Metal-ion mediated deoxygenation of sulfoxides

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CONTENTS

ABSTRACT

Over the past two decades, the deoxygenation (i.e. the reduction of the sulfinyl group) of free sulfoxides, $R_2S{=}O$, has been extensively studied and described in a number of reviews. However, the deoxygenation of coordinated sulfoxide ligands and metal-ion mediated deoxygenation of sulfoxides has received much less attention and no general overview of these processes has been presented. Correcting that omission is the major goal of this review. Although details of syntheses that involve the deoxygenation of sulfoxide ligands are presented, particular emphasis is placed on discussion of both the common features and differences in the reactions of S- and O-bonded sulfoxides. Along with general consideration of experimental results, an attempt is made to show that most of the methods for the reduction of the very strong S–O bond in S-coordinated R_2SO ligands are based on an initial activation of the sulfinyl oxygen by a reagent having a highly reactive electrophilic center. In contrast, in the case of O-bound sulfoxides, the metal ion itself plays the role of the electrophilic reagent and thus promotes the deoxygenation reaction. In order to provide a clearer picture of sulfoxide deoxygenation reactions, possible reaction pathways are discussed and evidence for these mechanisms is provided.

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1. INTRODUCTION

Interest in the chemistry of sulfoxides is largely due to the rôle that sulfoxides, $R_2S{=}O$, have played, and still play, in chemistry as ligands, reagents and solvents. One of the most fundamental chemical properties of R_2SO is their ability to undergo deoxygenation or, in other words, reduction of the sulfinyl group to give the corresponding sulfide R_2S. While a large amount of information is available on the deoxygenation of free sulfoxides (Table 1), no comprehensive work has been pre-

TABLE 1
Selected articles on deoxygenation of free sulfoxides (books and reviews)

Description of article	Authors and year of publication	Reference
First brief compilation of literature data (until 1960) on deoxygenation of sulfoxides	H.H. Szmant, 1961	1
Oxidations by activated dimethyl sulfoxide	W.W. Epstein and F.W. Sweat, 1967	2
Deoxygenation of DMSO by some metals and metal ions, hydrohalic acids, B- and P-containing reductants, as well as reduction of activated Me_2SO; a review of kinetic studies on the interaction of DMSO and HX acids	D. Martin and H.G. Hauthal, 1975	3
Reductions with HX, P(III)- and S-reducing agents, various metal hydrides, some metal ions, as well as deoxygenation of sulfoxides activated by acid halides	J. Drabowicz, T. Numata, and S. Oae, 1977	4
Reactions of dimethyl sulfoxide activated by electrophiles	A.J. Mancuso and D. Swern, 1981	5
Deoxygenations by P(III)-, P(V)-, S-, and B-containing reductants; reductions with organosilicon, some metal ions and Grignard reagents	J. Drabowicz, H. Togo, M. Mikolajczyk and S. Oae, 1984	6
Comprehensive review of the reduction of sulfoxides by P-, B-, and Si-containing reagents, by $Na[BH_4]$ and by metals	J.S. Grossert, 1988	7
Comprehensive review of the reduction of sulfoxides by HX, P-, S-, B-, and Si-containing reagents, by $Na[BH_4]$ and by some metal ions	M. Madesclaire, 1988	8
Reduction by metal hydrides, carbenes, P(III)-, I-, and S-containing reductants; brief survey of deoxygenation by metals and metal ions	S. Oae, 1991	9

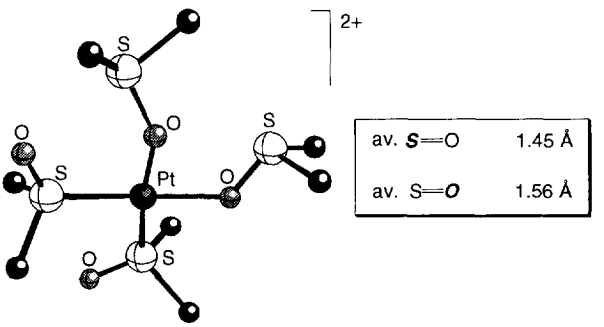
sented on metal-ion mediated deoxygenations of R_2SO with an emphasis on the reduction of coordinated ligands. Correcting that omission is the goal of this review.

Wood has determined the standard redox potential of the $Me_2S{=}O/Me_2S$ couple

$$Me_2S{=}O + H^+ + 2e^- \rightleftharpoons Me_2S + 2H_2O$$

in water at pH 7, which is equal to +0.16 V [10]. This value and values of redox potentials for some other R_2SO [11, 12] show that free sulfoxides posess only weak oxidizing abilities. However, the reactivity of R_2SO molecules changes significantly when coordinated. It is possible to evaluate these changes by consideration of the S–O bond distances in free, O-protonated, and both S- and O-coordinated sulfoxides (Table 2).

The S–O bond lengths given in Table 2 are averages calculated from data for a large number of sulfoxides and sulfoxide complexes [13]. Structural data for *cis*-$[Pt(O{-}Me_2SO)_2(S{-}Me_2SO)_2][CF_3SO_3]_2$ illustrate specifically a difference in the S–O bond distances between O- and S-bound ligands [14]:



Inspection of the data in Table 2 and those presented above indicates that (i) the S–O bond lengths in O-protonated or O-bound sulfoxides are longer than those in the corresponding free R_2SO molecule, and (ii) the S–O bonds in *S*-bound sulfoxides are shorter than those in the corresponding free R_2SO molecules. Although the S–O bond dissociation energies of coordinated sulfoxides have not yet been measured, it is probably reasonable to assume that the S–O bonds are stronger in S-bound and weaker in O-bound R_2SO ligands than in free sulfoxides. In turn, this implies that it will be more difficult to abstract oxygen from S-bound sulfoxides than

TABLE 2

Average S–O bond lengths in free, O-protonated, and both O- and S-coordinated sulfoxides [13]

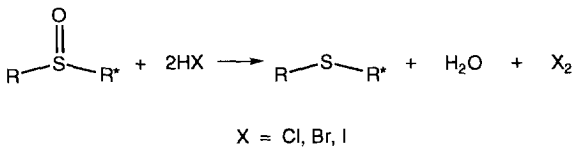
Type of R_2SO	Free $R_2S{=}O$	$[R_2S{=}OH]^+$	$M{-}S(=O)R_2$	$M{-}O{=}SR_2$
Average S–O (Å)	1.492(1)	1.585(8)	1.473(1)	1.540(2)

from O-bound sulfoxides. It is noteworthy that the S–O bond distances in S-coordinated sulfoxides are very close to those found in sulfones R_2SO_2 (average 1.45 Å [15]), which contain one of the strongest S–O bond types known. This property of the S=O group in R_2SO_2 is reflected in the chemistry of sulfones, which are normally unreactive towards a variety of deoxygenation reagents [7].

Here we attempt to show that most of the methods for the reduction of the very strong S–O bond in *S*-coordinated R_2SO are based on an initial activation of the sulfinyl oxygen by a reagent having a highly reactive electrophilic center. In contrast, in the case of *O*-bound sulfoxides, a metal ion itself plays the part of the electrophilic reagent and thus promotes the deoxygenation reaction.

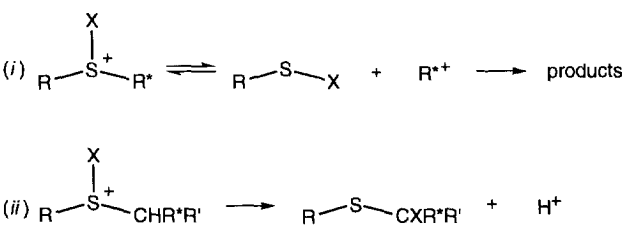
2. REACTIONS INVOLVING HYDROHALIC ACIDS

The first studies on the deoxygenation of free sulfoxides involving HX (X = Cl, Br, I) were carried out at the begining of the 20th century [16–20]. It was noted [4] that in general the reductions of R_2SO by HX may be represented by Scheme 1.



Scheme 1.

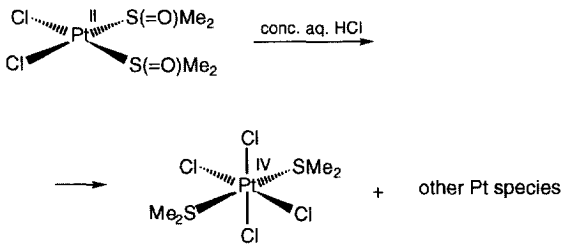
It was established also that the intermediate in this process is the halosulfonium salt $[R\text{-}S(X)\text{-}R^*]^+X^-$ which, depending on X and also the nature of R and R*, is either readily reduced to the corresponding sulfide RSR* or decomposes to form a mixture of products, among which halogenated alkyl sulfides, alkyl halides and methanesulfonic acid thioalkyl ester have been identified. Martin and Hauthal [3] have pointed out that in the case of the reaction between Me_2SO and HCl, formulation of the final products as Me_2S and Cl_2 is somewhat doubtful and it is more likely that the reaction yields $MeSCH_2Cl$. In a general sense, the halosulfonium ion formed during the initial step of the interaction between R_2SO and HX can, apart from reduction of the S=O bond, undergo cleavage of the C–S bond (i) or undergo a Pummerer-type rearrangement (ii), Scheme 2.



