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Aerobic oxygenation of organic sulfides using diruthenium activators

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ABSTRACT

Diruthenium compounds supported by carboxylate or mixed carboxylate/carbonate bridging ligands were found to be active catalysts for aerobic oxygenation of organic sulfides. $Ru_2(OAc)_3(CO_3)$ (**A**), $Ru_2(O_2CCF_3)_3(CO_3)$ (**B**) and $Ru_2(OAc)_4Cl$ (**C**) promote the conversion of organic sulfide to sulfoxide, and subsequently sulfone in an oxygen atmosphere at ca. 90 °C. The order of catalytic activity is **A** > **B** ≫ **C**. Catalytic reactions are operative in a number of 1:1 co-solvent–H_2O combinations, and the highest reactivity was found in aqueous media.

1. Introduction

Catalytic oxygenation of organic sulfur compounds is a reaction of practical use for both pharmaceutical and petroleum industries: chiral sulfoxides are important intermediates in medicinal chemistry [1,2]; and oxygenation of refractory sulfides such as dibenzothiophene is recognized as a promising method for deep desulfurization of fossil fuels [3,4]. Facile and selective conversion of organic sulfide to the corresponding sulfoxide and/or sulfone is also significant for the decontamination of chemical warfare agents such as muster gas and V-agents [5,6]. During the last few years, our laboratory has developed several efficient catalytic systems for the oxygenation of organic sulfides by either H_2O_2 or ^{t}BuOOH [7–10]. Both H_2O_2 and ^{t}BuOOH are inexpensive and non-toxic terminal oxidants [11–14], but have disadvantages such as thermal instability (H_2O_2) and low reactivity (^{t}BuOOH) for practical applications such as battlefield decontamination.

Aerobic oxidation of organic sulfides is a very appealing alternative to those based on H_2O_2 and ^{t}BuOOH because of both the ready access of oxidant, and, more importantly, its environment-friendly nature [15]. Development of systems capable of facilitating aerobic oxidation has been a key stimulus for the understanding of small molecule activation and the related mechanisms [16–18]. Functional catalysts for aerobic sulfide oxygenation, although rare, include those based on gold-polyoxometalates [19,20] and iron-polyoxometalates [21,22], all developed in the laboratory of Hill. Aerobic sulfide oxygenations were also achieved with Co(II) catalysts in the presence of excess aldehydes [23], and with *N*-hydroxyphthalimide as the catalyst in the presence of alcohols [24]. Catalytic oxidation of alcohol with molecular oxygen is more frequently studied, and many well-defined catalysts have been reported [25–27]. We were particularly intrigued by the report that water soluble diruthenium complexes, $Ru_2(OAc)_3(CO_3)$ (**A**) and $[Ru_2(OAc)_4](OAc)$, catalyze the oxidation of alcohols under an oxygen atmosphere [28]. Described in this contribution is the successful aerobic oxygenation of various organic sulfides facilitated by both an active catalyst generated in situ from either $Ru_2(OAc)_4Cl$ and K_2CO_3 (1:1, **A**) or $Ru_2(tfa)_5$ and K_2CO_3 (1:1, **B**) combination, and $Ru_2(OAc)_4Cl$ (**C**) shown in Scheme 1.

2. Results and discussion

Diruthenium(II,III) tetraacetate (**C**) was prepared using a procedure modified from that of Wilkinson and Stephenson [29]. As shown in Scheme 1, "$Ru_2(OAc)_3(CO_3)$" (**A**) was prepared from treating **C** with 1 equiv of K_2CO_3(aq) as described by Komiya et al. [28]. ^{1}H NMR spectrum of **A** generated in situ displayed two CH_3 peaks in 2:1 ratio, paramagnetically shifted down field and broadened, with chemical shifts very similar to those reported by Komiya. "$Ru_2(O_2CCF_3)_3(CO_3)$" (**B**) was similarly prepared in situ from diruthenium(II,III)(tetrakis-μ-trifluoroacetate)(η^1-trifluoroacetate), which was in turn prepared using a protocol developed by Cotton et al. [30].

