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Tantalum(V) or niobium(V) catalyzed oxidation of sulfides with 30% hydrogen peroxide

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ABSTRACT

Tantalum(V) and niobium(V) are effective catalysts for the oxidation of sulfides with 30% hydrogen peroxide. The reaction of sulfides with 30% hydrogen peroxide catalyzed by tantalum(V) chloride or niobium(V) chloride in acetonitrile, *i*-propanol or *t*-butanol selectively provided the corresponding sulfoxides in high yields. The corresponding sulfones are efficiently obtained from the reaction of sulfides with 30% hydrogen peroxide in methanol catalyzed by tantalum(V) or niobium(V).

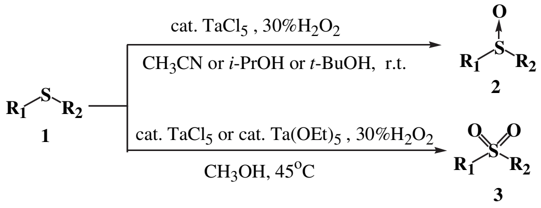
1. Introduction

Sulfoxides and sulfones are important and useful functional groups in organic synthesis, because they are frequently used as the intermediates for the construction of several important organic molecules.[1] In addition to this, there are many biologically important compounds containing a sulfoxide- or sulfone moiety. They are mainly prepared from the oxidation of corresponding sulfides; however, it is sometimes difficult to stop the oxidation at the sulfoxide stage. For instance, in the synthesis of sulfones from sulfides, other oxidizable functional groups, such as alcohols or olefins, sometimes react as well, producing undesirable compounds.

A large number of methods have been developed to overcome these drawbacks, however, most of these reactions require a stoichiometric amount of oxidant, resulting in undesirable waste.[2] Aqueous 30% hydrogen peroxide has recently been utilized as an attractive and environmentally benign oxidant[3] for the oxidation of sulfides, because 30% hydrogen peroxide is inexpensive, easy to handle, safely stored and produces only water as a side-product. Because the oxidation of sulfides with aqueous hydrogen peroxide in the absence of any catalysts requires a long reaction time, several transition metal (Ti,[4b] Mo,[4c] Fe,[4d] V,[4e,f] W,[4g,h] Re,[4i] Cu,[4j] Mn[4k,l] and Au[4m]) compounds have been used as catalysts.[4]

Although transition metal-catalyzed reactions produce the products in high yields, there are still problems, such as the use of hazardous solvents and/or reagents (Mo, V, Cu, Mn), extended times (Fe, Mo), low chemoselectivity (Ti, Fe, V, W, Re), and rare elements (Re, Au).

Recently, we reported several new synthetic methods for environmentally benign reactions using aqueous 30% hydrogen peroxide.[5] During the course of these studies, we found that tantalum(V) compounds, which have seldom been used as oxidation catalysts, are an excellent catalyst for the oxidation of sulfides using aqueous 30% hydrogen peroxide.[6] As we recently reported in a preliminary communication, [6] the reaction of sulfides (**1**) with 30% hydrogen peroxide catalyzed by tantalum(V) chloride in acetonitrile, *i*-propanol, or *t*-butanol selectively produces the corresponding sulfoxides (**2**). The reaction of **1** with 30% hydrogen peroxide catalyzed by tantalum(V) chloride or tantalum(V) ethoxide in methanol effectively afforded the corresponding sulfones (**3**) (Scheme 1). Tantalum(V) catalyzed oxidations of **1** with hydrogen



Scheme 1.

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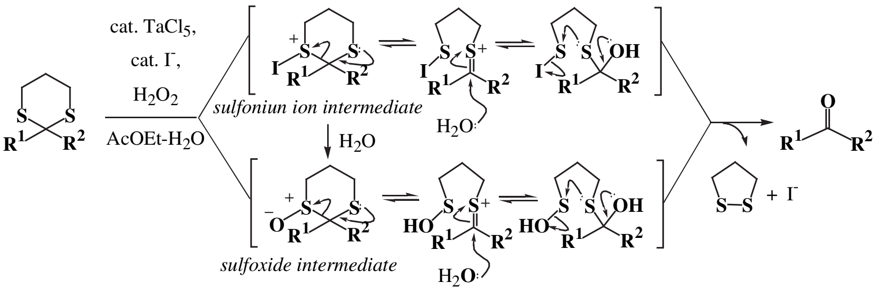


Scheme 2.

peroxide are highly chemoselective, and tantalum compounds are ideal for 'green chemistry', because they are non-toxic to animals.[7]

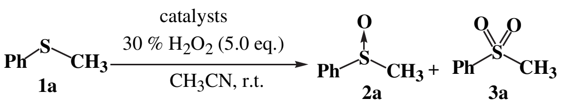
This paper further describes the details of the tantalum(V) catalyzed oxidation of sulfides with 30% hydrogen peroxide and also reports niobium(V)-catalyzed oxidation of sulfides with 30% hydrogen peroxide.

2. Tantalum(V)-catalyzed oxidation of sulfides with 30% hydrogen peroxide

Recently, we found that the treatment of 1,3-dithianes with 30% hydrogen peroxide in the presence of a catalytic amount of tantalum(V) chloride and sodium iodide provided the carbonyl compounds in high yield.[5b] This reaction is the result of oxidation of the sulfur atom of the 1,3-dithiane via a sulfonium ion and/or sulfoxide intermediate (Scheme 2); therefore, by extension, it should be possible to oxidize sulfides under similar reaction conditions.