Scheme 2.

In summary, despite uncertainty in the nature of some of the products of the reactions, it is clear that hydrohalic acids are able to deoxygenate sulfoxides to produce sulfides.

Deoxygenation of dimethyl sulfoxide (DMSO) in a metal complex was carried out for the first time in 1968 [21] during a study of the reaction between $[PtCl_2(Me_2SO)_2]$ and hydrochloric acid. From IR spectroscopic data and elemental analysis the reaction product was identified as $[PtCl_4(Me_2S)_2]$, Scheme 3. It was



Scheme 3.

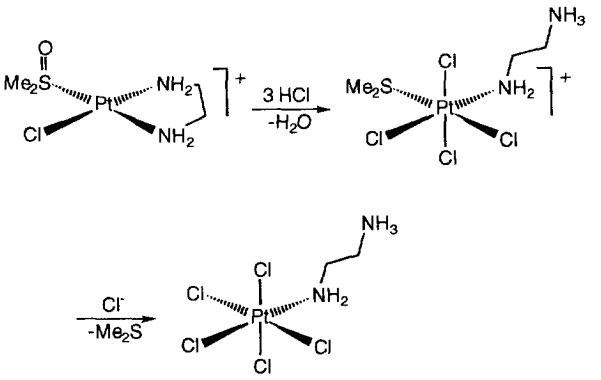
noted, however, that this reaction was accompanied by a number of side reactions and the resulting Pt(IV) complex was contaminated with unidentified Pt-containing products.

Concurrent with the publication just mentioned, Meek et al. [22] reported that when tetramethylene sulfoxide, $(CH_2)_4S{=}O$, reacted with $PdCl_2$ in a hot acetone solution saturated with anhydrous HCl, the teramethylene sulfide compound $[PdCl_2\{(CH_2)_4S\}_2]$ was formed. The authors [22] did not study or discuss the mechanism of this reaction.

In the 1970s the chemistry of sulfoxide complexes started to undergo rapid development [23–29]. However, to our knowledge, only three reports [30–32] on the deoxygenation of metal-bound R_2SO appeared in the literature. Tobe and co-workers [30] observed that $[PtCl(amine)_2(Me_2SO)]Cl$ (amine = various alicyclic primary amines) complexes in aqueous solution containing $HClO_4$ in concentrations stronger than 1.0 M are converted to platinum(IV) compounds with coordinated dimethyl sulfide. These products were neither isolated nor characterized in solution. Later, Romeo and Tobe [31] studied the kinetics of the displacement of amines from *trans*-$[PtCl_2(amine)(Me_2SO)]$ by chloride in an aqueous perchloric acid medium and reported that the $[PtCl_3(Me_2SO)]^-$ complex formed undergoes further reaction at a rate that increases with both the acid and chloride concentrations. Boucher and Bosnich [32] have described a method for the preparation of the complex *cis*-$[PtCl_2(\eta^2\text{-}C_2H_4)(Me_2SO)]$ starting from $K[PtCl_3(Me_2SO)]$ and ethylene in aqueous HCl. It was noted in this case that an excess of acid leads to the Pt-catalyzed reduction of DMSO. However, in this report [32] as well, no experimental details are given.

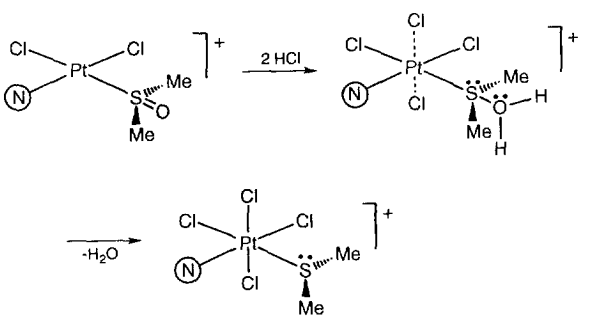
Studies on the deoxygenation of S-bound sulfoxides have recently begun to be more actively pursued. Natile and co-workers reported [33] that the complex

[PtCl(En)(Me_2SO)]Cl reacted with concentrated hydrochloric acid for 2 days at room temperature to give the platinum(IV)-thioether derivative, *cis*-[$PtCl_4$(HEn)(Me_2S)]Cl. The overall process included stages of deoxygenation of S-bound dimethyl sulfoxide, oxidation of Pt(II) to Pt(IV) and one-end displacement of the diamine ligand. On prolonged reaction further substitution, now of Me_2S, was observed and [$PtCl_5$(HEn)] was isolated. The process can be depicted by Scheme 4.



Scheme 4.

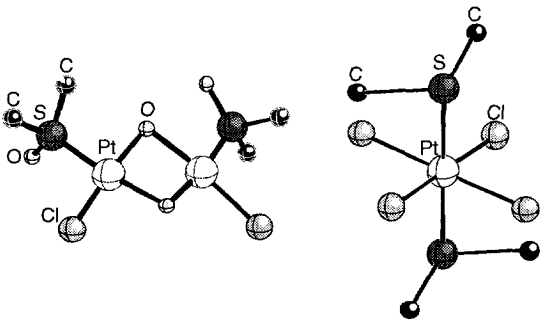
The authors [33] assumed that deoxygenation takes place after ring-opening via a mechanism involving protonation of the S-coordinated DMSO and a concerted two-electron reduction of the ligand and two-electron oxidation of the metal center, Scheme 5 (Ⓝ denotes the monoprotonated diamine ligand).



Scheme 5.

Pakhomova et al. [34] have studied oxo-chloride transformations on interaction of the oxo-bridged dimer H_2[PtCl(μ-O)(Me_2SO)]$_2$ and aqueous HCl at different molar ratios of the reagents. With a molar ratio of 1:3 the chloro-bridged dimer [Pt(μ-Cl)Cl(Me_2SO)]$_2$ is formed. With an increase in the concentration of HCl (molar ratio 1:10) the [Pt(μ-Cl)Cl(Me_2SO)]$_2$ is cleaved out and monomeric H[$PtCl_3$(Me_2SO)] is formed. A side reaction in the treatment of H_2[PtCl(μ-O)(Me_2SO)]$_2$ with HCl leads to the formation of the sulfide complex

trans-$[PtCl_4(Me_2S)_2]$ in isolated yields of 10%–15%. The structures, both for the starting material and the sulfide derivative, were confirmed by X-ray diffraction [34,35]:



The above results [34] clearly show that a Pt(II) sulfoxide complex when treated with concentrated HCl is converted to a dimethyl sulfide derivative of Pt(IV).

The processes discussed above [21,22,30–34] have not been of importance in preparative chemistry. Kukushkin and co-workers [36,37] observed that the deoxygenation of S-bound sulfoxides in Pt(II) complexes may have synthetic value and may be used to prepare sulfide derivatives of platinum(IV). In such cases the syntheses should be carried out not in an aqueous suspension but in non-aqueous solution. For example, on treatment of acetonitrile or nitromethane solutions of $(Et_4N)[PtCl_3(R_2SO)]$, where R = Me, Et, *n*-Pr, CH_2Ph, with gaseous HCl at room temperature, the corresponding $(Et_4N)[PtCl_5(R_2S)]$ complexes are rapidly formed. After subsequent work-up these compounds were isolated in 70%–80% yield. If HBr is used instead of HCl, the reduction of the sulfoxide and oxidation of Pt(II) is accompanied by Cl/Br exchange. As a result of the overall process, $(Et_4N)[PtBr_5(R_2S)]$ complexes were isolated.

Reaction of *cis*-$[PtCl_2(Me_2SO)_2]$ and HCl in acetonitrile, nitromethane or acetone solutions has been monitored by ^1H NMR spectroscopy and TLC [36,37]. It has been observed that *cis*-$[PtCl_4(Me_2S)(Me_2SO)]$ and *cis*-$[PtCl_4(Me_2S)_2]$ are the primary products of the reaction. Over time, the two complexes are subject to *cis–trans* isomerization. A gradual disappearance of *cis*- and *trans*-$[PtCl_4(Me_2S)(Me_2SO)]$ occurs concurrently with the rearrangement. Simultaneously, the concentration of *trans*-$[PtCl_4(Me_2S)_2]$ increases and the latter is the final product in the series of transformations.

In the context of mechanistic pathways for deoxygenations involving HCl, it is important to note that that the reactivity of coordinated and free $(PhCH_2)_2SO$ towards HCl is substantially different. The reaction of S-bound dibenzyl sulfoxide in $(Et_4N)[PtCl_3\{(PhCH_2)_2SO\}]$ with HCl occurs almost completely in favor of formation of the sulfide complex $(Et_4N)[PtCl_5\{(PhCH_2)_2S\}]$ [36,37]. This observation contrasts with the results of Smythe [16] who studied the reaction between free

TABLE 3

Organic products and yields of the reaction between free dibenzyl sulfoxide, $(PhCHa)_2SO$, and HCl [16]

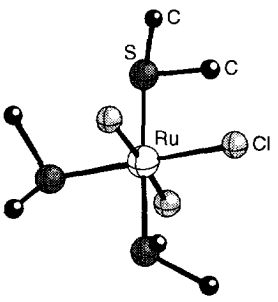
Solvent	Product				
	PhCHO	$PhCH_2Cl$	$(PhCHa)_2S_2$	$(PhCHa)_2S$	$(PhCH_2)S_2O_2$
Ethanol	2	36	15	16	31
Acetic acid	14	33	46	2	7
No solvent	15	30	35	9	12
Water	21	11	34	26	9
Chloroform	28	7	39	26	0

$(PhCH_2)_2SO$ and HCl in different solvents. Such reactions gave several products (Table 3) from which dibenzyl sulfide was isolated with a low yield.