Organic sulfide substrates examined in this study, shown in Scheme 2, include methyl phenyl sulfide (MPS), methyl *p*-tolyl sulfide (MTS), diphenyl sulfide (DPS), ethyl phenyl sulfide (EPS), 2-chloroethyl ethyl sulfide (CEES) and 2-chloroethyl phenyl sulfide (CEPS). For all catalytic runs, the catalyst was prepared in situ by mixing either $Ru_2(OAc)_4Cl$ or $Ru_2(O_2CCF_3)_5$ with appropriate equivalents of K_2CO_3(aq), and the solution mixture changed from the reddish brown to dark brown immediately. The substrate was

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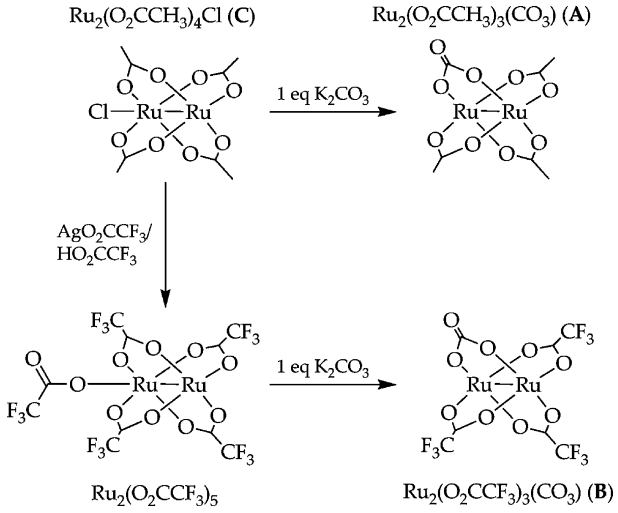
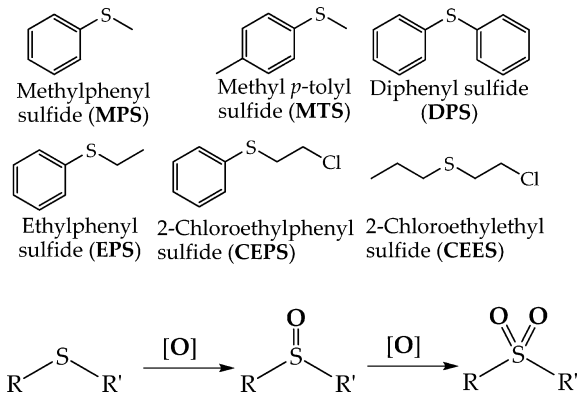


Scheme 1. Diruthenium catalysts and their syntheses.



Scheme 2. Organic sulfides and their stepwise oxygenation.

added to the reaction mixture as an oily suspension over the aqueous phase. The reaction mixture was then heated at the specified temperature and the progress of reaction was monitored periodically via GC analysis. The results obtained from all reactions catalyzed by catalyst **A** (5 mol% loading) are summarized in Table 1. As experienced in our past studies on sulfide oxygenation, all reactions produce sulfoxide and sulfone as indicated in Scheme 2.

As shown by the data from Table 1, most of methylphenyl sulfide (MPS) was converted to its sulfoxide during the first 24 h, while sulfone was not detected. During the second 24 h, the sulfide was all consumed and a small amount of sulfone appeared (7%). The amount of sulfone was increased to 37% at the expense of sulfoxide at the end of the 72 h run. These data seem to indicate that the conversion of sulfoxide to sulfone is slower than the conversion of sulfide. The reaction of methyl *p*-tolyl sulfide (MTS) is slightly faster than that of MPS, which is attributed to the comparable electron richness of the sulfur centers. In comparison, the reaction mixture of diphenyl sulfide (DPS) still contains a small fraction of sulfide even after 72 h, indicating a reduced reactivity of DPS owing to the decreased electron richness at the sulfur center. The conversion of ethyl phenyl sulfide (EPS) was also slow, and by-products derived from disulfide were also detected [8]. In all of the aforementioned catalytic reactions, the solution remained dark brown throughout the course of reaction, which may indicate a long-lived active species. To test the robustness of catalyst, the dark brown material was recovered at the end of MPS oxygenation

