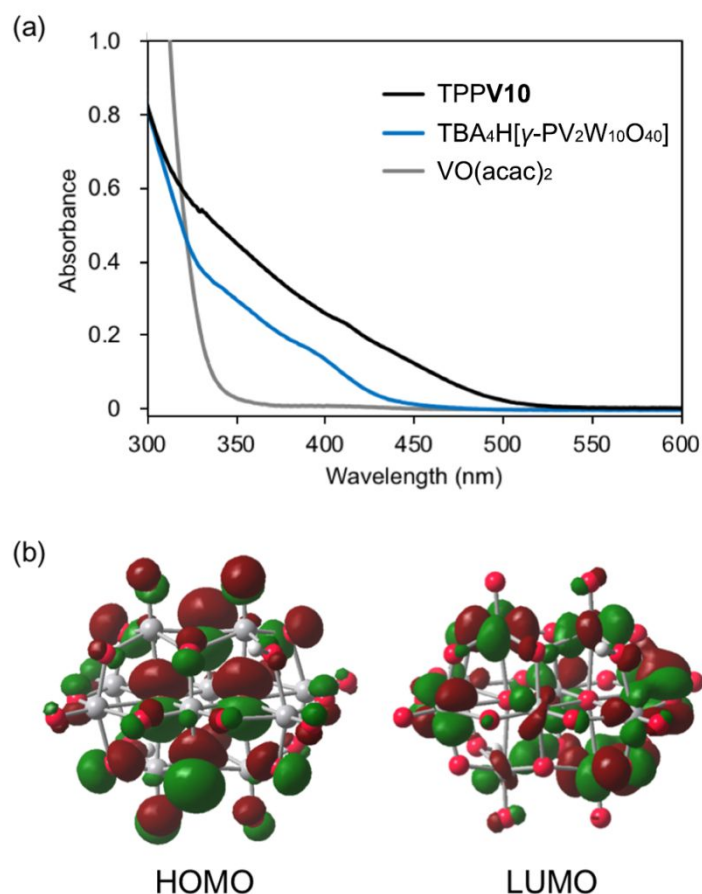


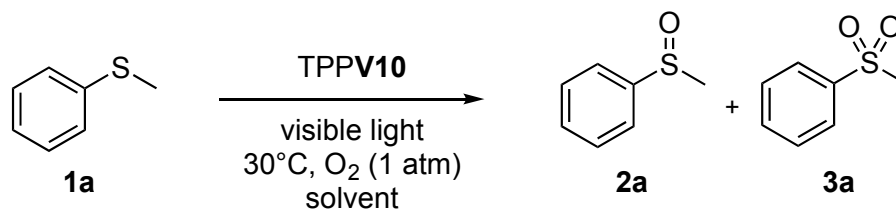
Fig. 1 (a) UV-Vis spectra of TPPV10 (0.05 mM), TBA₄H[γ-PV₂W₁₀O₄₀] (0.05 mM), and VO(acac)₂ (0.1 mM) in acetonitrile (1 cm cell). (b) Representations of the HOMO and LUMO of V₁₀ as determined by way of DFT calculations; the orbitals are represented by dark red and green lobes.

Optimization of the reaction conditions

The catalytic activity of TPPV10 in the oxygenation of thioanisole (**1a**), achieved through irradiation with visible light ($\lambda > 400$ nm) using a xenon lamp under an O₂ atmosphere, was examined in various solvents (Table 1). TPPV10 was soluble in these solvents, and the photocatalytic reactions were carried out under homogeneous conditions. Evidence indicated that the reaction hardly proceeded in organic solvents like acetonitrile, ethyl acetate, methanol, ethanol, or dimethyl sulfoxide (Table 1, entries 4–8). By contrast, and to our surprise, use of simple ketone solvents, such as MEK and diethyl ketone, was associated with significant improvements in the described photocatalytic activity, with the oxygenation of **1a** to form the corresponding sulfone (**3a**) proceeding with high efficiency and selectivity (Table 1, entries 1 and 3). Notably, although the photocatalytic oxygenation of **1a** to produce the corresponding sulfoxide (**2a**) proceeded to some extent in acetone, *N,N*-dimethylformamide, or *N,N*-dimethylacetamide, formation of **3a** was hardly observed when the oxygenation reaction was conducted in these solvents (Table 1, entries 9–11). Furthermore, the product selectivity of the

oxygenation reaction could be made to switch by simply adding water to the reaction mixture; when the reaction was carried out in a mixture of MEK and water (95/5, v/v), the corresponding sulfoxide **2a** was selectively obtained (Table 1, entry 2 vs. entry 1). Importantly, only one recent report exists describing a photocatalytic system that enables users to selectively access both sulfides and sulfoxides; this system, however, relies on highly toxic uranyl acetate catalyst, so that its utilization might be limited.^{12a}