Although the deoxygenation conditions for free and coordinated dibenzyl sulfoxide are not comparable, the differences in the pathways suggest a process assisted by Pt(II) for the deoxygenation of S-bound dibenzyl sulfoxide. The oxidation state of platinum changes during deoxygenation, in support of a Pt-mediated pathway. To the best of our knowledge this example provides the first evidence that the reduction of S-coordinated sulfoxides by HCl is Pt(II) mediated.

Examples of deoxygenation in the systems "[M]-DMSO–HX" are not restricted only to Pt(II) complexes, although examples of reductions involving other metal complexes are scarce. Apart from the previously cited work of Meek et al. [22] on Pd(II), attention should also be paid to the reports of James and co-workers [38]. These authors [38] have studied the reaction between $RuCl_3 \cdot 3H_2O$ and Me_2SO under various conditions. When ruthenium(III) chloride was heated in dimethyl sulfoxide in the presence of concentrated HCl at 85°C for 30 min, followed by concentration and cooling of the solution, crystals of $[(Me_2SO)_2H][RuCl_4(S\text{-}Me_2SO)_2]$ slowly separated out. The latter was structurally characterized.

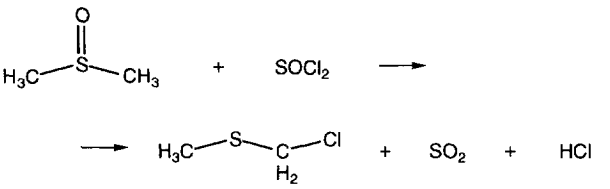
The course of the reaction was different when $RuCl_3 \cdot 3H_2O$ was heated in DMSO at 130–140°C for 1.5 h. In this case *mer*-$[RuCl_3(Me_2S)_3]$ crystallized on cooling of the solution. The structure of *mer*-$[RuCl_3(Me_2S)_3]$ was also determined by X-ray diffraction:



When HBr was used in the synthesis instead of HCl, $[RuBr_3(Me_2S)_3]$ was formed. The authors [38] stated that Me_2S almost certainly arises from reduction of Me_2SO in the acid solution, but the nature of the reductant remains unknown. The results of James and co-workers [38] were later duplicated by Sinitsyn and co-workers [39–41]. Complexes with tetramethylene sulfide, $[RuX_3\{(CH_2)_4S\}_3]$ (X = Cl, Br), have been prepared analogously to those with dimethyl sulfide [42].

3. REACTIONS BETWEEN COORDINATED DMSO IN Pt(II) COMPLEXES AND $SOCl_2$

The ability of thionyl chloride, $SOCl_2$, to deoxygenate free alkyl and aryl sulfoxides is well documented [43–48]. Usually reduction of the sulfinyl group in R_2SO proceeds along with chlorination of R and results in the formation of chloroalkyl or chloroaryl sulfides. For instance, Bordwell and Pitt [43] studied the interaction between Me_2SO and a two-fold excess of $SOCl_2$ in dichloromethane. This reaction gave rise to α-chloromethylmethylsulfide, CH_3SCH_2Cl, which was isolated from the reaction mixture in 92% yield, Scheme 6.

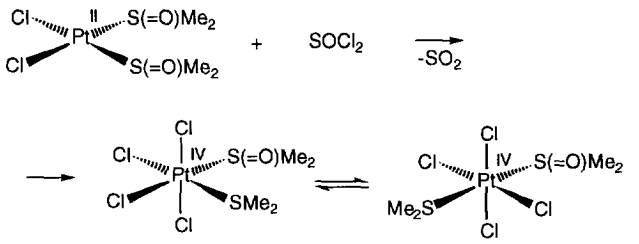


Scheme 6.

When diphenyl sulfoxide, Ph_2SO, reacts with $SOCl_2$, a mixture of diphenyl sulfide and chlorinated diaryl sulfides — Ph_2S, $(p\text{-}ClC_6H_4)SPh$, and $(p\text{-}ClC_6H_4)_2S$ — is formed in the ratio 0.36 : 0.59 : 0.05 respectively [45].

Remarkably, Me_2SO coordinated to Pt(II) reacts with $SOCl_2$ in a different way to free DMSO. It has been reported [46] that the reactions of $(Et_4N)[PtCl_3(Me_2SO)]$ and *cis*-$[PtCl_2(Me_2SO)(Me_2S)]$ with $SOCl_2$ at 20°C in an acetonitrile solution proceed within several minutes and produce dimethyl sulfide derivatives of Pt(IV), $(Et_4N)[PtCl_5(Me_2S)]$ and *cis*-$[PtCl_4(Me_2S)_2]$, as the main reaction products. No Pt-containing complexes with $MeSCH_2Cl$ were either isolated or detected in solution by ^1H NMR spectroscopy.

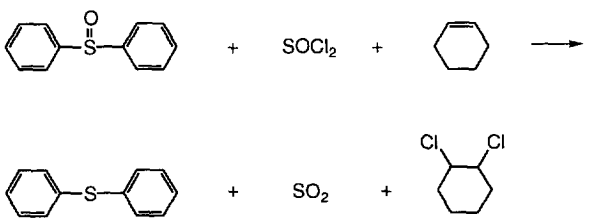
From the viewpoint of understanding a mechanism for deoxygenation, the reaction between the *bis*-sulfoxide complex *cis*-$[PtCl_2(Me_2SO)_2]$ and thionyl chloride is important [46]. Treatment of the starting material with a five-fold excess of $SOCl_2$ gave rise to *cis*-$[PtCl_4(Me_2SO)(Me_2S)]$. The latter has been isolated in the solid phase as the *cis*-isomer, which equilibrates with the *trans*-form on dissolution, Scheme 7.



Scheme 7.

These observations suggest that (i) even with an excess of thionyl chloride only one dimethyl sulfoxide ligand is deoxygenated, and (ii) the two-electron reduction of the ligand occurs in concert with the two-electron oxidation of the Pt ion; the reaction is complete when all of the Pt(II) is consumed.

Deoxygenations of coordinated sulfoxides in Pt(II) complexes discussed above have parallels in organic chemistry. In particular, it was shown that the formation of chlorinated alkyl sulfides can be avoided if the deoxygenation of R_2SO with thionyl chloride is carried out in the presence of cyclohexene [47] or sodium iodide [48]. Both of these compounds are external Cl_2-scavangers and are oxidized instead of the S-containing species. For example, the overall reaction of Ph_2SO with $SOCl_2$ in the presence of cyclohexene is represented by Scheme 8.



Scheme 8.

It may be assumed that in the reaction of Pt(II) sulfoxide complexes with $SOCl_2$, Pt(II) also acts as a Cl_2-scavanger and this drives the reaction towards the formation of unsubstituted dimethyl sulfide Pt(IV) complexes.

To conclude this section it should be mentioned that the deoxygenation reactions of coordinated sulfoxides in Pt(II) complexes involving $SOCl_2$ have parallels not only in organic but also in organometallic chemistry. In a number of studies Himmelreich and Fischer [49] and Mayr and co-workers [50,51] have shown that metal acyls can be deoxygenated with thionyl chloride or other acid halides to form alkylidyne complexes. For example, one of the processes studied [50] is depicted in Scheme 9.

$$(Me_4N)[(OC)_5M{-}\overset{\overset{O}{\|}}{C}{-}R] + SOCl_2 \longrightarrow$$

$$\longrightarrow Cl(OC)_4M{\equiv}C{-}R + SO_2 + CO + (Me_4N)Cl$$

M = Mo, W R = Me, Ph

Scheme 9.

In these reactions also there is a concerted two-electron reduction of the acyl ligand and a two-electron oxidation of the metal ion on treatment with $SOCl_2$.

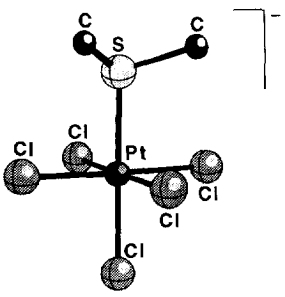
4. DEOXYGENATION OF SULFOXIDES COORDINATED TO Pt(II) BY SUCCESSIVE REACTION WITH PCl_5 AND ROH

It is now well established that phosphorus(V) pentachloride, PCl_5, can serve as a solid chlorine equivalent and is able to oxidize Pt(II) complexes to form the corresponding Pt(IV) derivatives, Scheme 10 [52–56].

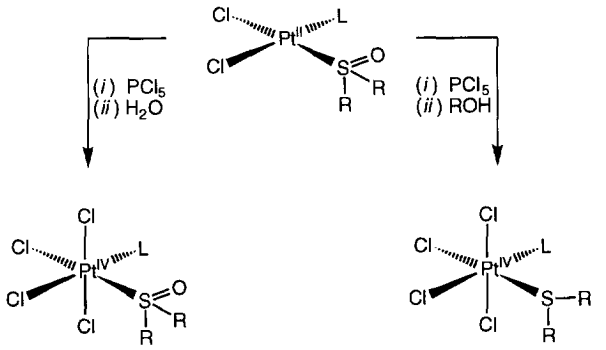
$$-Pt^{II}- + P^{V}Cl_5 \longrightarrow \begin{array}{c}|\\ -Pt^{IV}-\\ |\end{array} + P^{III}Cl_3$$

Scheme 10.

