Stereospecific rhenium catalyzed desulfurization of thiiranes

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Methyltrioxorhenium catalyzes the efficient and stereospecific desulfurization of thiiranes by triphenylphosphine at room temperature, moreso when MTO has been pretreated with hydrogen sulfide, with a Re^V species as the active form of the catalyst.

Desulfurization of thiiranes (episulfides) occurs thermally,¹ photochemically² and chemically.³⁻¹¹ One of the most widely used reactions of thiiranes is the stereospecific desulfurization by trivalent phosphorus compounds such as PPh₃.⁴ These are very slow reactions, the rate constant for the reaction between PPh₃ and but-1-ene sulfide being $(0.9-1.8) \times 10^{-5} 1 \text{ mol}^{-1} \text{ s}^{-1}$ at 40 °C in different solvents. Recent studies of oxygen atom transfer^{12–14} might be extended to sulfur atom transfer reactions, using organorhenium catalysts. Herein we report the results of our investigations.

Treatment of propylene sulfide with PPh₃ gave no direct reaction until catalytic amounts of MeReO₃ (MTO) were added.[†] Propylene was then formed, albeit quite slowly (Fig. 1) and only after a long induction period. The active catalyst, a Re^V species, from MTO and Ph₃P, is formed by a similar induction period.¹⁵ Plausibly, an unspecified thiorhenium intermediate arises during that time.

Rhenium(v)¹⁶ is proposed to be the active catalyst species here as well. Substitution of an oxygen atom on MTO by sulfur might perhaps eliminate the induction period, in that Re^{VII} transfers a sulfur atom to a phosphine faster than it does an oxygen atom. MTO exchanges oxygens with water^{17,18} and could use H₂S to exchange one or more oxygen atoms with sulfur. As a test, H₂S was first bubbled through MTO in CD₃CN and the reaction repeated [eqn. (1)]. As predicted, the rate was significantly enhanced (Fig. 1).

$$Ph_{3}P + \sum_{k=1}^{S} R \xrightarrow{\text{cat. MeReO}_{3}, H_{2}S} Ph_{3}P = S + \underline{\qquad} R$$
(1)

Removal of H_2S by bubbling argon through the reaction prior to the addition of the phosphine and episulfide did not diminish the reactivity.[‡] The general reaction with episulfides^{19,20} occurs efficiently on a 2 g scale at room temperature for many thiiranes



Fig. 1 Kinetics of the reaction of propylene sulfide with PPh₃ in the presence of MTO as followed by ¹H NMR: (\Box) no H₂S, [propylene sulfide] = 50 mM, [PPh₃] = 200 mM, [MTO] = 20 mM; (\bigcirc) MTO solution (2 mM) rapidly pre-treated with H₂S, followed by an argon sparge, [propylene sulfide] = 100 mM, [PPh₃] = 200 mM.

(Table 1). This desulfurization process is tolerant of various functional groups. With both epoxy and episulfido groups (entry 10), only the episulfide undergoes atom transfer. Stereochemistry is retained completely, as indicated by entries 12 and 13.

In the absence of H_2S the reaction proceeds as shown in Scheme 1. H_2S alters the reaction by forming thiorhenium complexes in exchange processes [eqn. (2)]. Direct reaction

with H_2S yields Re_2S_7 from $KReO_4$ and MoS_3 from $(NH_4)_2MoO_4$.²¹ The same components at elevated temperatures (>450 °C) form reduced (Re^V and Mo^{IV}) sulfides.²²

On bubbling H_2S through a solution of MTO in CD_3CN , a black solid separates out within a few minutes. It proved insoluble in all common organic solvents and in water, complicating its characterization. Excess H_2O_2 dissolved the black solid product, but the ¹H NMR chemical shift of the new species does not match that of the well-established diperoxo complex of MTO.