Detailed reaction profiles revealed that the present **V10**-catalysed oxygenation of **1a** is characterised by significant solvent dependence (Fig. 2). In particular, when the photocatalytic oxygenation of sulfide **1a** was carried out in MEK, **1a** was oxygenated to produce initially the corresponding sulfoxide **2a** and, subsequently, sulfone **3a** (Fig. 2a). As a result, in this system, the selective synthesis of sulfoxide **2a** was very difficult to achieve at any reaction time. By contrast, when the reaction was carried out in MEK/H₂O (95/5, v/v), the oxygenation of sulfide **1a** to sulfoxide **2a** was accelerated, whereas the further oxygenation of this compound to produce sulfone **3a** was significantly suppressed, resulting in the selective oxygenation of sulfide **1a** to sulfoxide **2a** (Fig. 2b).

Table 1 Photocatalytic aerobic oxygenation of **1a** using TPPV10 as catalyst in various solvents^a

Entry	Solvent	Conv. (%)	Yield (%)	
			2a	3a
1	Methyl ethyl ketone (MEK)	98	<1	96
2^b	MEK/H₂O (95/5, v/v)	98	93	3
3	Diethyl ketone	>99	17	81
4	Acetonitrile	2	2	<1
5	Ethyl acetate	<1	<1	<1
6	Methanol	1	<1	<1
7	Ethanol	<1	<1	<1
8	Dimethyl sulfoxide	2	<1	<1
9	Acetone	10	10	<1
10	<i>N,N</i> -Dimethylformamide	17	8	<1
11	<i>N,N</i> -Dimethylacetamide	42	31	1

^aReaction conditions: **1a** (0.2 mmol), TPPV10 (0.4 mol%), solvent (4 mL), 30°C, visible light ($\lambda > 400$ nm, xenon lamp), O₂ (1 atm), 8 h. ^b4 h.

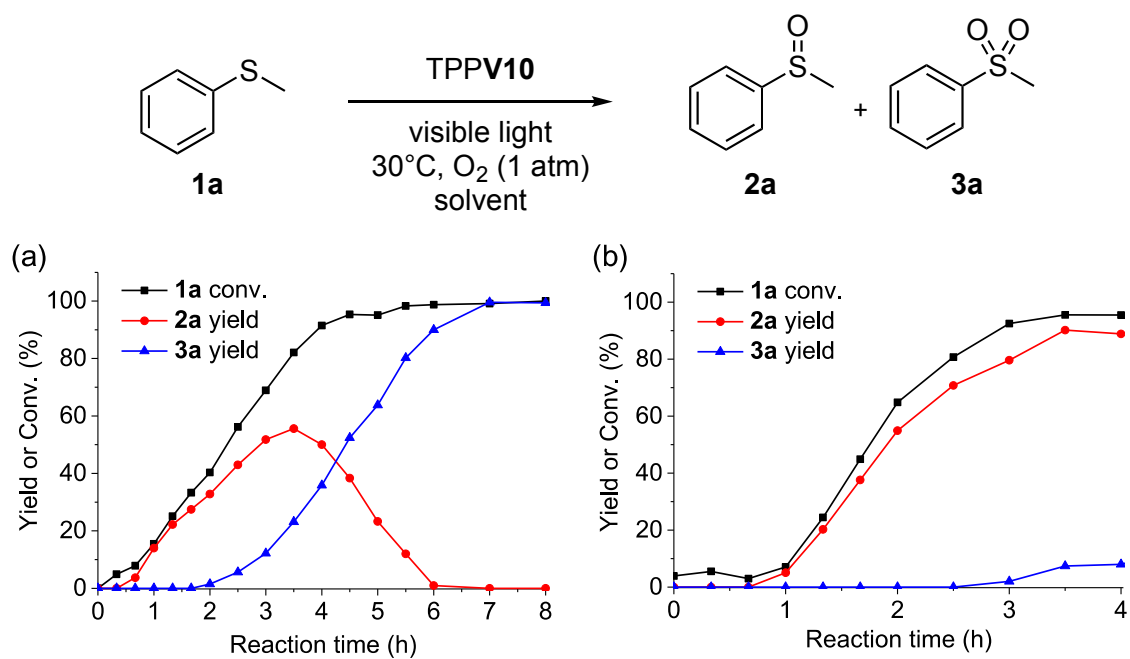
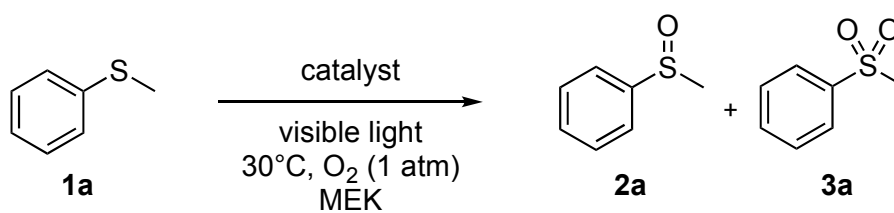


Fig. 2 Reaction profiles of the photocatalytic aerobic oxygenation of **1a** using TPPV10 as a catalyst in (a) MEK and (b) MEK/H₂O (95/5, v/v) under visible light ($\lambda > 400$ nm) irradiation realised with a xenon lamp. Reaction conditions: **1a** (0.2 mmol), TPPV10 (0.4 mol%), solvent (4 mL), 30°C, visible light ($\lambda > 400$ nm, xenon lamp), O₂ (1 atm).