In accord with these observations it has been shown that the reactions of the complexes $K[PtCl_3(Me_2SO)]$ and $[PtCl_2(R_2SO)L]$ (R = Me, Et, $\frac{1}{2}C_2H_4OC_2H_4$, L = R_2SO; R = Me, L = Me_2S; NH_3, piperidine, pyridine, 2- and 4-methylpyridine) with PCl_5 in acetonitrile or nitromethane result in the formation of the corresponding sulfoxide complexes of Pt(IV) [57–59]. In particular, by reacting $K[PtCl_3(Me_2SO)]$ with a five-fold excess of PCl_5 in acetonitrile, followed by decomposition of the unreacted PCl_5 with water or ethanol and addition of tetraethylammonium chloride to the mixture, $(Et_4N)[PtCl_5(Me_2SO)]$ was isolated and structurally characterized [58]. The reaction proceeds in a different way if 2-propanol is used instead of water or ethanol. In this case the overall process leads to the formation of the dimethyl sulfide derivative $(Et_4N)[PtCl_5(Me_2S)]$, whose structure has also been confirmed by X-ray diffraction analysis:



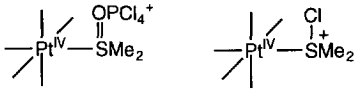
Similar reactions are typical for other Pt(II) sulfoxide derivatives, such as complexes of the type $[PtCl_2(R_2SO)L]$. The latter react with PCl_5 and H_2O and with PCl_5 and ROH in different ways, Scheme 11.



Scheme 11.

It should be mentioned, in particular, that on addition of EtOH or 2-PrOH to a mixture of $[PtCl_2(R_2SO)L]$ and PCl_5, the dialkyl sulfide derivatives $[PtCl_4(R_2S)L]$ are formed in all cases. A mixture of $K[PtCl_3(Me_2SO)]$ and PCl_5 reacts with alcohols in a different way. Thus, addition of 2-propanol leads to formation of the complex $[PtCl_5(Me_2S)]^-$, while addition of ethanol gives a $[PtCl_5(Me_2SO)]^-$ complex. It follows from a comparison of the results obtained that, in at least one case (the reaction with $K[PtCl_3(Me_2SO)]$ or with $[PtCl_2(R_2SO)L]$), a coordinated rather than free sulfoxide molecule is deoxygenated.

It may be assumed that in the reactions of the complexes $K[PtCl_3(Me_2SO)]$ and $[PtCl_2(R_2SO)L]$ with PCl_5, oxidation of the Pt(II) ion to Pt(IV) occurs and the intermediates **A** or **B** are formed:



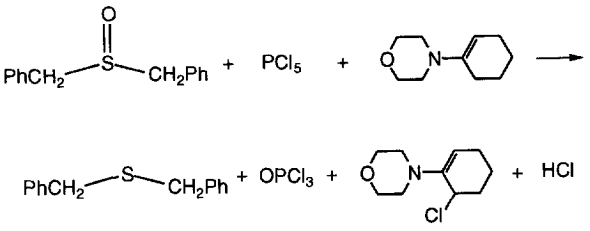
A **B**

The subsequent addition of water leads to the hydrolysis of **A** and/or **B** with the formation of a Pt(IV) dialkyl sulfoxide complex while, when 2-propanol is added, the Pt(IV) intermediate is reduced and Pt(IV) dialkyl sulfide derivative is formed. It is interesting to compare the reactions of platinum(II) sulfoxide complexes with PCl_5 and with PCl_3. The latter reagent is not able to oxidize the Pt(II) center and therefore refluxing of *cis*-$[PtCl_2(Me_2SO)_2]$ in neat PCl_3 for ≈ 1 h leads to $[PtCl_2(Me_2S)_2]$ in isolated yield of $\approx 30\%$ [60].

It is known that deoxygenations of free sulfoxides with PCl_5 occur quite readily. However, there are significant differences in the reduction of coordinated and uncoordinated dialkyl sulfoxides. Thus, the reaction between free Me_2SO and excess

PCl_5 gives rise to the chlorosulfonium salt $[Me_2SCl][PCl_6]$, which rearranges into α-chloromethylmethylsulfide, $MeSCH_2Cl$, via a Pummerer rearrangement [61,62]. However, no complexes with chloromethylmethylsulfide were detected among the products of the reaction of Pt-bound Me_2SO and PCl_5 and ROH [57–59].

The formation of Pummerer-type products can be avoided if the conversion of free R_2SO into R_2S by the action of PCl_5 is carried out in the presence of reducing agents such as NaI [48], *N,N*-diallylaniline [63], or certain enamines [63]. For example, Ishimaru and co-workers [63] reported that the deoxygenation of various dialkyl sulfoxides by PCl_5 proceeds smoothly below 0°C in the presence of 1-morpholino-1-cyclohexene, Scheme 12.



Scheme 12.

It seems reasonable to assume that on successive addition of PCl_5 and ROH to a sulfoxide complex of Pt, ROH plays the role of an external reducing agent, similar to 1-morpholino-1-cyclohexene.

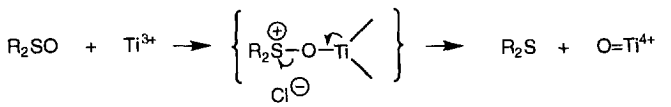
5. REDUCTION OF SULFOXIDES ON TREATMENT WITH LOW OXIDATION STATE METAL IONS

McMurray indicated in his review [64] that Ti^{3+} compounds are mild, specific and effective reducing agents. Titanium has a strong affinity for oxygen and this is partly responsible for its remarkable ability to deoxygenate nitro- and nitroso compounds, aromatic and aliphatic *N*-oxides, azoxy compounds and oximes [64]. The ability of Ti^{3+} to abstract an oxygen from organic compounds has also been extended to deoxygenation of sulfoxides. This clean and rapid reaction has been proposed as a method for the quantitative determination of R_2SO [65–67]. Abbott et al. [68] have used this method for the reduction of $C_5H_{10}NCHMeS(=O)(p\text{-tol})$ with the formation of $C_5H_{10}NCHMeS(p\text{-tol})$, but no details of the preparation have been given.

Ho and Wong have shown [69] that the reaction of R_2SO, where R_2SO = Ph_2SO, $(p\text{-}ClC_6H_4)_2SO$, $(PhCH_2)_2SO$, $PhMe_2SO$, and $(n\text{-}Bu)_2SO$, with $TiCl_3$ is of synthetic utility for preparation of the corresponding sulfides. Reactions were carried out for 2–4 h by refluxing a sulfoxide and titanium(III) chloride (15% w/v aqueous solution) in a methanol + chloroform solvent mixture. The corresponding sulfides were isolated in 70%–90% yields. The synthetic method [69] was subsequently adopted by Stirling [70], Tuck [71] and their co-workers for the deoxygenation of

some other sulfoxides. In the latter case [71] titanium(III) species were electrochemically generated from a Ti-anode and used in situ for the reduction of Ph_2SO.

The authors [69] assumed that the reaction proceeded according to the following mechanism, which includes the step of O-coordination of the R_2SO ligand, Scheme 13.



Scheme 13.

Baliah and Satyanarayana [72] have confirmed the above assumption on studying the kinetics of reduction of *ortho*-, *metha*- and *para*-substituted phenyl methyl sulfoxides with $TiCl_3$ in aqueous ethanol. They found that the deoxygenation is overall second order — first order each for the sulfoxide and the titanium(III) chloride. Analysis of the kinetic data obtained indicates that the attack of Ti(III) on the sulfinyl oxygen is the rate-determining step.

The reducing ability of Ti^{2+} is known to be greater than that of Ti^{3+} [64]. It has also been established that Ti^{2+} salts do not exist in aqueous solution since they are oxidized by water. However, Ti^{2+} compounds can be successfully generated in non-aqueous media, for example by the reduction of titanium(IV) tetrachloride with zinc dust or some other reducing agents [73]. Titanium(II) species obtained by this method were used [74] for the reduction of R_2SO (R = Alk, $PhCH_2$, Ph) to the corresponding sulfides. The process was carried out in a diethyl ether at 20°C and was completed in less than 1 min. In another study [75], when $TiCl_4$ was treated with LiH in THF at a 1:4 molar ratio of reagents, "low-valent titanium complexes" were generated in situ. On refluxing alkyl or aryl sulfoxides with these compounds in THF for 10 h, the corresponding sulfides were formed. The prolonged time and relatively high temperature required for the synthesis should be noted.

The possibility of reducing sulfoxides with tin(II) chloride in the presence of HCl was first demonstrated in 1947 [76]. Later this method was improved [77,78]. The reaction is carried out by refluxing a solution of dialkyl, dibenzyl or diaryl sulfoxide and $SnCl_2 \cdot H_2O$ in methanol in the presence of HCl. Aliphatic sulfoxides are reduced much faster (ca. 2 h) than aromatic ones (ca. 20 h) [77].