Table 1
Oxidation of organic sulfides with catalyst **A** ($Ru_2(OAc)_4Cl + K_2CO_3$) at 90 °C

Substrate	Rxn time (h)	Sulfide (%)	Sulfoxide (%)	Sulfone (%)	Others[c]	TOF[a]
MPS	24	9.6	90.4			0.75
	48		93	7		0.45
	72		63	37		0.38
R1[b]	24	1.8	98.2			0.82
R2[b]	24	7.6	92.4			0.77
R3[b]	24	44.6	55.3			0.46
MTS	24	7.6	90.9	1.5		0.78
	48	0.2	80.4	19.4		0.50
	72		58	42		0.39
DPS	24	55.8	43.3	0.9		0.38
	48	23.1	73.6	3.3		0.33
	72	7.1	84.1	8.8		0.28
EPS	24	60.8	25.3		13.9	0.21
	48	14.4	50.1	6.2	29.3	0.26
	72		34.6	42.7	22.7	0.33
CEES	24–48	100				
CEPS	24–48	100				

[a] Turnover frequency (h^{-1}) = {[RR′SO] + 2[RR′SO_2]}/{[cat] * time (h)}.
[b] The aqueous phase at the end of above 72 h run was collected and washed with EtOAc and hexanes several times to remove all organics and dried in vacuo. The solid residue was used for a new oxygenation reaction (R1). The same procedure was used to recover the catalyst for runs R2 and R3.
[c] "Others" include by-product disulfide (PhSSPh) and its respective oxidation products (PhS(O)SPh, or PhS(O)S(O)Ph, $PhS(O)_2SPh$).

by **A** and reused several times for the same reaction with freshly added substrate. The same level of catalytic activity was maintained in the recycled catalyst, as shown in Table 1.

It was surprising and somewhat disappointing that no oxygenation activity was found for either CEPS or CEEP substrate under the same conditions used for other sulfides (Table 1). It was noticed that the dark brown color characteristic of catalyst **A** quickly faded to light yellow upon the addition of Cl-containing sulfides at 90 °C. It is possible that the Cl-containing sulfide forms a tight complex with diruthenium species, and effectively "poisons" the catalyst.

The effect of the number of μ-carbonate ligands on aerobic oxygenation was studied with the use of catalysts prepared in situ from the combination of $Ru_2(OAc)_4Cl$ with 2, 3 or 4 equiv of K_2CO_3. The capacity of this series of catalysts and $Ru_2(OAc)_4Cl$ (**C**) in promoting aerobic oxygenation of MPS were examined and the results are given in Table 2 along with that of **A**. Clearly, the highest reactivity was achieved with **A**, and the activity decreases as the equivalent of carbonate increases. We speculate, as sketched in Scheme 3, that the introduction of the first μ-carbonate promotes facile dissociation of the *trans*-acetate, which creates open sites for O_2 binding. Presence of additional μ-carbonate ligands generally reduces the solubility of diruthenium moiety and consequently the catalytic efficiency. Our observation is also consistent with the inactivity of $[Ru_2(CO_3)_4]^{3-}$ in alcohol oxidation reported by Komiya et al. [28]. Surprisingly, $Ru_2(OAc)_4Cl$ is also effective in sulfide oxygenation, albeit significantly less active than **A**.

Table 2
Oxygenation of MPS with catalysts {$Ru_2(OAc)_4Cl + nK_2CO_3$} and $Ru_2(OAc)_4Cl$ at 90 °C

Catalyst	Rxn time (h)	Sulfide (%)	Sulfoxide (%)	Sulfone (%)	TOF
$Ru_2(OAc)_4Cl + K_2CO_3$(**A**)	24	9.6	90.4		0.75
$Ru_2(OAc)_4Cl + 2\ K_2CO_3$	24	16.0	84.0		0.70
$Ru_2(OAc)_4Cl + 3\ K_2CO_3$	24	43.5	54.5	2.0	0.49
$Ru_2(OAc)_4Cl + 4\ K_2CO_3$	24	63.7	36.3		0.30
$Ru_2(OAc)_4Cl$	24	69.6	30.4		0.25