Several control experiments we conducted revealed that the oxygenation of **1a** did not proceed in the absence of the catalyst (TPPV**10**, Table S2, entry 2), visible light irradiation (Table S2, entry 3), or O₂ (Table S2, entry 4). Notably, the reaction proceeded efficiently even under an air atmosphere (Table S2, entry 5). A blue LED light ($\lambda = 420$ nm) could also be used as a light source, instead of the xenon lamp, to trigger the catalytic reaction (Table S2, entry 6). Use of a TBA salt of **V10** (TBA**V10**) as a photocatalyst afforded similar results as use of TPPV**10** (Table 2, entries 1 and 2), indicating that the identities of the counter cations have little effect on photocatalytic activity. The photocatalytic activity of TPPV**10** (or TBA**V10**) was much superior to those of vanadium-free POM TBA₃[α -PW₁₂O₄₀] and other vanadium-containing POMs, including TBA₄H[γ -PV₂W₁₀O₄₀], TBA₄H₂[γ -SiV₂W₁₀O₄₀], TBA₄[α -PV₁W₁₁O₄₀], TBA₆[α -PV₃W₉O₄₀], and TPP₂[V₆O₁₃(C₅H₉O₄)₂]¹⁸ (Table 2, entries 1 and 2 vs. entries 4–8). In particular, TPPV**10** showed much higher catalytic activity than TBA₄H[γ -PV₂W₁₀O₄₀], which, in a previous study conducted by our group, displayed the highest activity among the complexes tested in the photocatalytic oxygenation of sulfides to sulfoxides (Table 2, entries 1 and 2 vs. entry 4).^{7c} Simple vanadium compounds, such as VO(acac)₂, V₂O₅, and NaVO₃, showed much lower photocatalytic activity than TPPV**10** in the oxygenation of **1a** (Table S3). In addition, various transition-metal complexes hardly showed photocatalytic activity in the described reaction (Table S3). The catalytic activity of TPPV**10** was even higher than that of the TBA salt of decatungstate [W₁₀O₂₈]⁴⁻ (TBA**W10**, Table S4, entry 2 vs. entry 1). Other commonly utilised visible-light-responsive molecular photocatalysts, such as Ru(bpy)₃Cl₂, Eosin Y, methylene blue, and rose bengal, were also tested in the aerobic oxygenation of sulfide **1a** under the same conditions detailed above (Table S4, entries 3–6). Use of these catalysts afforded sulfoxide **2a** as the major product; however, in these cases, the **2a** yields were moderate, and the formation of the corresponding disulfide side-product **4a** was also observed.

Table 2 Photocatalytic aerobic oxygenation of **1a** using various catalysts and methyl ethyl ketone (MEK) as a solvent^a



