

The first example of direct oxidation of sulfides to sulfones by an osmate molecular oxygen system†

Boyapati M. Choudary,* Chinta Reddy V. Reddy, Billakanti V. Prakash, Mannepalli L. Kantam and B. Sreedhar

Indian Institute of Chemical Technology, Hyderabad 500007, India. E-mail: choudary@iict.ap.nic.in; Fax: 91-40-27160921

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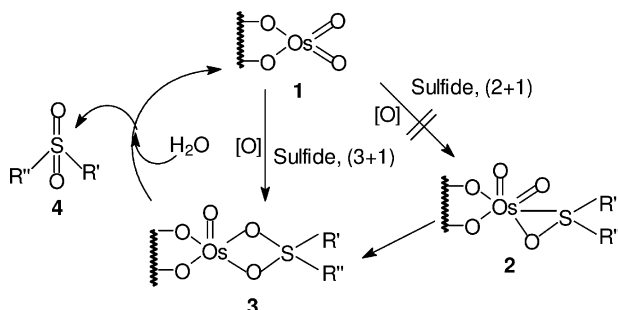
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Osmate-exchanged Mg–Al layered double hydroxides catalysed the delivery of two oxygen atoms simultaneously via a 3 + 1 cycloaddition to sulfide to form sulfone directly for the first time, reminiscent of 3 + 2 cycloaddition in asymmetric dihydroxylation reactions.

The oxidation of sulfides to sulfones has been the subject of extensive studies, since sulfones are useful synthons for the construction of various chemically and biologically significant molecules.^{1,2} The reaction path for the oxidation of sulfides to sulfones involves formation of sulfoxides as intermediates that contaminate the sulfone products, which are difficult to separate.^{2b} With inherent advantages such as ready availability and low price, molecular oxygen is widely used as an oxidant in many organic transformations, but reports on the oxidation of sulfides are still scarce.^{3,4} These include the *in situ* generated peracid from the O₂–aldehyde and cobalt system,³ the singlet oxygen produced under photochemical conditions.³ Recent disclosure of the deactivation of thioether mustard analogue by the oxidation of its sulfide to sulfoxide using an Au(III)-based homogeneous catalyst represents the sole catalytic protocol using molecular oxygen directly.⁵ Therefore, there is an incentive to develop direct oxidation of sulfides to sulfones. We chose an osmium catalyst for the direct oxidation of sulfides to sulfones, since it is known to activate molecular oxygen⁶ and deliver two oxygen atoms simultaneously to the olefin in the dihydroxylation reactions.⁷

In this communication, we report the effective oxidation of sulfides directly to sulfones without sulfoxide contamination in excellent yields at a faster rate for the first time using molecular oxygen as the stoichiometric oxidant and osmate exchanged layered double hydroxide (LDH–OsO₄) as a recyclable catalyst. The examination of transient surface intermediate species, prepared on interaction of LDH–OsO₄ with the sulfides, by using XPS and TGA–DTA–MS and kinetic studies, provides evidence for the simultaneous delivery of two oxygen atoms via 3 + 1 cycloaddition (Scheme 1).

Exchanger–OsO₄ catalysts immobilized on Mg–Al-LDH and resin⁸ by the ion-exchange technique designed and developed



Scheme 1 Plausible mechanism for the exchanger–OsO₄ catalyzed oxidation of sulfides using molecular oxygen as stoichiometric oxidant.

† Electronic supplementary information (ESI) available: experimental details; TGA–DTA–MS thermogram of LDH–OsO₄® with thioanisole. See <http://www.rsc.org/suppdata/cc/b2/b212749k/>

recently and their homogeneous analogue were used in the direct oxidation of thioanisole to methyl phenyl sulfone using molecular oxygen as stoichiometric oxidant at 55 °C in phosphate buffer and *t*-butanol (Table 1, entry 1) and no sulfoxide was detected by GC. LDH–OsO₄ (cat 1) exhibits faster activity over the resin–OsO₄ (cat 2) and K₂OsO₄·2H₂O catalysts in oxidation of thioanisole (Fig. 1). The large positive electric potential and spatial organisation of the LDH–OsO₄ may be responsible for the superior performance; this result is in consonance with asymmetric dihydroxylation reactions⁸ and oxidative bromination.⁹