The oxidation of thioanisole (**1a**) in acetonitrile with 5 equiv of 30% hydrogen peroxide[8] using tantalum(V) chloride as a catalyst in the presence or absence of sodium iodide was investigated first (Table 1). Thioanisole (**1a**) was oxidized with hydrogen peroxide in the absence of a catalyst to produce the sulfoxide (**2a**); however, it took quite some time to complete the oxidation (run 1). Tantalum(V) chloride was an excellent oxidation catalyst and was effective even in the absence of sodium iodide (runs 2–4). The sulfoxide (**2a**) was efficiently obtained in all cases. The sulfone (**3a**) was a minor product (less than 10% yield) even for a long reaction time (24 h, run 4). Urea hydrogen peroxide (UHP) was not a good oxidant for the oxidation of sulfide catalyzed by tantalum(V) chloride (run 5). Interestingly, a stoichiometric amount of sodium iodide inhibited the oxidation of thioanisole with hydrogen peroxide catalyzed by tantalum(V) chloride (run 7).

Table 1

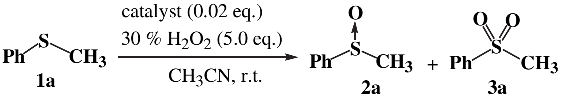


Run	$TaCl_5$ (equiv)	NaI (equiv)	Time (h)	Yield[a] (%)		
				1a	**2a**	**3a**
1	—	—	20.0	0	98.0	2.0
2	0.10	—	0.5	0	93.8	6.2
3	0.02	—	1.75	0	95.2	4.8
4	0.02	—	24.0	0	90.8	9.2
5[b]	0.02	—	30.0	43.2	56.8	0
6	0.10	0.10	1.0	0	88.2	11.8
7	0.10	1.00	24.0	94.9	5.1	0

[a] Determined by ^1H NMR (methyl protons).

[b] UHP was used instead of 30% H_2O_2.

Table 2



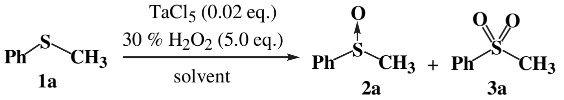
Run	Catalyst	Time (h)	Yield[a] (%)		
			1a	**2a**	**3a**
1	**$TaCl_5$**	1.75	0	96	4
2	**$Ta(OEt)_5$**	5.0	0	72	28
3	**Ta_2O_5**	20.0	0	94	6
4	—	20.0	0	92	2

[a] Determined by ^1H NMR (methyl protons).

The oxidation of **1a** with 30% hydrogen peroxide was then investigated using several other tantalum(V) compounds as catalysts in acetonitrile (Table 2). Tantalum(V) chloride and tantalum(V) ethoxide have catalytic activities for the oxidation of **1a** with hydrogen peroxide. However, tantalum(V) oxide was ineffective.

The oxidations of **1a** with 30% hydrogen peroxide using tantalum(V) chloride as a catalyst were examined in several solvents (Table 3). The less polar solvents constituting a heterogeneous solvent system with aqueous hydrogen peroxide were not effective (runs 1–3). In polar solvents, **1a** was efficiently oxidized into the corresponding sulfoxide (**2a**) and/or sulfone (**3b**) (runs 4–14). The oxidative ability of this reaction system in more polar (or less sterically hindered) solvents (run 4: CH_3CN, run 7: CH_3OH, run 10: EtOH) is greater than that in less polar (or more sterically hindered) solvents (run 5: CH_3CH_2CN, run 11: *i*-PrOH, run 13: *t*-BuOH). The best conditions for preparation of the sulfoxide (**2a**) selectively are the reaction in CH_3CN at rt (run 4), in *i*-PrOH at 45 °C (run 12), or in

Table 3



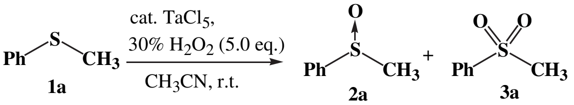
Run	Solvent	Time (h)	Temp.	Yield[a] (%)		
				1a	**2a**	**3a**
1	CH_2Cl_2	5.5	rt.	28	23	49
2	toluene	5.5	rt.	50	2	48
3	AcOEt	5.5	rt.	17	52	25
4	CH_3CN	3.0	rt.	0	95	5
5	CH_3CH_2CN	3.0	rt.	11	82	7
6	CH_3CH_2CN	7	rt.	0	19	21
7	CH_3OH	0.5	rt.	0	86	14
8	CH_3OH	8.5	rt.	0	3	97
9	CH_3OH	1.5	45 °C	0	1	99
10	EtOH	0.5	rt.	7	87	6
11	*i*-PrOH	0.5	rt.	34	66	0
12	*i*-PrOH	0.3	45 °C	0	95	5
13	*t*-BuOH	0.5	rt.	36	64	0
14	*t*-BuOH	1.5	45 °C	1	96	3

[a] Determined by ^1H NMR (methyl protons).

t-BuOH at 45 °C (run 14). The ideal condition for synthesis of the sulfone (**3a**) is the reaction in CH_3OH at 45 °C (run 9).

The amount of tantalum(V) chloride (Table 4) and 30% hydrogen peroxide (Table 5) required to prepare the sulfoxide (**2a**) via the oxidation of **1a** in acetonitriles was further examined. The optimum conditions are the treatment of **1a** with 5 equiv of peroxide in the presence of 0.02 equiv of tantalum.