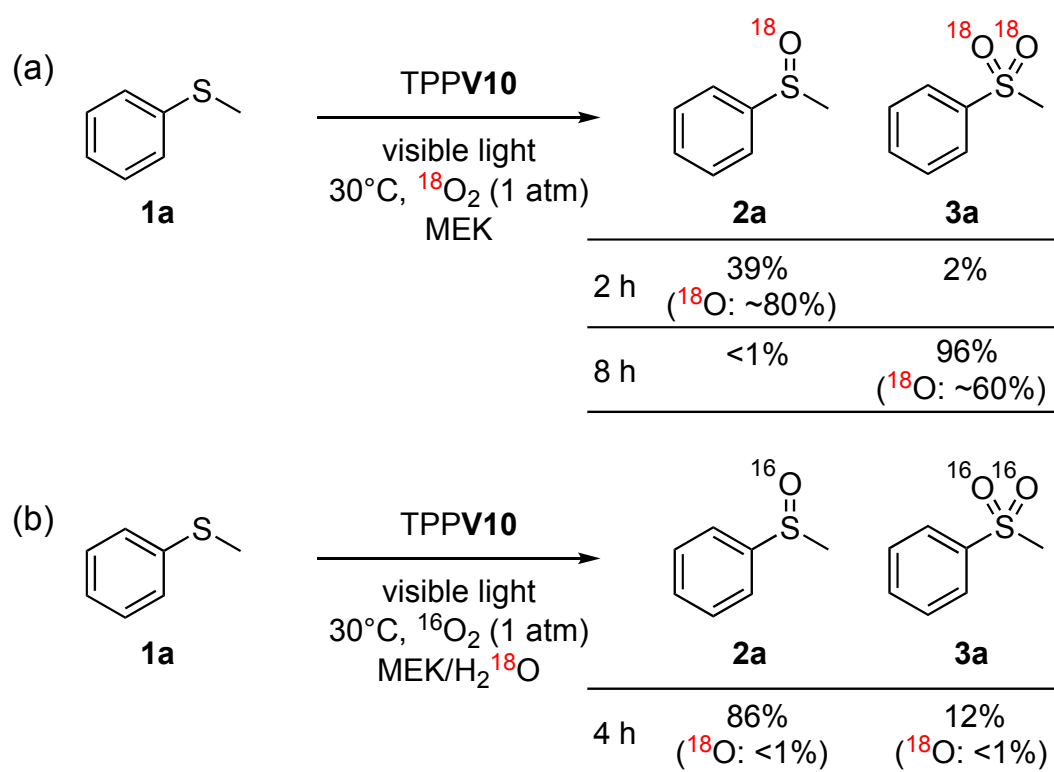
Entry	Catalyst (mol%)	Conv. (%)	Yield (%)	
			2a	3a
1	TPPV10 (0.4)	98	35	59
2	TBAV10 (0.4)	>99	48	52
3	TBA ₃ [α -PW ₁₂ O ₄₀] (2)	5	2	<1
4	TBA ₄ H[γ -PV ₂ W ₁₀ O ₄₀] (2)	96	80	16
5	TBA ₄ H ₂ [γ -SiV ₂ W ₁₀ O ₄₀] (2)	15	8	<1
6	TBA ₄ [α -PV ₁ W ₁₁ O ₄₀] (2)	1	<1	<1
7	TBA ₆ [α -PV ₃ W ₉ O ₄₀] (2)	21	15	<1
8	TPP ₂ V ₆ O ₁₃ (C ₅ H ₉ O ₄) ₂ (2)	5	<1	<1

^aReaction conditions: **1a** (0.2 mmol), MEK (4 mL), 30°C, visible light ($\lambda > 400$ nm, xenon lamp), O₂ (1 atm), 4 h.

Reaction mechanism

In order to investigate the mechanism of the **V10**-catalysed photocatalytic oxygenation of sulfides, the relevant oxygenation of **1a** was carried out in the presence of radical scavengers (Table S5). When (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), a widely used radical scavenger,¹⁹ was added to the reaction mixture, the reaction was significantly suppressed (Table S5, entry 2). Similarly, the presence of either 1,4-dimethoxybenzene, a scavenger of sulfide cation radical species (Table S5, entry 3),²⁰ or benzoquinone, a scavenger of superoxide anion radical species (Table S5, entry 4), also suppressed the oxygenation reaction.²¹ However, the reaction was hardly affected by the presence of isopropanol, a hydroxy radical ($\bullet\text{OH}$) scavenger (Table S5, entry 5).²² The emission of singlet oxygen ($^1\text{O}_2$, 1270 nm) was not observed following the excitation of **TBAV10** with a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser in MEK. These results indicated the possible involvement of a single electron transfer (SET) mechanism in the formation of the sulfide cation radical and superoxide anion radical species in the catalytic cycle²³; on the other hand, the formation of the $\bullet\text{OH}$ radical and $^1\text{O}_2$ was less likely to occur during the catalytic cycle.

A set of ^{18}O -labelling experiments were subsequently conducted to investigate the oxygen-transfer process. Firstly, the **TPPV10**-catalysed oxygenation of **1a** was performed using $^{18}\text{O}_2$ as an oxidant, under the reaction conditions described in Scheme 2a. After 2 h, ^{18}O -labelled sulfoxide **2a** was formed as the main reaction product (39% yield, 95% selectivity), with the ^{18}O content in this product measured to be $\sim 80\%$, which demonstrates that the main oxygen source for the oxygenation of **1a** to **2a** is dioxygen. After 8 h, the corresponding sulfone was exclusively obtained (96% yield, $>99\%$ selectivity). However, evidence indicated that the ^{18}O content in the sulfone product was only 60%. Therefore, an oxygen source other than O_2 also appears to be involved in the oxygenation of **2a** to **3a**, which raises the question of what this oxygen source may be. In order to clarify this issue, we performed the several control experiments described in the rest of this section. When the **TPPV10**-catalysed oxygenation of **1a** was carried out in a mixture of MEK/ H_2^{18}O (95/5, v/v) under $^{16}\text{O}_2$ atmosphere, no ^{18}O was found to be present in the sulfone **3a** produced (Scheme 2b). Therefore, water can be ruled out as an oxygen source in the reaction. In addition, considering that the amount of **TPPV10** used for the reaction was very small (only 0.4 mol%) and that the oxygen atom in **TPPV10** was not replaced by ^{18}O in the presence of $^{18}\text{O}_2$ (as indicated by the results of CSI mass analysis), oxygen atoms derived from **TPPV10** are unlikely to participate directly in sulfone formation.