LDH–OsO₄, the best-evolved catalyst, was further subjected to the oxidation of various aliphatic and aromatic sulfides† and the results are summarised in Table 1. All the substrates irrespective of the nature of the substituents present on the phenyl ring as shown in Table 1 afforded excellent yields without formation of sulfoxide. It is interesting to note that

Table 1 Oxidation of sulfides to sulfones catalysed by LDH–OsO₄ (cat 1) using molecular oxygen as oxidant^a

Entry	R'	R''	Time/h	Yield (%) ^b
1	C ₆ H ₅	CH ₃	8 24	99 (93) ^c NR ^d
2	<i>p</i> -Cl-C ₆ H ₄	CH ₃	5	96
3	<i>p</i> -MeO-C ₆ H ₄	CH ₃	5	95
4	C ₆ H ₅	C ₂ H ₅	16	96
5	<i>p</i> -Cl-C ₆ H ₄	C ₂ H ₅	15	95
6	<i>p</i> -Br-C ₆ H ₄	CH ₃	10	96
7	<i>n</i> -C ₁₀ H ₂₁	CH ₃	12	95

^a Reaction conditions as exemplified in the ESI. ^b Isolated yields. ^c Yield after 4th cycle. ^d No reaction without catalyst.

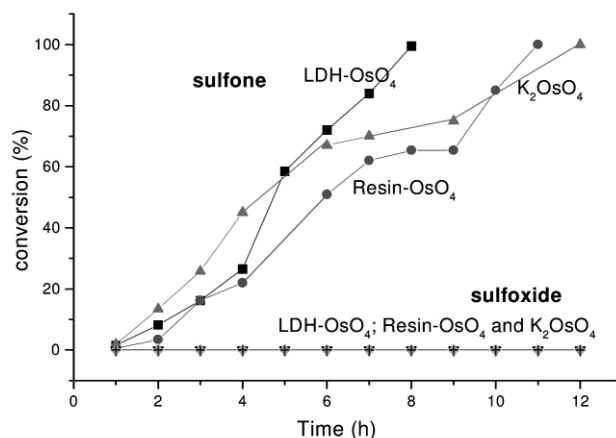


Fig. 1 Selectivity as a function of time in the oxidation of thioanisole using different osmate catalysts.

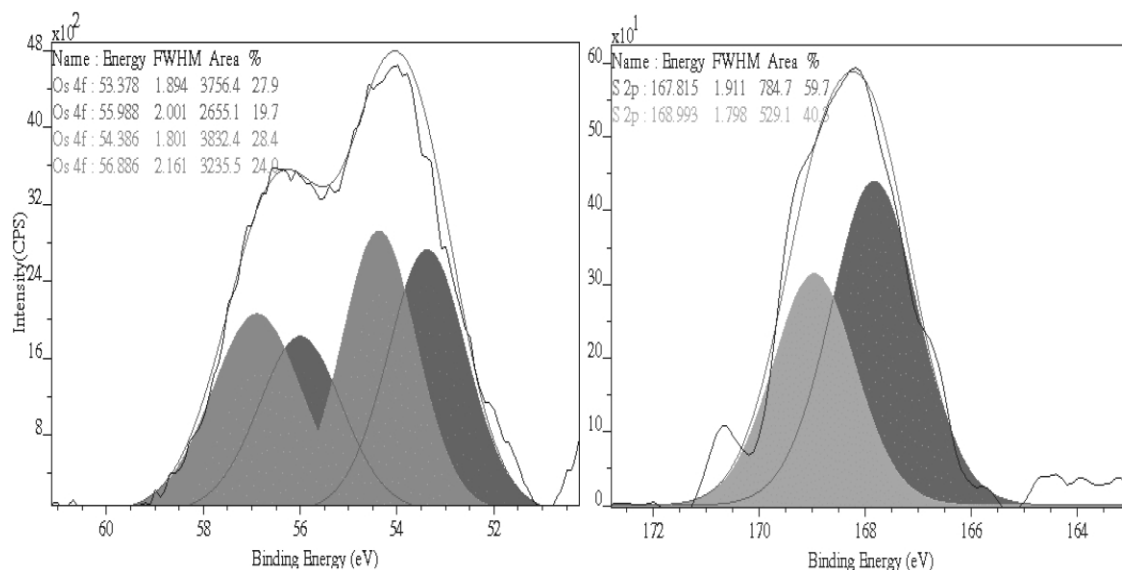


Fig. 2 XPS spectra of Os 4f and S 2p of LDH-OsO₄[®].