Tin(II) chloride has also been used [79–81] for the reduction of *S*-bound DMSO. It was shown that the reaction of the platinum(II) complex *cis*-$[PtCl_2(Me_2SO)_2]$, or a mixture of $K_2[PtCl_4]$ and dimethyl sulfoxide, in hydrochloric acid with $SnCl_2 \cdot H_2O$ for 5–7 min at 70–90°C produced *cis*- and *trans*-$[PtCl_4(Me_2S)_2]$ platinum(IV) complexes respectively. The complexes $[PtCl_4(R_2S)_2]$, where R = Et or *n*-Pr, were synthesized in a similar way. The authors [79–81] assumed that the reactions leading to the formation of the $[PtCl_4(R_2S)_2]$ complexes could occur in both the inner and outer spheres of the complexes.

In concluding Section 5 we note that the deoxygenation of sulfoxides can also

be achieved using low oxidation state chromium [82], vanadium [83], molybdenum [83–85], tungsten [84,86], and samarium [87,88].

6. DEOXYGENATIONS INVOLVING $M^{n+} \rightarrow M^{(n+2)}{=}O$ TRANSFORMATIONS

Oxygen atom transfer between a metal center and a substrate is one of the most fundamental and important reactions of metal oxo complexes [89,90]. These processes have received attention because of their importance in biological systems, in organic synthesis, and in industrial processes. Since the present review concerns deoxygention of sulfoxides, in Section 6 we consider reactions of the type

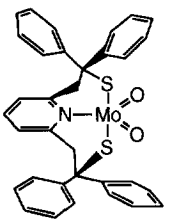
$$M^{n+} + R_2S{=}O \rightarrow M^{(n+2)}{=}O + R_2S$$

with sulfoxides as substrates.

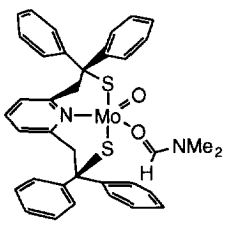
The molybdenum-containing oxo-transferases (hydroxylases) catalyze the two-electron oxidation or reduction of substrates X/XO in a process which can be formally represented as

$$X + H_2O \rightleftharpoons XO + 2H^+ + 2e^-$$

In a number of studies Holm and co-workers [90–97] have demonstrated that complexes **C** and **D**:

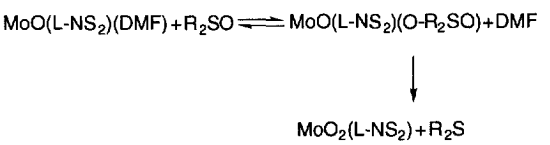


C



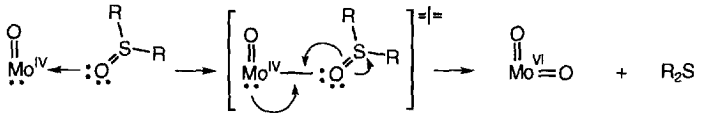
D

which contain the sterically hindered tridentate ligand abbreviated as L-NS_2, are reasonable structural models of certain enzyme sites and convenient for the study of oxygenation and deoxygenation processes in models of biological systems. In particular, it was shown [93] that complex **D**, in which molybdenum is in a relatively low oxidation state, can effectively deoxygenate alkyl and aryl sulfoxides. The authors have studied the kinetics and mechanism of the deoxygenations and were led to the conclusion that the process occurs in two steps, Scheme 14.



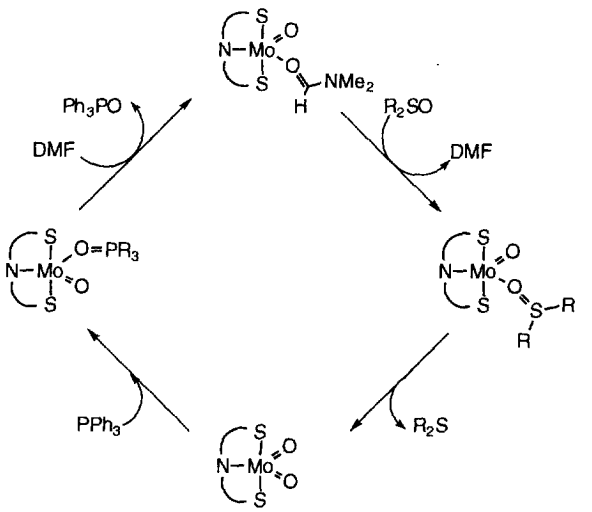
Scheme 14.

In the first step, the coordinated dimethylformamide ligand (DMF) is substituted by R_2SO and, in the second step, deoxygenation of the *O*-bound sulfoxide is followed by elimination of the corresponding sulfide. The authors argued that the reaction proceeds via the following route, Scheme 15 [93–97].



Scheme 15.

It has been shown in one of these studies [93] that the dioxomolybdenum complex MoO_2(L-NS_2), **C**, oxidizes triphenylphosphine to triphenylphosphine oxide and the deoxygenation of R_2SO by PPh_3 is catalyzed by the complexes **C** and **D**, Scheme 16.



Scheme 16.

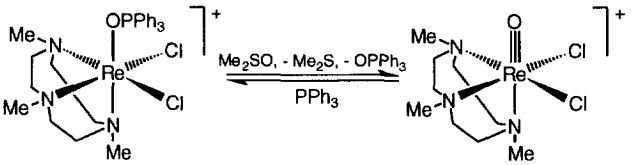
The results of other studies [98–108], which are compiled in Table 4, indicate that certain other Mo complexes can effectively deoxygenate dialkyl sulfoxides to produce the corresponding sulfides.

To the best of our knowledge, deoxygenations of sulfoxides involving $M^{n+} \rightarrow M^{(n+2)}{=}O$ transformations have received systematic study only in the case of molybdenum complexes. Reactions involving $Sn^{2+} \rightarrow Sn^{4+}{=}O$ transformations were examined in the previous section. Examples of reduction of the sulfinyl group in R_2SO by other $M^{n+}/M^{(n+2)}{=}O$ systems are listed in the paragraphs that follow.

Conry and Mayer [109] described the first example of simple oxygen atom transfer from dimethyl sulfoxide to a rhenium center. They found that $[ReCl_2(Me_3tacn)(OPPh_3)]^+$, where Me_3tacn is 1,4,7-trimethyltriazacyclononane, reacts with Me_2SO to give the corresponding oxo complex and Me_2S, Scheme 17.

TABLE 4
Deoxygenation of sulfoxides by Mo complexes

Starting complex/sulfoxide	Final products	Reference
$MoO(L\text{-}NS_2)(DMF)/R_2SO$, R = Me, p-C_6H_4F	$MoO_2(L\text{-}NS_2)(DMF)/R_2S$	89–97
$MoO(S_2CNEt_2)/Me_2SO$	$MoO_2(S_2CNEt_2)/Me_2S$	98–101
$MoO_2(SCNEt_2)_2/R_2SO$ and PPh_3, R = Me, Ph, CH_2Ph, n-octyl	R_2S (63%–97%), no information was given about other products	102
$\{HB(Me_2pz)_3\}MoO\{S_2P(OEt)_2\}/Me_2SO$	$\{HB(Me_2pz)_3\}MoO_2\{S_2P(OEt)_2\}/Me_2S$	103
$Mo(CO)_nL_2/Me_2SO$, n = 2, L = S_2CNEt_2; n = 3, L = S_2CPh, $S_2CC_5H_4FeCp$	$MoOL_2/Me_2S$ and CO	104
MoOL, H_2L = salicylaldehyde thiosemicarbazone and salicylaldehyde 4-phenylthiosemicarbazone/Me_2SO	MoO_2L and Me_2S	105
$Mo(Ntol)(S_2CNEt_2)_2/Me_2SO$	$MoO(Ntol)(S_2CNEt_2)_2/Me_2S$	106, 107
$[MoOCl(dttd)]^-/Me_2SO$, $dttdH_2$ = 2,3 : 8,9-dibenzo-1,4,7,10-tetrathiadecane	$[MoO_2Cl(dttd)]^-/Me_2S$	108



Scheme 17.

The oxo complex was converted back to the original $OPPh_3$ complex on addition of triphenylphosphine. The authors [109] provided arguments in favor of the following mechanistic pathway for the Re-mediated deoxygenation of sulfoxides:

$$[ReCl_2(Me_3tacn)(OPPh_3)]^+ \xrightarrow[-OPPh_3]{} [ReCl_2(Me_3tacn)]^+ \xrightarrow[+Me_2SO]{\text{fast}}$$

$$[ReCl_2(Me_3tacn)(OSMe_2)]^+ \rightarrow [Re(O)Cl_2(Me_3tacn)]^+ + Me_2S$$

The loss of triphenylphosphine oxide appeared to be the rate-determining step.