Scheme 2 Photocatalytic oxygenation of **1a** using TPPV10 as a catalyst in the presence of (a) $^{18}\text{O}_2$ (1 atm) in MEK as a solvent and (b) $^{16}\text{O}_2$ (1 atm) in MEK/ H_2^{18}O (95/5, v/v) as a solvent. Reaction conditions: **1a** (0.2 mmol), TPPV10 (0.4 mol%), solvent (4 mL), 30°C, visible light ($\lambda > 400$ nm, xenon lamp), O_2 (1 atm).

Notably, the oxygenation of sulfoxide **2a** to afford sulfone **3a** proceeded when commercially available MEK peroxide in place of O_2 was used as an oxidant, even in the absence of visible light irradiation (Table S6, entries 1 and 2). Therefore, the photocatalytic oxygenation of **2a** to produce **3a**, using TPPV10 as the catalyst, probably involved the formation of MEK-derived peroxide species. This conclusion is in good agreement with the results of the above-described labelling experiment involving the use of $^{18}\text{O}_2$ as the terminal oxidant, and we assume that a part of the oxygen atoms in the oxygenation from **2a** to **3a** can be originated from MEK-derived peroxide species. (Scheme 2a). Importantly, the reaction products derived from MEK were hardly observed after the photocatalytic oxygenation of **1a** using TPPV10, suggesting that MEK may have acted as a catalyst of the oxygenation reactions in this photocatalytic system. When the photocatalytic oxygenation of **2a** by TPPV10 was carried out in MEK, the rate of the photocatalytic oxygenation of **2a** was extremely slower than that of the corresponding oxygenation of **2a** taking place following the oxygenation of **1a** (Fig. S7 vs. Fig. 2a). This observation probably descends from the fact that, in the presence of **1a** and O_2 , the MEK-derived peroxide species get formed as a result of the TPPV10-catalysed photoredox reaction (*i.e.*, the reaction consisting in the oxidation of **1a** to produce the corresponding sulfide cation

radical and the reduction of O_2 to produce the superoxide anion radical). This TPPV10-catalysed photoredox reaction seems to be difficult to proceed when **2a** is used as a substrate, because of the high oxidation potential of **2a** (~ 2.5 V vs. normal hydrogen electrode).²⁴

The proposed V10-catalysed photocatalytic oxygenation of sulfides may thus proceed *via* the mechanism depicted in Fig. 3. The reaction is initiated by the formation of a sulfide cation radical resulting from a SET from the sulfide substrate to the photo-activated V10 (V10*). The reduced V10 is then reoxidised by O_2 to afford a superoxide anion radical. The corresponding sulfoxide is then obtained as a result of the reaction between the sulfide cation radical and the superoxide anion radical. As to the formation of a sulfone product, the MEK-derived peroxide species are probably involved in the oxygenation of sulfoxides to produce sulfones. Importantly, the oxygenation of sulfoxide **2a** by MEK-derived peroxide species to produce sulfone **3a** was not suppressed by the addition of water (Table S6, entries 3 and 4). Therefore, the selectivity switch for the photocatalytic reaction relying on V10 as catalyst realised by addition of water is most likely achieved *via* suppression of the formation of MEK-derived peroxide.

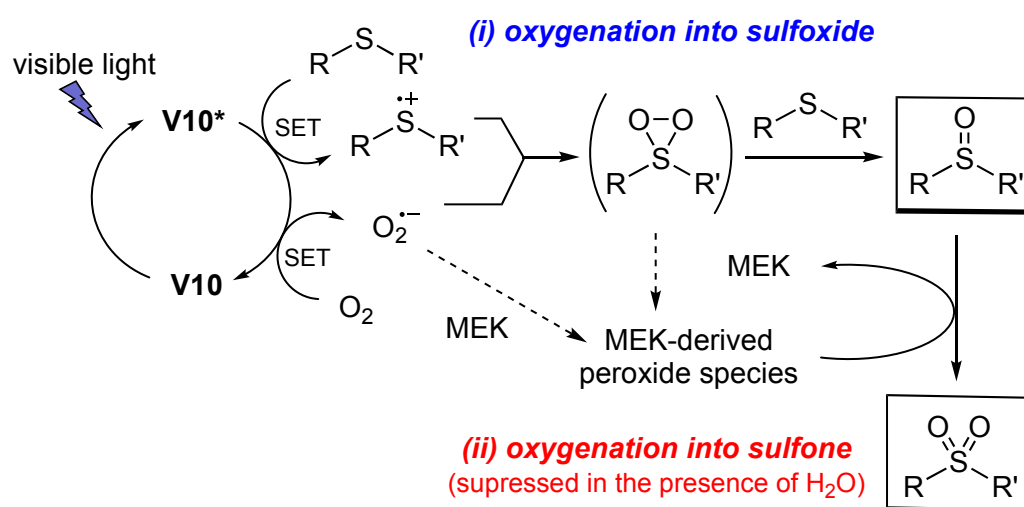


Fig. 3 Proposed mechanism of V10-catalysed photocatalytic oxygenation of sulfides.