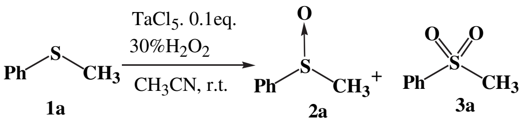
Table 4



Run	$TaCl_5$ (equiv)	Time (h)	Ratio[a]		
			1a	**2a**	**3a**
1	0.08	0.5	0	96	4
2	0.06	1	0	96	4
3	0.04	1	5	93	2
4	0.02	2.5	0	95	5
5	0.01	3	0	92	7
6	0	20	0	98	2

[a] Determined by ^1H NMR (methyl protons).

Table 5

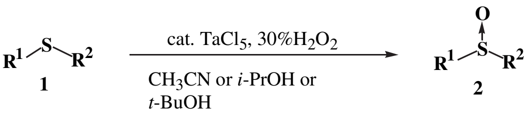


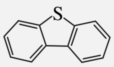
Run	30% H_2O_2 (equiv)	Time (h)	Ratio[a]	
			b	c
1	5.0	0.5	94	6
2	4.0	0.75	94	6
3	3.0	0.83	89	11
4	2.0	0.83	88	12

[a] Determined by ^1H NMR (methyl protons).

In order to further examine the sulfoxide (**2**) synthesis, several sulfides (**1**) were treated with 30% hydrogen peroxide in the presence of catalytic amounts of tantalum(V) chloride in acetonitrile, *i*-propanol and *t*-butanol (Table 6). The sulfoxides (**2**) were selectively obtained in all cases. It is notable that the olefin moiety was not oxidized at all (entry 2). Although, 0.1 equiv of tantalum and 20 equiv of peroxide were required for the diaromatic sulfides, the corresponding sulfoxides were still obtained in relatively high yields (entries 9–12).

Table 6

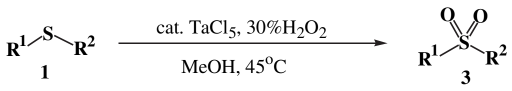


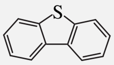
Entry	R^1	R^2	Solvent	$TaCl_5$ (equiv)	H_2O_2 (equiv)	Time (h)	Temp.	Yield[a] (%)
1	Ph	$CH_2{=}CHCH_2$	CH_3CN	0.02	5	1.5	rt.	95
2	Ph	$PhCH_2$	CH_3CN	0.02	5	2	rt.	95
3			*i*-PrOH	0.02	5	3.25	45 °C	94
4			*t*-BuOH	0.02	5	3	45 °C	99
5	$PhCH_2$	$PhCH_2$	CH_3CN	0.02	5	1	rt.	99
6			*i*-PrOH	0.02	5	0.3	45 °C	94
7			*t*-BuOH	0.02	5	0.7	45 °C	92
8	$PhCH_2$	CH_3	CH_3CN	0.02	5	0.5	rt.	96
9	Ph	Ph	CH_3CN	0.1	20	2	rt.	90
10			*i*-PrOH	0.1	20	1.25	45 °C	83
11			*t*-BuOH	0.1	20	2	45 °C	81
12			CH_3CN	0.1	20	8.5	50 °C	16

[a] Isolated yields.

The treatment of several sulfides with 30% hydrogen peroxide in the presence of catalytic amounts of tantalum(V) chloride in methanol at 45 °C effectively afforded the corresponding sulfones (**3**) in all cases (Table 7). The olefin moiety remained inactive under the reaction conditions (entry 1). For the less reactive diaromatic sulfides, 0.1 equiv of tantalum chloride and 20 equiv of hydrogen peroxide were required to produce **3** in high yields (entries 5, 6).

Table 7



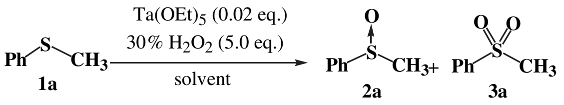
Entry	R^1	R^2	$TaCl_5$ (equiv)	H_2O_2 (equiv)	Time (h)	Yield[a] (%)
1	Ph	$CH_2{=}CHCH_2$	0.02	5	3	99
2	Ph	$PhCH_2$	0.02	5	2.5	96
3	$PhCH_2$	$PhCH_2$	0.02	5	2.5	99
4	PhCH	CH_3	0.02	5	0.25	97
5	Ph	Ph	0.1	20	3.5	90
6			0.1	20	20	98

[a] Isolated yields.

The oxidation of **1a** with 30% hydrogen peroxide using tantalum(V) ethoxide as a catalyst was then examined in several solvents (Table 8). Although **2a** was not selectively obtained in all cases, **3a** was efficiently produced in methanol at 45 °C (run 6).

Based on these results, the oxidation of several sulfides with 30% hydrogen peroxide in methanol using tantalum(V) ethoxide as a catalyst was further examined in methanol to obtain the corresponding sulfone (Table 9). The sulfones (**3**) were obtained in almost quantitative yields. As in the cases of tantalum(V) chloride, the olefin moiety did not react at all (entry 2). For the less reactive diaromatic sulfides, 0.1 equiv of tantalum(V) and 20 equiv of peroxide were required to complete the reaction (entry 5).