Our next approach was to prepare and study MTO complexes to establish the mechanism. Nitrogen donor ligands give welldocumented complexes with MTO,¹⁴ but complexes of MTO with phenanthroline, bipyridine and 8-hydroxyquinoline failed

 Table 1
 Yields obtained in the MTO-catalyzed desulfurization of thiiranes§

Entry	Substrate	Product	Time	Yield (%)
1	s		3 h	100
2	S	\bigcirc	5 min	100
3	∕/──\S		5 min	96
4	Ph	Ph	5 min	100
5	s		1 h	100
6	S Ph	─Ph	4 h	89
7	S OPh		6 h	100
8	SF	F	9 h	50
9	S C ₈ H ₁₅	C ₈ H ₁₅	1 h	90
10	S (CH ₂) ₄	(CH ₂) ₄	2 h	100
11	(CH ₂) ₄	(CH ₂) ₄	1 h	100
12	Ph Ph	Ph Ph	30 min	100
13	Ph S Ph	Ph Ph	30 min	100





to react with H₂S. Reaction with 2-mercaptomethylthiophenol^{23,24} gave a new dimeric yellow rhenium(v) complex **D** [eqn. (3)], as reported earlier.²⁵



With **D** in hand it was possible to test the mechanism in Scheme 1, according to which 2 equiv. of episulfide should be desulfurized without phosphine. Fig. 2 shows the kinetics of an experiment with **D** and a four-fold excess of propylene sulfide. According to the amounts of material formed and remaining, **D** reacts with 2 equiv. of the thiirane, establishing rhenium(v) as the active catalyst. Furthermore, the reaction can be made catalytic in rhenium by the addition of PPh3 and the use of much less **D** at the outset, although a longer time is required than with the use of the aforementioned MTO/H₂S procedure. The same rate of desulfurization as given by MTO/H₂S was achieved by bubbling H₂S through the dimer solution before the addition of the episulfide and phosphine (Fig. 2). Addition of H₂S changes the color of the solution from yellow to pink, consistent with conversion of the Re=O group of D to Re=S; the species responsible could not be isolated.

The question still remains, regarding the original MTO/H₂S system, of whether the reactions utilize a sulfur analogue of MTO or a rhenium(v) species that might have been formed in the system. The black solid obtained on reaction of MTO with H₂S is an oligomeric alkylrhenium sulfide. Transition metal sulfides, including high oxidation state rhenium sulfides, are known to oligomerize and some of them have been characterized. ²⁶ When the black solid obtained on reaction with H₂S was treated with propylene sulfide, 4% desulfurization was observed in 2 h (starting with 5 mM MTO), suggesting the formation of at least some rhenium(v). The constitution of the major part was deduced by these experiments. First H₂S was bubbled through 20 mM MTO in CD₃CN until all the MTO had reacted (by ¹H NMR), the excess then being removed by an argon purge. Its reaction with successive 5 mM increments of PPh₃ was then monitored by ³¹P NMR. Only Ph₃P=S was



Fig. 2 Decrease in the concentration of propylene sulfide as followed ¹H NMR: (\Box) stoichiometric experiment, with [propylene sulfide] = 30 mM, [**D**] = 7.5 mM; (\bigcirc) catalytic experiment, with [propylene sulfide] = 100 mM, [PPh₃] = 125 mM and [**D**] = 2 mM, at room temperature.

observed, and no PPh₃ detected, on addition of 15 mM PPh₃. Addition of a further 5 mM increment of PPh₃ showed very small amounts of PPh₃. Beyond that, more phosphine did not lead to more Ph₃P=S. These findings indicate the presence of a rhenium(VII) sulfide that easily transfers a sulfur atom to a phosphine to generate Re^V and phosphine sulfide. Most of product of the MTO/H₂S reaction exists as Re^{VII} on reaction with H₂S. On the basis of direct information, however, we cannot claim that another valence state, such as Re^{VI}, is not involved.

This is a novel catalytic system that effects the desulfurization of episulfides at ambient temperature and pressure. The reaction is stereospecific and tolerant to functional groups.

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Notes and references

[†] MTO, propylene sulfide and cyclohexene sulfide were purchased. The other episulfides were synthesized. NMR spectra were referenced to solvent peaks: δ 7.15 for C₆D₆ and δ 1.93 for CD₃CN.

‡ In a typical experiment, hydrogen sulfide was bubbled into 2 mM MTO in CD₃CN for about 5 min, as a black solid separated. The excess of H_2S was removed by sparging with argon, whereupon PPh₃ and the episulfide were added. The reaction was monitored by NMR, and yields obtained based on proton integration relative to the solvent or to an internal standard of Ph₃CH. The chemical shifts of the olefin products agreed well with reference data.

§ In a typical experiment, carried out at room temperature, H_2S was bubbled through a 2 mM MTO in CD₃CN for 5 min; excess H_2S was then removed by purging with argon. To this solution PPh₃ (125 mM) was added, followed by the thiirane (100 mM). The reaction was followed by ¹H NMR at 25 °C. The reaction also worked very well on a 2 g scale.

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