Substrate scope

Finally, the substrate scope of the described photocatalytic oxygenation of sulfides was investigated under visible light irradiation at $\lambda > 400$ nm in the presence of O_2 (1 atm) as the oxidant and TPPV10 as the catalyst (Fig. 4). In MEK, in the presence of catalytic amounts of TPPV10 (0.35 mol%), thioanisole and its derivatives having either electron-donating or electron-withdrawing substituents on the aromatic ring were all efficiently and selectively converted to the desired sulfones (**3a–3f**). Sulfides

possessing chloro, cyclopropyl, and pyridyl groups were all selectively oxygenated to produce the corresponding sulfones (**3e**, **3h**, and **3j**), without any observed side reactions. Notably, this photocatalytic system could also be applicable to the oxygenation of 4-nitrothioanisole to produce the corresponding sulfone **3c**, whereas a reactivity has not been achieved by reported photocatalytic systems.²⁵ Importantly, substrates with alkyl functional groups, as well as alkyl sulfides like pentamethylene sulfide and dibutyl sulfide were also efficiently converted into the desired sulfones (**3g–3i**, **3k** and **3l**). Most remarkably, when we changed the reaction solvent from MEK to MEK/H₂O (95/5 or 92/8, v/v), sulfoxides could be obtained with high selectivity from sulfides. Unfortunately, diphenyl sulfide and dibenzothiophene could not be converted to the corresponding sulfoxides because of the low stability of these substrates in the MEK/H₂O mixed solvent. By contrast, the other sulfides tested in this study were all selectively oxygenated to produce the corresponding sulfoxides in MEK/H₂O.