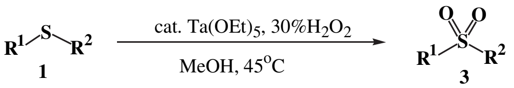
Table 8



Run	Solvent	Time (h)	Temp.	Yield[a] (%)		
				1a	2a	3a
1	CH_3CN	5	rt.	0	72	28
2	CH_3OH	0.17	rt.	0	77	23
3	CH_3OH	4	rt.	0	0	100
4	CH_3OH	2	35 °C	0	0	100
5	CH_3OH	1.3	40 °C	0	0	100
6	CH_3OH	1	45 °C	0	0	100
7	EtOH	0.17	rt.	0	86	14
8	EtOH	20	45 °C	0	15	85
9	*i*-PrOH	1	rt.	2	90	8
10	*i*-PrOH	20	45 °C	0	46	54
11	*t*-BuOH	3	rt.	2	90	8
12	*t*-BuOH	20	45 °C	0	64	36

[a] Determined by H NMR (methyl protons).

Table 9



Entry	R^1	R^2	$TaCl_5$ (equiv)	H_2O_2 (equiv)	Time (h)	Yield[a] (%)
1	Ph	CH_3	0.02	5	1	99
2	Ph	$CH_2{=}CHCH_2$	0.02	5	1.3	quant.
3	Ph	$PhCH_2$	0.02	5	2.5	99
4	$PhCH_2$	$PhCH_2$	0.02	5	2.5	97
5	Ph	Ph	0.1	20	3	98

[a] Isolated yields.

3. Oxidation of sulfides with 30% hydrogen peroxide catalyzed by niobium(V)

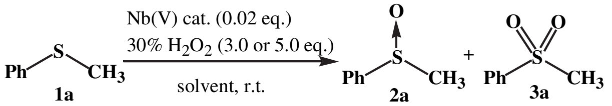
Although niobium is also in Group VB with tantalum, some niobium compounds have been studied as catalysts for the oxidation of organic compounds. For example, $LiNbMoO_6$ catalyzes the selective oxidation of allylic sulfides by hydrogen peroxide,[9] and Nb(salen) catalyzes the asymmetric sulfoxidation of sulfides by urea–hydrogen peroxide adducts.[10] However, simple niobium(V) salts, such as niobium(V) chloride or niobium(V) ethoxide, have not been examined for their catalytic activity toward the oxidation of sulfides with hydrogen peroxides. Simple niobium(V) salts are expected to have catalytic activity similar to the simple tantalum(V) salts [$TaCl_5$ and $Ta(OEt)_5$] with respect to the oxidation of sulfides.

The reaction of**1a** with 30% hydrogen peroxide was examined in the presence of 0.02 equiv of niobium(V) salt in several solvents (Table 10). All showed catalytic activity for the oxidation of **1a** with hydrogen peroxide.

It is interesting that niobium(V) oxide possesses catalytic activity (runs 7–9), in sharp contrast to tantalum(V) oxide, which did not show any catalytic activity (Table 2 run 3). Furthermore, the catalytic activity of niobium(V) chloride and niobium(V) ethoxide was higher than that of the corresponding tantalum(V) salts.

Because of this, and based on the results shown in Table 10, niobium(V) chloride was expected to be a good catalyst for the selective synthesis of sulfoxides, and niobium(V) ethoxide was expected to be an ideal catalyst for the selective synthesis of sulfones.

Table 10

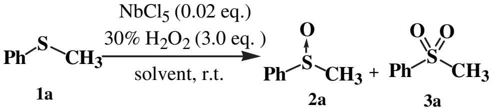


Run	Catalyst	Solvent	Time (h)	Yield[a] (%)	
				2a	3a
1	$NbCl_5$	CH_3CN	0.2	92	8
2	3.0 equiv H_2O_2	CH_3OH	4.0	0	100
3		*i*-PrOH	0.1	66	34
4	$Nb(OEt)_5$	CH_3CN	0.1	0	100
5	5.0 equiv H_2O_2	CH_3OH	0.17	0	100
6		Org. Solv. Free	0.5	0	100
7	Nb_2O_5	CH_3CN	7.0	91	9
8	5.0 equiv H_2O_2	CH_3OH	3.0	96	4
9		CH_3OH	24.0	0	100
10	No catalyst	CH_3CN	20.0	98	2
11	5.0 equiv H_2O_2	CH_3OH	14.0	90	10

[a] Determined by ^1H NMR (methyl protons).

Therefore, the oxidation of **1a** with 30% hydrogen peroxide using niobium(V) chloride as a catalyst was further examined for the effect of the solvent (Table 11). The less polar solvents (toluene and ethyl acetate) were similarly ineffective, as in the case of the tantalum(V) analog (runs 1 and 2). Acetonitrile was the best solvent for the synthesis of the sulfoxide (**2a**) (run 6).

Table 11

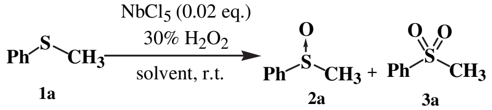


Run	Solvent	Time	Yield[a] (%)		
			1a	2a	3a
1	Toluene	6.5 h	1	7	93
2	AcOEt	5.0 h	2	57	41
2	CH_3OH	2 min	0	26	74
4	CH_3OH	1.0 h	0	2	98
5	EtOH	2 min	0	34	66
6	CH_3CN	7 min	0	92	8

[a] Determined by ^1H NMR (methyl protons).