molecular oxygen served as a better stoichiometric oxidant for aliphatic and aromatic sulfides than H₂O₂. The catalyst was used for four cycles in the oxidation of thioanisole, which shows consistent selectivity and a small decrease in activity. Osmium was not present even in traces in solution after the reaction.

Sulfoxide, which is generally initially formed in the oxidations of sulfide, is transformed into sulfone on further oxidation during the reaction. The higher nucleophilicity of sulfide allows nucleophilic reaction with the oxygen to form sulfoxide, while the sulfoxide undergoes electrophilic reaction with the oxidant to form sulfone.¹⁰ An unprecedented direct oxidation of sulfide to sulfone without formation of sulfoxide as intermediate is demonstrated here: the oxidation of thioanisole was studied as a function of time using LDH-OsO₄, resin-OsO₄, and K₂OsO₄ catalysts. Sulfoxide was not formed even in the initial stages of the reaction (Fig. 1).

The XPS of the transient surface intermediate LDH-OsO₄[®] obtained by the interaction of LDH-OsO₄ with thioanisole in the presence of molecular oxygen in anhydrous acetonitrile (55–60 °C) shows Os 4f_{7/2} lines at 53.378 and 54.386, Os 4f_{5/2} at 55.988 and 56.886 eV, respectively. This suggests the possible presence of a surface Os-sulfone complex along with the unreacted LDH-OsO₄ (Scheme 1, intermediate **3**) in +VI oxidation state.¹¹ The XPS of LDH-OsO₄[®] shows S 2p_{3/2} and 2p_{1/2} lines at 167.8 and 168.9 eV, respectively, characteristic of the formation of sulfone (Fig. 2).¹² The reported binding energies for S–O of sulfoxide and metallic sulfides are 2–7 eV lower than the corresponding sulfone binding energies. Therefore, the higher binding energies observed are presumably ascribed to the formation of an Os-sulfone complex (Scheme 1, intermediate **3**) on the surface, which is indeed confirmed by TGA-DTA-MS. The *m/z* values 79, 77, and 64 amu[†] observed are assigned to radical cations of CH₃SO₂, C₆H₅, SO₂, fragments from the surface Os-sulfone intermediate (Fig. A, ESI; † Scheme 1, intermediate **3**) obtained as above. The XPS of LDH-OsO₄[®], which does not show any direct Os–S bond, indicates that the possible reaction path *via* complex **2** by 2 + 1 cycloaddition is ruled out. Thus, kinetic, XPS and TGA-DTA-MS studies unambiguously establish the concerted 3 + 1 cycloaddition *via* the delivery of two oxygens simultaneously as detailed in Scheme 1, similar to the 3 + 2 cycloaddition for asymmetric dihydroxylation and heterogeneity of the reaction.⁶

The LDH-OsO₄ catalyst is successfully employed for oxidation of sulfides to sulfones with excellent yields for the first time. The simple ecofriendly procedure, easily recoverable and reusable catalytic system described here is a potential

candidate and practical alternative to the currently practiced process.

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Notes and references

‡ LDH-OsO₄ (10 mg, 0.0134 mmol) was taken in a round-bottomed flask containing aqueous buffer solution (12.5 mL, pH 10.4) and tBuOH (5 mL) and stirred at 1 bar O₂, 55 °C in an oil bath. Then sulfide (1 mmol) was added in one portion and the reaction mixture was stirred vigorously. After completion of the reaction (as monitored by TLC), the catalyst was filtered and washed with ethyl acetate. After removing the solvent, the crude material was chromatographed on silica gel to afford the corresponding sulfone.

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