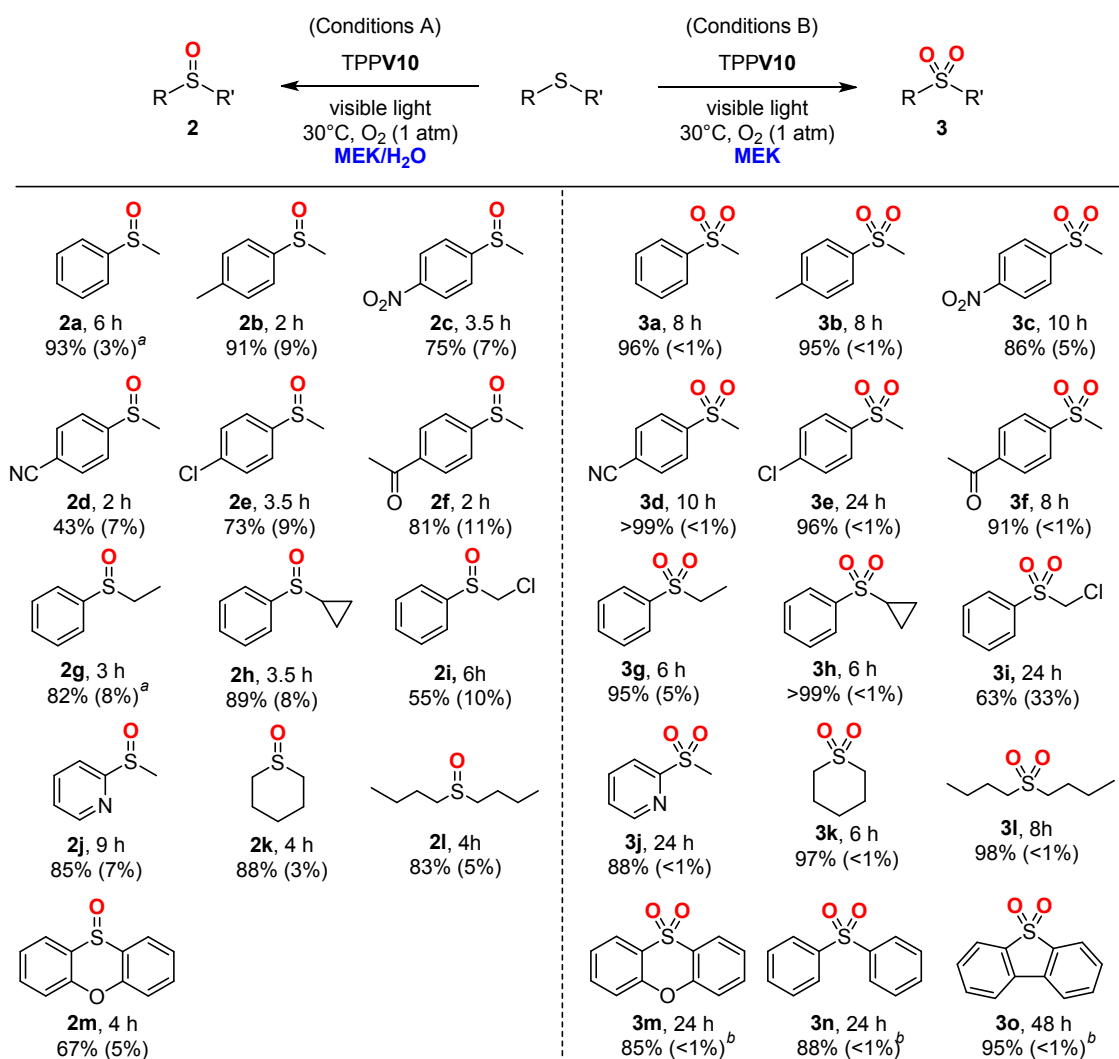


Fig. 4 Substrate scope for the **V10**-catalysed oxygenation of sulfides to produce sulfoxides and sulfones. Reaction conditions A: substrate (0.1 mmol), **TPPV10** (0.35 mol%), 30°C, visible light ($\lambda > 400$ nm, xenon lamp), O₂ (1 atm), MEK/H₂O (4 mL, 92/8, v/v). Reaction conditions B: substrate (0.2 mmol), **TPPV10** (0.35 mol%), 30°C, visible light ($\lambda > 400$ nm, xenon lamp), O₂ (1 atm), MEK (4 mL). Yields were determined by GC using dodecane as an internal standard. Isolated yields are shown in ESI. ^aSubstrate (0.2 mmol), MEK/H₂O (4 mL, 95/5, v/v). ^bSubstrate (0.1 mmol), **TPPV10** (1.4 mol%), MEK (4 mL). The values in the parentheses are the yields of sulfoxides (for reaction conditions A) and sulfones (for reaction conditions B).

Conclusion

In this article, we reported the visible-light-induced selective oxygenation of sulfides to produce both sulfoxides and sulfones using O₂ (1 atm) as an oxidant. In particular, we report two important findings: (i) a well-known decavanadate (**V10**) showed remarkable visible-light-responsive photocatalytic activity in the oxygenation of sulfides; (ii) the selectivity of the oxygenation products (*i.e.*, sulfoxides *vs.* sulfones) can be switched by simply changing the solvent. In the presence of catalytic amounts of **V10**, various aromatic and alkyl sulfides can be transformed directly into the corresponding sulfoxides or sulfones with high efficiency and selectivity, by irradiating the reaction mixture with visible light ($\lambda > 400$ nm). We believe that the photocatalytic activity of decavanadate might be exploited to effect oxidative transformations of various organic functional groups using O₂ as an oxidant. This new strategy is not simply a means to realize the photocatalytic oxygenation of sulfides, but to highlight the considerable potential of the development of green photocatalytic oxidation systems using O₂ and MEK solvent.

Experimental section

Reagents

Sulfides (TCI), acetonitrile (Kanto Chemical), acetone (Kanto Chemical), MEK (TCI), diethyl ketone (TCI), 3-hexanone (TCI), cyclohexanone (TCI), dimethyl sulfoxide (Kanto Chemical), *N,N*-dimethylacetamide (TCI), *N,N*-dimethylformamide (Kanto Chemical), methanol (Wako), ethanol (Kanto Chemical), trifluorotoluene (TCI), benzonitrile (Kanto Chemical), dodecane (TCI), VO(acac)₂ (Aldrich), V₂O₅ (Kanto Chemical), NaVO₃ (Nacalai Tesque), 30% H₂O₂ (Kanto Chemical), and methyl ethyl ketone peroxide (~50% in dimethyl phthalate, TCI) were used as received. H₃PW₁₂O₄₀ was obtained from Wako. TBA₄[W₁₀O₃₂],²⁶ TBA₃H₄[γ -PW₁₀O₃₆],²⁷ TBA₄[α -PV₁W₁₁O₄₀],²⁸ TBA₄H[γ -PV₂W₁₀O₄₀],²⁹ TBA₄H₂[γ -SiV₂W₁₀O₄₀],³⁰ and TBA₃H₃[V₁₀O₂₈] (**TBAV10**)³¹ were synthesised according to the reported procedures. The syntheses of these compounds were confirmed by CSI mass spectroscopy, IR spectroscopy, and/or NMR spectroscopy.