The amount of niobium(V) chloride and 30% hydrogen peroxide required to prepare **2a** from **1a** in acetonitrile was then examined, and it was found that the reaction of **1a** with 1.3 equiv of 30% hydrogen peroxide in the presence of 0.02 equiv of niobium(V) chloride at rt was ideal (Table 12).

Table 12

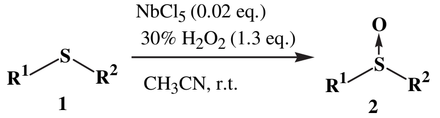


Run	30% H_2O_2 (equiv)	Time (h)	Yield[a] (%)		
			1a	2a	3a
1	3.0	0.1	0	92	8
2	2.0	0.4	0	92	8
3	1.3	0.5	0	93	7

[a] Determined by ^1H NMR (methyl protons).

A variety of sulfides was reacted with peroxide in the presence of niobium(V) using these ideal reaction conditions to effectively produce the corresponding sulfoxides (Table 13). The olefin moiety of

Table 13



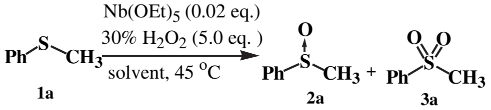
Entry	R^1	R^2	Time (h)	Yield[a] (%)
1	Ph	CH_3	0.5	86
2	Ph	CH_2Ph	1.5	76
3	Ph	$CH_2{=}CHCH_2$	0.4	80
4	$PhCH_2$	$PhCH_2$	0.8	93
5	Ph	Ph	2.0	78

[a] Isolated yield.

the sulfide was unchanged under the reaction conditions (entry 3). Even in the case of the less reactive diaromatic sulfide, the corresponding sulfoxide was effectively obtained (entry 5).

The solvent effect on the oxidation of **1a** with 30% hydrogen peroxide using niobium(V) ethoxide as a catalyst was examined next (Table 14). The corresponding sulfone (**3a**) was efficiently obtained in most cases. The more polar solvents such as methanol provided **3a** within a shorter reaction time. The amounts of 30% hydrogen peroxide required to oxidize **1a**–**3a** in methanol were then examined, and it was found that the reaction of **1a** with 3.0 equiv of 30% hydrogen peroxide in the presence of 0.02 equiv of niobium(V) chloride at 45 °C was ideal (Table 15).

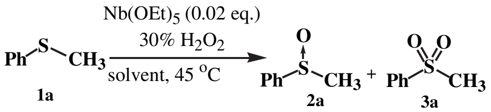
Table 14



Run	Solvent	Time (h)	Yield[a] (%)		
			1a	**2a**	**3a**
1	Toluene	2.5	20	6	74
2	AcOEt	2.5	0	0	100
3	CH_3OH	0.1	0	0	100
4	EtOH	0.1	0	0	100
5	CH_3CN	0.7	0	0	100
6	Org. Solv. Free	0.5	0	0	100

[a] Determined by ^1H NMR (methyl protons).

Table 15

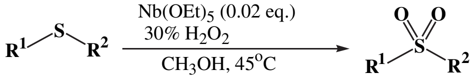


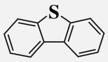
Run	30% H_2O_2 (equiv)	Time (h)	Yield[a] (%)	
			2a	**3a**
1	5.0	0.1	0	100
2	4.0	0.25	0	100
3	3.0	1.0	0	100
4	2.1	12.0	9	91

[a] Determined by ^1H NMR (methyl protons).

Several sulfides were treated with 30% hydrogen peroxide in the presence of niobium(V) ethoxide under the ideal reaction conditions to afford the corresponding sulfones in excellent yields (Table 16). The olefin moiety of the sulfide did not react under the reaction conditions (entry 3). In the case of the less reactive diaromatic sulfides, 4 equiv of 30% hydrogen peroxide were required to produce the sulfones (entries 6 and 7).

Table 16

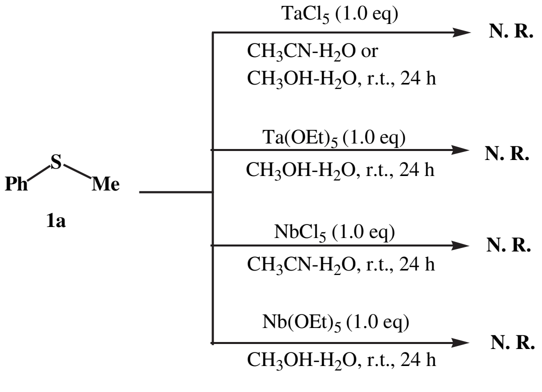


Entry	R^1	R^2	30% H_2O_2 (equiv)	Time (h)	Yield[a] (%)
1	Ph	CH_3	3.0	1.0	quant.
2	Ph	$CH_2{=}CHCH_2$	3.0	1.0	98
3	Ph	$PhCH_2$	3.0	1.5	98
4	$PhCH_2$	CH_3	3.0	0.75	quant.
5	$PhCH_2$	$PhCH_2$	3.0	1.5	95
6	Ph	Ph	4.0	3.0	98
7			4.0	3.0	98

[a] Isolated yield.