Complexes $[WCl_2(PR_3)_4]$ ($PR_3 = PMe_3$ and $PMePh_2$) react with dimethyl sulfoxide to produce the terminal oxo complex $[W(=O)Cl_2(PR_3)_3]$ but the fate of the product formed by reduction of the DMSO is not reported [110]. Davison and co-workers [111] have reported that the technetium(III) thiolate, $[Tc(tmbt)_3(py)_2]$ (tmbt = 2,3,5,6-tetramethylbenzenethiolate), readily deoxygenates dimethyl sulfoxide to produce the technetium(V) oxo-complex, $[TcO(tmbt)_3(py)]$ and dimethyl sulfide. In turn, the Tc(V) product reacts further with DMSO and this reaction gives rise

to the formation of $[TcO_4]^-$. It was also observed that addition of a catalytic amount of $[TcO(tmbt)_3(py)]$ to a solution containing DMSO and PPh_3 causes deoxygenation of dimethyl sulfoxide to yield the phosphine oxide and Me_2S.

7. PROCESSES INVOLVING HIGH-VALENT METAL IONS AND EXTERNAL REDUCING AGENTS

In Section 5 we considered deoxygenation reactions of sulfoxides involving low oxidation state metal ions which act simultaneously as electrophiles for substrate activation and reducing agents. However, metal ions in relatively high oxidation states, which usually do not possess reducing properties, can also be used to deoxygenate sulfoxides but, in this case, chlorinated Pummerer-type products are formed. Thus, in studies of the reaction of dimethyl sulfoxide with $NbQX_4$(Q = X = Cl; Q = X = Br; Q = Me, X = Cl) compounds, XCH_2SCH_3 products were observed in all cases [112–114]. The authors of all three studies concluded that the process consists of two steps. In the first step oxygen is transferred to form an oxo-complex and a halosulfonium salt:

$$NbQX_4 + 3Me_2S{=}O \rightarrow Nb(=O)QX_2 \cdot 2Me_2SO + [Me_2S^+X]X^-$$

In the second step the halosulfonium salt $[Me_2S^+X]X^-$ is converted to a haloalkylsulfide XCH_2SCH_3. The formation of XCH_2SCH_3 can be avoided if the deoxygenation process is carried out in the presence of external reducing agents. Details of some of the "metal ion–external reducing agent" systems are compiled in Table 5.

Boron and aluminium hydrides [130] are commonly used as reducing agents for these processes. For example, in accord with the recommended procedure [118], the reduction of sulfoxides was carried out by slow addition of $TiCl_4$ to a solution of R_2SO and $Li[AlH_4]$ in diethyl ether at 0°C. In the vast majority of cases the authors (for instance, Drabowicz and Mikolajczyk [118], Lin and Zhang [121]) assumed that the process included a step of electrophilic activation of R_2SO by complexation with high-valent metal ions via oxygen. Complex formation would weaken the S–O bond and render the sulfur atom more susceptible to nucleophilic attack by hydride. Two-electron reduction terminates this process.

Babu and Bhatt have reported [127] the results of a study in which the conversions of dibutyl, dibenzyl, and diphenyl sulfoxides to the corresponding sulfides using aluminium(III) iodide, AlI_3, in acetonitrile were observed. It would appear that in these reactions the aluminium ion functioned as the electrophilic activator and the I^- ions reduced the *O*-coordinated sulfoxides.

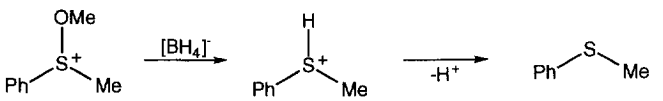
The reactions considered in this section and the proposed mechanisms have parallels in organic chemistry and, in particular, among reductions of alkoxysulfonium salts, $[RR^*S\text{-}OR']^+$, with boron hydrides [131,132]. Johnson and Philips [132] have reported that these salts were efficiently converted to the corresponding sulfides, RR^*S, when treated with $Na[BH_4]$ in alcohols or tetrahydrofuran. The authors [132] have argued that the reaction occurs by the mechanism shown by Scheme 18.

TABLE 5

Deoxygenation of sulfoxides by "high-valent metal ion–external reducing agent" systems

Starting reagent	Reducing agent	R_2SO	Product(s)	Reference
$MoCl_5$	None	Me_2SO	$MoOCl_3 \cdot Me_2SO$[a]	115
$Nb(CH_3)Cl_4$	None	Me_2SO	$NbO(CH_3)Cl_2 \cdot 2Me_2SO$ and CH_3SCH_2Cl	113
NbX_5, X=Cl, Br	None	Me_2SO	$NbOX_3 \cdot 2Me_2SO$ and CH_3SCH_2X	112, 114
$TiCl_4$	$Na[BH_4]$	Variety of diaryl, and alkylaryl sulfoxides	Corresponding R_2S	116, 117
$TiCl_4$	$Li[AlH_4]$	Dialkyl, diaryl and alkylaryl sulfoxides	Corresponding R_2S	118
$TiCl_4$	NaI	Dialkyl, dibenzyl, diaryl, alkylaryl and alkylbenzyl sulfoxides	Corresponding R_2S	119
$TiCl_4$	Zn	Substituted-α-haloalkyl phenyl sulfoxides	Corresponding phenyl vinyl sulfoxides[b]	120
$FeCl_3$	$Na[BH_4]$	Me_2SO and diaryl sulfoxides	Corresponding R_2S	121
Fe(tpp)Cl[c]	$Na[BH_4]$[d]	Variety of diaryl, and alkylaryl sulfoxides	Corresponding R_2S, reaction is catalyzed by Fe(tpp)Cl	122, 123
$BF_3 \cdot OEt_2$	NaI	Alkylaryl and diaryl sulfoxides	Corresponding R_2S	124
BF_3	NaI	Dialkyl, dibenzyl and diphenyl sulfoxide	Corresponding R_2S	125
$B(OPh)_3$	$Na[BH_4]$	Dialkyl, dibenzyl and diphenyl sulfoxide	Corresponding R_2S	126
AlI_3	AlI_3	R=*n*-Bu, CH_2Ph_2, Ph	Corresponding R_2S	127
$CoCl_2 \cdot 6H_2O$[e]	$Na[BH_4]$	R=Me, *n*-Bu, $\frac{1}{2}(CH_2)_4$, CH_2Ph_2 and various diaryl sulfoxides	Corresponding R_2S, reaction is catalyzed by Co(II) species [106]	128, 129

[a] A "strong odor of mercaptans" has been reported [115] but products have not been isolated or identified. [b] Eliminative deoxygenation. [c] $tppH_2$ is tetraphenylporphyrine. [d] 1-benzyl-1,4-dihydronicotinamide was also employed as a reducing agent. [e] Co(II) does not belong to the class of high oxidation state metal ions, nevertheless deoxygenation proceeds as described in this section for other systems that do involve high-valent metal ions.

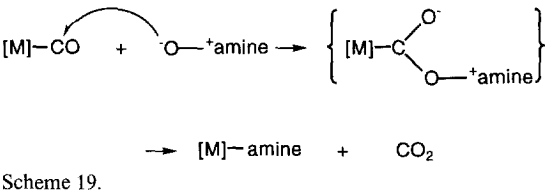


Scheme 18.

The deoxygenation of sulfoxides with reagent systems of the type "Lewis acid or non-aqueous protic acid–reducing agent" (see Table 5), $BF_3 \cdot OEt_2$–NaI [124], BF_3–NaI [125], $BI_3 \cdot NEt_2Ph$ [133], $B(OPh)_3$–$Na[BH_4]$ [126], RSO_3H (R = *p*-tol, CF_3, Cl)–NaI [134] occurs via the same route.

8. REDUCTION OF SULFOXIDES ON REACTION WITH COORDINATED CARBONYLS OR CARBENE LIGANDS

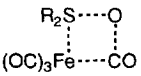
It is now well documented that electrophilically activated coordinated carbonyl groups are subject to nucleophilic oxygenation by a variety of oxygen donors. Amine oxides, nitro- and nitrosoarenes, and iodosobenzene [130,135–140] have been widely used as oxygen donors in order to carry out such processes. The mechanism of these types of reactions was established on the basis of broad kinetic investigations [140] and can be represented by Scheme 19.



Scheme 19.

Albers and Coville have pointed out [139] that dialkyl sulfoxides can also act in a fashion similar to amine oxides as oxygen donors for nucleophilic oxidations, but no experimental data supporting this statement have been given.

The reduction of sulfoxides by carbonyl complexes was first reported by Alper and Keung [141]. It was established that the reaction of various dialkyl, diaryl, and heterocyclic sulfoxides as well disulfoxides with $Fe(CO)_5$ at 130–135°C in either diglyme or di-*n*-butyl ether under remarkably simple conditions leads to the deoxygenation of R_2SO with the formation of the corresponding sulfides in fair to excellent yields. The authors [141] did not isolate or characterize other products of the redox conversion but suggested that the interaction proceeds via intermediate formation of **E** or **F**:

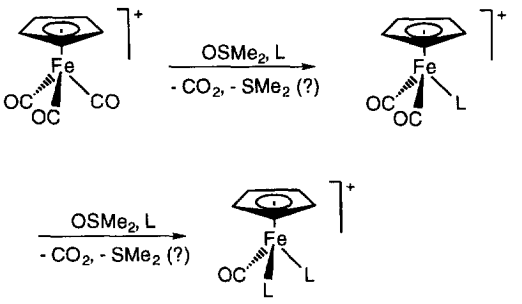


E

$[Fe(R_2SO)_6][Fe_4(CO)_{13}]$

F

Davies [142] observed the stepwise nucleophilic oxygenation of $[(\eta^5\text{-Cp})Fe(CO)_3][PF_6]$ by Me_2SO in the presence of phosphine and phosphite ligands L, where $L = \frac{1}{2}\ PPh_2(CH_2)_nPPh_2$ ($n = 2, 3$), PPh_3 or $P(OMe)_3$, Scheme 20.