Instrumentation

IR spectra were measured on a JASCO FT/IR-4100 spectrometer using KCl disks. UV-Vis spectra were measured on a Jasco V-570 spectrometer with a quartz cell of 1 cm path length. Gas

chromatography (GC) analyses were performed on a Shimadzu GC-2014 instrument with a flame ionization detector equipped with a TC-1 capillary column. GC mass spectra were recorded on a Shimadzu GCMS-QP2010 instrument at an ionization voltage of 70 eV. CSI mass spectra were recorded on a JEOL JMS-T100CS spectrometer. NMR spectra were recorded on a JEOL JNM ECA-500 spectrometer (^{31}P , 202.47 MHz; ^{51}V , 130.23 MHz;) using 5 mm tubes. Chemical shifts (δ) were reported in ppm downfield from H_3PO_4 (solvent: D_2O) for ^{31}P NMR spectra and NaVO_3 (solvent: D_2O) for ^{51}V NMR spectra. Thermogravimetric and differential thermal analyses were performed using a Rigaku Thermo plus TG 8120 instrument. Inductively coupled plasma atomic emission spectroscopy analyses for V and P were performed with a Shimadzu ICPS-8100 instrument. Elemental analyses were performed with an Elementar vario MICRO cube (for C, H, N) instrument at the Elemental Analysis Center of School of Science of the University of Tokyo.

Quantum calculations

Quantum calculations were performed using the Gaussian 09 software.³² Decavanadate (**V10**) was optimised at the CAM-B3LYP functional³³ with 6-31++G** (for H and O) and LanL2DZ (for V)³⁴ by using the conductor-like polarizable continuum model with the parameters of the integral equation formalism model for acetonitrile.

X-ray crystallography

Diffraction measurements were made using a Rigaku VariMax Saturn 724 diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$, 50 kV, 24 mA) at 123 K. The data were collected using CrystalClear and processed using CrysAlisPro.³⁵ Neutral scattering factors were obtained from the standard source. Lorentz and polarization corrections were applied for data reduction. Structural analyses were performed using WinGX.³⁶ All structures were solved by SHELXS-97 (direct methods) and refined by SHELXL-2018/3.³⁷ Vanadium, oxygen, carbon, and phosphorous atoms were refined anisotropically. CCDC-1974262 contains the supplementary crystallographic data for TPPV10. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of TPPV10

A solution of NaVO_3 (2.00 g, 16.4 mmol) was dissolved in water (66 mL, 50°C), and the pH of the

solution was adjusted to 4.8 adding dropwise to it HCl 3M. After filtration, the pH of the solution was further adjusted to 4.5 by adding dropwise to it HCl 3M; a solution of TPPBr (4.2 g, 10.0 mmol) in a mixture of water and acetonitrile (20 mL, 1/1, v/v) was then added to the NaVO₃ solution. The solution thus obtained was vigorously stirred for 1 min. The precipitate formed during stirring was filtered off and washed with water to afford crude TPP₄H₂[V₁₀O₂₈] (TPPV10) in the form of an orange powder. Orange crystals of TPPV10 were subsequently obtained from a solution of crude TPPV10 in a mixture of acetonitrile and ethyl acetate at 25°C. These crystals were then used for the photocatalytic reactions. Single crystals suitable for X-ray crystallographic analysis were obtained over 3 days from a solution of TPPV10 in a mixture of acetonitrile and ethyl acetate, or from a solution of TPPV10 in a mixture of acetonitrile and MEK, at 25°C. Results from X-ray crystallographic analysis, CSI mass and NMR spectroscopies, and elemental analysis support the synthesis of TPP₄H₂[V₁₀O₂₈]. Positive-ion MS (ESI, acetonitrile): *m/z* 2317.4 (calcd. 2317.8 for [TPP₄H₃V₁₀O₂₈]⁺). ⁵¹V NMR (130.23 MHz, acetonitrile-*d*₃): $\delta = -511.80$ ppm (4V), -487.92 ppm (4V), -410.93 ppm (2V). IR (KCl pellet, cm⁻¹): 390, 441, 526, 604, 688, 722, 760, 836, 965, 1107, 1166, 1189, 1317, 1335, 1437, 1481, 1583, 1630. Elemental analysis calcd. (%) for TPP₄H₂V₁₀O₂₈(CH₃CN)_{0.5}: C 49.84, H 3.60, N 0.30, P 5.30, V 21.79; found: C 49.35, H 3.62, N 0.25, P 5.34, V 22.90.

A typical procedure for the photocatalytic oxygenation of sulfides

Into a Pyrex Schlenk flask (volume: ~20 mL), TPPV10 (0.8 μ mol, 0.4 mol% with respect to **1a**), **1a** (0.2 mmol), dodecane (0.1 mmol), MEK (4 mL), and a Teflon-coated magnetic stir bar were successively placed under O₂ atmosphere (1 atm). The reaction was initiated at 30°C by irradiation with visible light ($\lambda > 400$ nm) from a xenon lamp equipped with a 400 nm cutoff filter. The detailed reaction conditions are described in the footnotes of Tables and Figures. The identities of the products were confirmed by comparison of their GC retention times and GC-MS spectra with those of authentic samples. The GC yields reported in Fig. 4 were determined using dodecane as an internal standard. The detailed GC conditions are summarized in ESI. Column chromatography was performed to isolate the products with silica gel and solvents were technical standard. The detailed isolation conditions and isolated yields are summarized in ESI.

Conflicts of interest

There are no conflicts to declare.

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