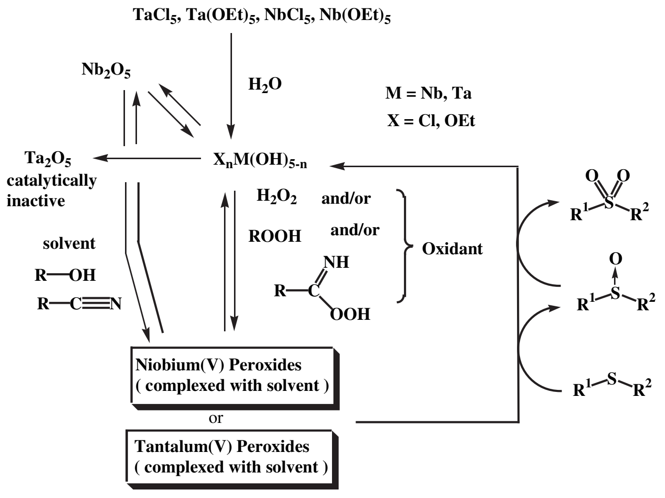
4. Reaction mechanism

To investigate the reaction mechanism, **1a** was treated with an equimolar amount of tantalum(V) or niobium(V) in aqueous acetonitrile or aqueous methanol in the absence of hydrogen peroxide. In all cases, **1a** was completely unreacted and was quantitatively recovered. These results indicate that tantalum(V) and niobium(V) themselves are not the oxidizing agent in the reaction system (Scheme 3).



Scheme 3.

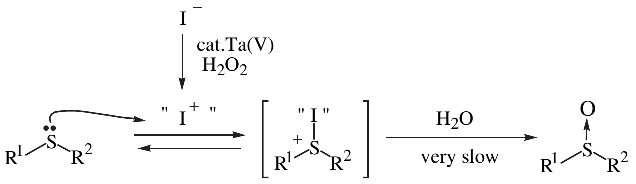
A plausible reaction mechanism is shown in Scheme 4. Tantalum(V) or niobium(V) immediately reacts with water to form tantalum(V) or niobium(V) hydroxides. The resulting hydroxides react with hydrogen peroxide or peroxides derived from the reaction of hydrogen peroxide with the solvents (alcohols or nitriles) to produce tantalum(V) or niobium(V) peroxides. Because tantalum(V) and niobium(V) compounds act as Lewis acid,[11,12] alcohols and nitriles coordinate with the metal peroxides to produce tantalum(V) or niobium(V) peroxide complexes. These peroxide complexes oxidize sulfides or sulfoxides and revert to tantalum(V) or niobium(V) hydroxides (or the complex of the solvent). The resulting tantalum(V) or niobium(V) hydroxides then react with peroxide to reform the tantalum(V) or niobium(V) peroxide complexes. Unfortunately, the chemistry of tantalum(V) and niobium(V) peroxides is fundamentally unknown, even in inorganic chemistry. Therefore, the exact structure of the peroxide complexes is unclear. Although the solvent effect is not perfectly clear, it is assumed that the coordinative properties of the solvents affect the oxidative ability of the tantalum(V) or niobium (V) peroxides. Tantalum(V) hydroxides gradually are converted into inactive tantalum(V) oxide.[13] Although niobium(V) hydroxides are also converted into niobium(V) oxide, niobium(V) oxide reacts with hydrogen peroxide (or peroxides derived from the reaction of



Scheme 4.

hydrogen peroxide with solvent) to produce niobium(V) peroxide complexes. Further details of the chemistry of tantalum(V) and niobium(V) peroxide complexes are currently under investigation.

In the presence of sodium iodide, iodo cation equivalents or iodine derived from the oxidation of the iodo anion react with a sulfide to produce an iodosulfonium ion intermediate. The intermediate subsequently reacts with water to form the sulfoxide (Scheme 5). It has been reported that the first step is fast and reversible and that the second step is very slow.[14] The formation of the iodosulfonium ion prevents the reaction of sulfide with a tantalum(V) peroxide complex; therefore, as expected, the sulfides did not produce oxidized products in the presence of a molar equivalent of sodium iodide.



Scheme 5.

5. Conclusion

Sulfides (**1**) were selectively oxidized to sulfoxides (**2**) in a reaction with 30% hydrogen peroxide catalyzed by tantalum(V) chloride or niobium(V) chloride in acetonitrile, *i*-propanol or *t*-butanol. The reaction of **1** with 30% hydrogen peroxide catalyzed by tantalum(V) or niobium(V) compounds in methanol efficiently produced the corresponding sulfones in high yields. The tantalum(V) or niobium(V) peroxides, derived from the reaction of tantalum(V) or niobium(V) with hydrogen peroxide, oxidized sulfides (**1**).

6. Experimental section

6.1. General

NMR spectra were acquired using a JEOL JNM-400 spectrometer. All NMR spectra were acquired using $CDCl_3$ solutions with tetramethylsilane as an internal standard, and the coupling constants (*J*) are given in Hertz (Hz). Mass spectra (electron impact) were recorded on a Shimadzu GC–MS-QP1100EX spectrometer. Melting points were determined with a Yanagimoto micro melting point apparatus and are uncorrected. Column chromatography was performed on silica gel (Merck Kieselger 60). The sulfides, tantalum(V) compounds and niobium(V) compounds were obtained from Wako Pure Chemical Industries, Kanto Kagaku, Nacalai Tesque, Tokyo Kasei Kogyo, or Aldrich, and used without further purification.