Scheme 20.

In accord with the method described, $[(\eta^5\text{-Cp})Fe(CO)_3][PF_6]$ and L were dissolved in dimethyl sulfoxide and stirred at room temperature for 10 min. Work-up gave the substituted $[(\eta^5\text{-Cp})Fe(CO)_2L][PF_6]$ compounds. Continuous stirring of the reaction mixture in DMSO yielded disubstituted products. Unfortunately, no information was given about the products formed by reduction of the dimethyl sulfoxide [142]. Chen et al. [143] reported that both aliphatic and aromatic silfoxides are readily deoxygenated when treated with $[(\eta^5\text{-Cp})_2Ti(CO)_2]$ in THF under nitrogen in the temperature range 25°C to refluxing the solvent. The authors pointed out the formal similarity of these reactions to the deoxygenation of amine oxides by metal carbonyls [135–140] but no experimental evidence supporting this analogy was given [143].

It has been shown [144] that molybdenum hexacarbonyl is quite an effective reagent for the deoxygenation of alkyl and aryl sulfoxides. The complex $Mo(CO)_6$ reduced sulfoxides on heating in a solution of dimethoxyethane.

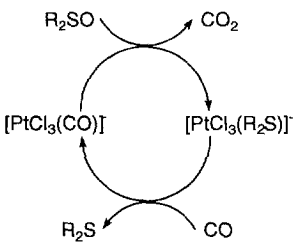
Analysis of a wide range of experimental data has shown that the frequencies of the ν(CO) absorption bands in IR spectra are useful indicators for elucidation of the reactivity of metal carbonyls in nucleophilic oxygenation [135–139]. It is well established that carbonyls with $\nu(CO) > 2000\ cm^{-1}$ are electrophilically active and subject to nucleophilic attack by at least the most common oxygen donor $ONMe_3$. Despite the fact that sulfoxides are less active *O*-donors than amine oxides, knowledge of the value of ν(CO) is nevertheless useful for estimation of electrophilic activity.

Pakhomova et al. [145] carried out the synthesis of *cis*-$[PtCl_2(Me_2SO)(CO)]$ ($\nu(CO) = 2138\ cm^{-1}$) via cleavage of the bridged dimer $[PtCl(\mu\text{-Cl})(CO)]_2$ with dimethyl sulfoxide in dry benzene. Heating of *cis*-$[PtCl_2(Me_2SO)(CO)]$ gives a mixture of products, among which CO_2 and CH_3Cl were identified by mass spectrometry. In the IR spectra of the solid products of thermolysis, the absorption bands characteristic of coordinated Me_2SO had disappeared. The authors [145] regarded these results as an indication of the redox nature of the interaction between the coordinated Me_2SO and CO ligands. As the overall product of these transformations, the polymeric complex $[PtCl(SMe)]_n$ was isolated.

Deoxygenation of R_2SO molecules also occurs in processes involving another platinum(II) carbonyl compound, the complex $(Ph_3PCH_2Ph)[PtCl_3(CO)]$ (ν(CO)=

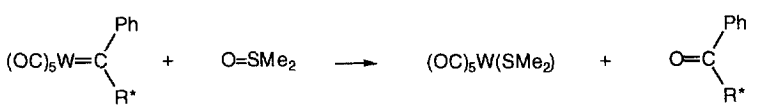
2081 cm^{-1}). Thus, it was shown [146] that reaction of this complex with sulfoxides R_2SO (R = Me, Et, *n*-Pr, CH_2Ph) in a nitromethane + acetic acid solvent mixture for several hours led to the formation of $(Ph_3PCH_2Ph)[PtCl_3(R_2SO)]$. On exposure of the complex $(Ph_3PCH_2Ph)[PtCl_3(CO)]$ and the sulfoxide to an atmosphere of CO (1 atm, 20°C, 5–7 days) in $MeNO_2 + MeCO_2H$, deoxygenation of the sulfoxides occurs and the sulfides R_2S are formed. Reduction of the sulfoxides by carbon monoxide does not occur in the absence of $(Ph_3PCH_2Ph)[PtCl_3(CO)]$.

It was also shown in the same study [146] that reaction of the $(Ph_3PCH_2Ph)[PtCl_3(R_2SO)]$ complexes with CO under the conditions described above yields R_2S and $(Ph_3PCH_2Ph)[PtCl_3(CO)]$ as the major products. The reaction of $(Ph_3PCH_2Ph)[PtCl_3(Ph_2SO)]$ with CO produces Ph_2S and a mixture of unidentified platinum-containing products. The results obtained [146] suggest that the deoxygenation of R_2SO using CO in the presence of $(Ph_3PCH_2Ph)[PtCl_3(CO)]$ is catalytic, Scheme 21.



Scheme 21.

The carbon that is bound to the central atom in carbene complexes is known to be electrophilically activated and can be attacked by various *O*-donor nucleophiles, for example by trimethylamine oxide [147–149]. Fischer et al. [150] have reported that Me_2SO can be deoxygenated by the benzylidene tungsten complexes $(OC)_5W[C(R^*)Ph]$ (R = H, Ph, OMe) in dichloromethane solution at −15°C, Scheme 22.

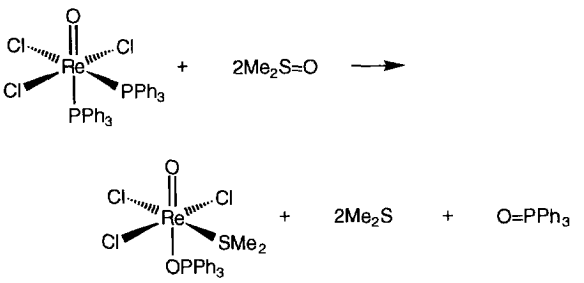


Scheme 22.

As a result of the redox reaction, the dimethyl sulfide complex $(OC)_5W(SMe_2)$ and $O=C(R^*)Ph$ are formed. Other groups have observed oxygen abstraction from Me_2SO by carbene complexes of Cr and W [151–154] but corresponding dimethyl sulfide complexes have neither been isolated nor identified in solution by spectroscopic methods.

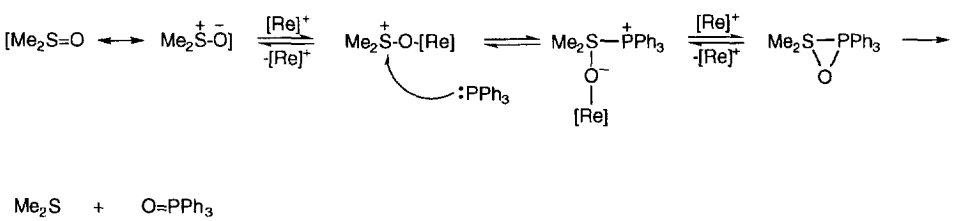
9. DEOXYGENATION OF METAL-BOUND R_2SO IN SULFOXIDE–PHOSPHINE COMPLEXES

Mayer and co-workers [155] have observed that $[ReOCl_3(PPh_3)_2]$ reacts in benzene or toluene with dimethyl sulfoxide in the presence of HCl to yield the dimethyl sulfide complex $[ReOCl_3(OPPh_3)(Me_2S)]$ and triphenylphosphine oxide, Scheme 23.



Scheme 23.

The formation of $[ReOCl_3(OPPh_3)(Me_2S)]$ occurs in the presence of hydrogen chloride, which is itself a reagent capable of deoxygenating Me_2SO (See Section 2) and is an effective catalyst for the dimethyl sulfoxide oxidation of PPh_3. However, the process can also take place in the absence of HCl. In this case the yield of $[ReOCl_3(OPPh_3)(Me_2S)]$ is reduced slightly (75% vs. 95%). It was also noted that $[ReOCl_3(OPPh_3)(Me_2S)]$ is not formed when $[ReOCl_3(OPPh_3)_2]$ is treated with Me_2S or $OPPh_3$. Based on chemical and oxygen-18 labeling experiments, the authors [155] were led to the conclusion that oxygen atom transfer to triphenylphosphine occurs directly from a Me_2SO ligand activated by the rhenium center, without direct involvement of the Re oxo group. It was assumed that the reaction mechanism included a step involving *O*-coordination of the Me_2SO molecule, Scheme 24.



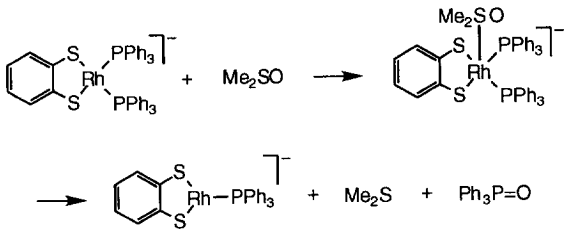
Scheme 24.