6.2. Selective oxidation of sulfides to sulfoxides with 30% hydrogen peroxide catalyzed by tantalum(V) chloride

A mixture of sulfide (**1**) (1.0 mmol), tantalum chloride (7.1 mg, 0.02 mmol; or 35.5 mg, 0.10 mmol), and 30% hydrogen peroxide (0.5 mL, 5 mmol; or 2.0 mL, 20 mmol) in a solvent (acetonitrile, *i*-propanol or *t*-butanol) (2 mL) was stirred at rt (acetonitrile) or 45 °C (*i*-propanol and *t*-butanol). The reaction was monitored by thin layer chromatography (TLC). After **1** disappeared from the TLC, saturated aqueous sodium thiosulfate (15 mL) was added to the reaction mixture, followed by extraction with ethyl acetate (3×20 mL). The combined organic phase was washed with brine, dried over anhydrous magnesium sulfate, and evaporated. Chromatography on silica gel gave the pure sulfoxides (**2**).

6.3. Selective oxidation of sulfides to sulfoxides with 30% hydrogen peroxide catalyzed by niobium(V) chloride

A mixture of sulfide (**1**) (1.0 mmol), niobium chloride (5.4 mg, 0.02 mmol), and 30% hydrogen peroxide (0.13 mL, 1.3 mmol) in acetonitrile (2 mL) was stirred at rt. The reaction was monitored by thin layer chromatography (TLC). After **1** disappeared from the TLC, saturated aqueous sodium thiosulfate (15 mL) was added to the reaction mixture, followed by extraction with ethyl acetate (3×20 mL). The combined organic phase was washed with brine, dried over anhydrous magnesium sulfate, and evaporated. Chromatography on silica gel gave the pure sulfoxides (**2**).

*6.3.1. Methyl phenyl sulfoxide (**2a**)*[4g]. Colorless oil. ^1H NMR ($CDCl_3$) δ: 2.72 (3H, s), 7.48–7.55 (3H, m), 7.64–7.66 (2H, m). ^{13}C NMR ($CDCl_3$) δ: 43.71, 123.28, 129.17, 130.85, 145.42. MS (*m*/*z*) 140 (M^+).

*6.3.2. Allyl phenyl sulfoxide (**2b**)*[15]. Colorless Oil. ^1H NMR ($CDCl_3$) δ: 3.49 (1H, dd, *J*=12.8, 7.6 Hz), 3.58 (1H, dd, *J*=12.8, 7.6 Hz), 5.19 (1H, d, *J*=17.2 Hz), 5.22 (1H, d, *J*=10.0 Hz), 5.59–5.69 (1H, m), 7.49–7.51 (3H, m), 7.56–7.60 (2H, m). ^{13}C NMR ($CDCl_3$) δ: 60.52, 123.60, 124.05, 124.97, 128.78, 130.84, 142.62. MS (*m*/*z*) 166 (M^+).

*6.3.3. Benzyl phenyl sulfoxide (**2c**)*[15]. Colorless crystals, mp 124–126 °C (MeOH), (lit[16]: 123–124 °C). ^1H NMR ($CDCl_3$) δ: 3.99 (1H, d, *J*=12.8 Hz), 4.09 (1H, d, *J*=12.8 Hz), 6.96–6.98 (2H, m), 7.22–7.30 (3H, m), 7.36–7.47 (5H, m). ^{13}C NMR ($CDCl_3$) δ: 63.57, 124.42, 128.24, 128.44, 128.84, 129.12, 130.35, 131.16, 142.74. MS (*m*/*z*) 216 (M^+).

*6.3.4. Dibenzyl sulfoxide (**2d**)*[17]. Colorless crystals, mp: 135 °C (EtOH/H_2O) (lit[17]: 135–136 °C). ^1H NMR ($CDCl_3$) δ: 3.85 (2H, d, *J*=12.8 Hz), 3.91 (2H, d, *J*=12.8 Hz), 7.25–7.38 (10H, m). ^{13}C NMR ($CDCl_3$) δ: 57.22, 128.32, 128.92, 130.11, 130.43. MS (*m*/*z*) 214 (M^+).

*6.3.5. Benzyl methyl sulfoxide (**2e**)*[18]. Colorless oil. ^1H NMR ($CDCl_3$) δ: 2.34 (3H, s), 3.82 (1H, d, *J*=11.4 Hz), 3.91 (1H, d, *J*=11.4 Hz), 7.19–7.27 (5H, m). ^{13}C NMR ($CDCl_3$) δ: 36.89, 59.71, 127.98, 128.52, 129.36, 129.67. MS (*m*/*z*) 154 (M^+).

*6.3.6. Diphenyl sulfoxide (**2f**)*[4g]. Colorless crystals, mp: 70 °C (benzene/pentane) (lit[19]: 72.0–73.0 °C). ^1H NMR ($CDCl_3$) δ: 7.41–7.43 (6H, m), 7.63–7.65 (4H, m). ^{13}C NMR ($CDCl_3$) δ: 124.70, 129.29, 131.03, 145.53. MS (*m*/*z*) 202 (M^+).

*6.3.7. Dibenzothiophen-5-oxide (**2g**)*[20]. Pale yellow crystals, mp: 195 °C (EtOH) (lit[20]: 189 °C). ^1H NMR ($CDCl_3$) δ: 7.48–7.52 (2H, m), 7.58–7.62 (2H, m), 7.81 (2H, d, J=7.8 Hz), 7.99 (2H, d, J=7.8 Hz). ^{13}C NMR (CDCl$_3$) δ: 121.87, 127.51, 129.52, 132.53, 137.07, 145.13. MS (m/z) 200 (M^{+}).

6.4. Oxidation of sulfides to sulfones with 30% hydrogen peroxide catalyzed by a tantalum(V) compound

A mixture of sulfide (**1**) (1.0 mmol), tantalum chloride (7.1 mg, 0.02 mmol; or 35.5 mg, 0.10 mmol) or tantalum pentaethoxide (8.1 mg, 0.02 mmol; or 40.5 mg, 0.10 mmol), and 30% hydrogen peroxide (0.5 mL, 5 mmol; or 2.0 mL, 20 mmol) in a methanol (2 mL) was stirred at 45 °C. The reaction was monitored by thin layer chromatography (TLC). After **1** disappeared from the TLC, saturated aqueous sodium thiosulfate (15 mL) was added to the reaction mixture, followed by extraction with ethyl acetate (3×20 mL). The combined organic phase was washed with brine, dried over anhydrous magnesium sulfate, and evaporated. Chromatography on silica gel gave the pure sulfones (**3**).

6.5. Oxidation of sulfides to sulfones with 30% hydrogen peroxide catalyzed by a niobium pentaethoxide

A mixture of sulfide (**1**) (1.0 mmol), niobium pentaethoxide (6.4 mg, 0.02 mmol), and 30% hydrogen peroxide (0.3 or 0.4 mL; 3 or 4 mmol) in methanol (2 mL) was stirred at 45 °C. The reaction was monitored by thin layer chromatography (TLC). After **1** disappeared from the TLC, saturated aqueous sodium thiosulfate (15 mL) was added to the reaction mixture, followed by extraction with ethyl acetate (3×20 mL). The combined organic phase was washed with brine, dried over anhydrous magnesium sulfate, and evaporated. Chromatography on silica gel gave the pure sulfones (**3**).

*6.5.1. Methyl phenyl sulfone (**3a**)*[4g]. Colorless crystals, mp: 86 °C (EtOH) (lit[21]: 89–90 °C). ^{1}H NMR (CDCl$_3$) δ: 3.06 (3H, s), 7.55–7.59 (2H, m), 7.64–7.67 (1H, m), 7.93–7.95 (2H, m). ^{13}C NMR (CDCl$_3$) δ: 44.92, 121.56, 122.14, 130.356, 131.58, 133.86, 137.68. MS (m/z) 156 (M^{+}).

*6.5.2. Allyl phenyl sulfone (**3b**)*[22]. Colorless oil. ^{1}H NMR (CDCl$_3$) δ: 3:81 (2H, d, J=7.2 Hz), 5.15 (1H, d, J=17.2 Hz), 5.33 (1H, d, J=10 Hz), 5.75–5.85 (1H, m), 7.54–7.58 (2H, m), 7.64–7.68 (1H, m) 7.87–7.89 (2H, m). ^{13}C NMR (CDCl$_3$) δ: 60.84, 124.60, 124.70, 128.47, 129.03, 133.73, 138.25. MS (m/z) 183 (M^{+}).

*6.5.3. Benzyl phenyl sulfone (**3c**)*[23]. Colorless crystals, mp: 147 °C (Et$_2$O–hexane) (lit[24]: 142–145 °C). ^{1}H NMR (CDCl$_3$) δ: 4.30 (2H, s), 7.06–7.08 (2H, m), 7.22–7.32 (3H, m), 7.42–7.45 (2H, m), 7.56–7.63 (3H, m). ^{13}C NMR (CDCl$_3$) δ: 62.74, 128.01, 128.45, 128.49, 128.64, 128.78, 130.71, 133.61, 137.74. MS (m/z) 232 (M^{+}).

*6.5.4. Dibenzyl sulfone (**3d**)*[4g]. Colorless crystals, mp: 152 °C (EtOH) (lit[18]: 150–152 °C). ^{1}H NMR (CDCl$_3$) δ: 4.11 (4H, s), 7.37–7.39 (10H, m). ^{13}C NMR (CDCl$_3$) δ: 57.99, 127.54, 128.31, 128.91, 128.94, 128.97, 130.13, 130.86. MS (m/z) 246 (M^{+}).

*6.5.5. Benzyl methyl sulfone (**3e**)*[25]. Colorless crystals, mp: 127 °C (MeOH) (lit[26]: 126–127 °C). ^{1}H NMR (CDCl$_3$) δ: 2.76 (3H, s) 4.26 (2H, s), 7.40–7.42 (5H, m). ^{13}C NMR (CDCl$_3$) δ: 39.03, 61.03, 128.33, 129.11, 130.54. MS (m/z) 170 (M^{+}).

*6.5.6. Diphenyl sulfone (**3f**)*[4g]. Colorless crystals, mp: 123 °C (petroleum ether) (lit[18]: 127 °C). ^{1}H NMR (CDCl$_3$) δ: 7.45–7.55 (6H, m), 7.93–7.95 (4H, m). ^{13}C NMR (CDCl$_3$) δ: 127.57, 129.27, 133.20, 141.52. MS (m/z) 218 (M^{+}).

*6.5.7. Dibenzothiophene-5,5-dioxide (**3g**)*[4g]. Pale yellow crystals, mp: 237 °C (EtOH) (lit[20]: 232.0–232.5 °C). ^{1}H NMR (CDCl$_3$) δ: 7.50–7.54 (2H, m), 7.61–7.65 (2H, m), 7.78–7.80 (2H, m), 7.81–7.83 (2H, m). ^{13}C NMR (CDCl$_3$) δ: 121.56, 122.14, 130.35, 131.58, 133.86, 137.68. MS (m/z) 216 (M^{+}).

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