The metal ion in this case functions as an electrophile in substrate activation, increasing the partial positive charge on sulfur and weakening the S–O bond. Subsequently there is a reaction with triphenylphosphine, which deoxygenates the Me_2SO molecule. In connection with this study [155] it is noteworthy that a process similar to that described had previously been reported in the organic chemistry literature [156]. It was established [155,156] that HCl catalyzes the deoxygenation

of Me_2SO by triphenylphosphine. This process also includes a step involving electrophilic activation of Me_2SO by protonation of the sulfinic oxygen.

Davies et al. [157] observed deoxygenation of dimethyl sulfoxide in the palladium(II) and platinum(II) complexes $[MCl(O\text{-}Me_2SO)(Dppe)][ClO_4]$, where Dppe is 1,2-bis(diphenylphosphino)ethane. On allowing the $[PdCl(O\text{-}Me_2SO)(Dppe)][ClO_4]$ complex to stand for 3 h in a $CH_2Cl_2 + Me_2SO$ (2:2, v/v) solvent mixture, the starting material was converted gradually to the sulfide complex $[PdCl(Dppe)(Me_2S)][ClO_4]$. The latter is unstable towards dimerization both in solution and in the solid state, giving the dimer $[\{MCl(Dppe)\}_2][ClO_4]_2$ and free Me_2S. The analogous Pt(II) complex $[PtCl(O\text{-}Me_2SO)(Dppe)]^+$ was more stable towards deoxygenation: the formation of $[PtCl(Dppe)(Me_2S)]^+$ was observed only after the $[PtCl(O\text{-}Me_2SO)(Dppe)]^+$ complex had stood in nitromethane-d_3 solution for 1 month. The authors [157] gave no information about the oxidation products or about the presence or absence of phosphine oxide in the mixture after completion of the reactions. It should also be pointed out that $[Pd(O\text{-}Me_2SO)_2(Dppe)]^{2+}$ proved to be surprisingly stable in solution and no dimethyl sulfide species were detected [157].

The rhodium(I) compound $(Me_4N)[Rh(PPh_3)_2(o\text{-}S_2C_6H_4)]$ reacts with Me_2SO in DMF-d_6 and catalyzes oxygen transfer from Me_2SO to triphenylphosphine [158]. Sellmann et al. [158] proposed that the reaction scheme included a step involving coordination of dimethyl sulfoxide to the rhodium(I) center in $[Rh(PPh_3)_2(o\text{-}S_2C_6H_4)]^-$, activation of the ligand, and formation of Me_2S, triphenylphosphine oxide and a three-coordinate Rh complex stabilized by the solvent, Scheme 25.



Scheme 25.

It should be noted that this mechanism, unsupported by experimental evidence, involves *S*-coordination of the sulfoxide to a Rh(I) ion bound to other "soft" ligands (two *S*- and two *P*-donor ligands) and this raises certain questions. As a general rule, for complexes with a number of "soft" ligands, Me_2SO is coordinated by oxygen rather than by sulfur [159]. If such an assumption is subsequently proved correct, it may be possible to indicate more definitively that there are similarities between the processes described in all three studies cited above [155,157,158].

10. CONVERSIONS OF DMSO IN SYSTEMS INVOLVING METALS AND RX (R = H, ALKYL; X = Cl, Br, I)

Lavrentev and co-workers have shown [160–170] that interaction between the components of M–DMSO–RX systems results in deoxygenation of Me_2SO with the

formation of Me_2S or secondary conversion products of dimethyl sulfide (Table 6). The mechanisms of these processes are quite complicated. Nevertheless, it has been found that an oxidizable metal mediates the reaction between the components of the redox system. It may also be assumed that, in the case of the reaction of M, DMSO and HX, the resulting halosulfonium ion $[Me_2SX]^+$ is reduced by metals or metal ions formed at an intermediate stage in the process.

For example, metallic silver interacts with solutions of HX (X=Br, I) in dimethyl sulfoxide at 70°C to give dimethyl sulfide, the trimethylsulfonium salts $(Me_3S)[AgX_2]$, $(Me_3S)[Ag_2X_3]$ and AgX. The authors [166,167] believe that on reaction of DMSO and HX the following processes take place:

$$Me_2SO + 2HX \rightleftharpoons H_2O + [Me_2S^+X]X^-$$

$$2Me_2SO + 2HX \rightleftharpoons 2[Me_2S^+{-}OH]X^- \rightarrow [Me_3S^+]X^- + [MeS^+{=}O]X^- + H_2O$$

When metallic silver is introduced into the system, the metal acts as a reducing agent:

$$[Me_2S^+X]X^- + Ag \rightarrow AgX + Me_2S + \tfrac{1}{2}X_2$$

TABLE 6
Starting materials and products for M–Me_2SO–RX systems

System	Products and comments	Reference
Pd–Me_2SO–*n*-$C_6H_{13}Br$	*trans*-$[PdBr_2(Me_2S)_2]$	160
Rh–Me_2SO–*n*-$C_6H_{13}Br$	Rh(III) dimethyl sulfide complex, no information on the structure was reported	160
Pt–Me_2SO–*n*-$C_6H_{13}Br$	Pt(IV) dimethyl sulfide complex, no information on the structure was reported	160
Au–Me_2SO–HX, X=Cl, Br	$[AuX(Me_2S)]$ (X=Cl, Br), $[AuBr_3(Me_2S)]$, $Q[AuBr_4]$ ($Q=Me_3S$, Me_3SO), $(Me_3S)[AuBr_4(Me_2S)]$, $(Me_3S)[Au_2Br_7(Me_2S)]$ and $(Me_3S)_2[Au_2Br_8]$; $[AuBr(Me_2S)]$ and $[AuBr_3(Me_2S)]$ were characterized by X-ray crystallography	161–163
M–Me_2SO–HX, M=Pd, Pt; X=Cl, Br	*trans*-$[PdCl_2(Me_2S)_2]$ and *trans*-$[PtBr_4(Me_2S)_2]$, both compounds were characterized by X-ray crystallography	164
Noble metal–Me_2SO–HX, X=Cl, Br	Oxidation products of noble metals; no information on the reduction products of Me_2SO was given	165
Ag–Me_2SO–HX, X=Br, I	$(Me_3S)[AgX_2]$, $(Me_3S)[Ag_2X_3]$ and AgX; X-ray structure of $(Me_3S)[AgBr_2]$	166, 167
M–Me_2SO–CCl_4, M=Fe, Co, Ni, Cu	Dimethyl sulfide, CO_2, $COCl_2$, C_2Cl_6 and metal oxidation products	168–172

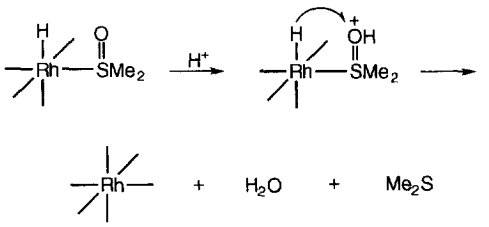
Secondary reactions of AgX with $[Me_3S]X$ lead to the formation of $(Me_3S)[AgX_2]$ and $(Me_3S)[Ag_2X_3]$.

In connection with the work cited in this section, attention should be paid to the paper by Amidzhanov and Kotegov [173] who reported reduction of $[Me_2SCl]^+$, obtained in situ in a reaction between DMSO and 6 M HCl, with $H_2[ReOCl_5]$. This process led to the formation of $[ReO_4]^-$ and dimethyl sulfide. Here a metal ion, instead of a metal itself, plays the role of a reducing agent.

11. MISCELLANEOUS METAL-ION MEDIATED DEOXYGENATIONS OF SULFOXIDES

In this section we have compiled material which does not belong to the categories described above. Thus, the reduction of coordinated dimethyl sulfoxide can occur when solid state thermolysis of complexes is carried out [174]. Antonov and Amantova have reported [175] that heating of the isomeric osmium(II) compounds $[OsCl_2(S\text{-}Me_2SO)_4]$ and $[OsCl_2(O\text{-}Me_2SO)(S\text{-}Me_2SO)_3]$ at 150°C in vacuo causes the disproportionation of dimethyl sulfoxide to dimethyl sulfone and the osmium(III) complexes $[Os_2Cl_4(\mu\text{-}SMe)_2(Me_2S)_2]$ and $[Os_2Cl_4(O\text{-}Me_2SO)(\mu\text{-}SMe)_2(Me_2S)]$ respectively. Arsenin et al. [176] have described the solid-state thermolysis of the zirconium and hafnium compounds $ZrCl_4 \cdot 9Me_2SO$ and $HfCl_4 \cdot 9Me_2SO$. Heating these compounds results in the formation of the hydroxo complexes $[MCl_2(OH)_2(Me_2SO)_2]$ during the initial stages through a reaction with atmospheric moisture. When the temperature is increased further, conversion of the Me_2SO ligands occurs. Dimethyl sulfide, HCl, and $Me_3S^+Cl^-$ were identified among the reaction products. The authors [176] believe that the formation of Me_2S occurs within the coordination sphere of the metal in a reaction involving HCl.

James et al. [177] observed that Me_2SO in the presence of $RhCl_3 \cdot 3H_2O$ or *cis*-$[RhCl_3(Et_2S)_3]$ can be catalytically reduced with H_2 under mild conditions. The kinetics of these reactions have been investigated, and the mechanism shown by Scheme 26, involving the formation of a rhodium(III) hydride, was proposed.

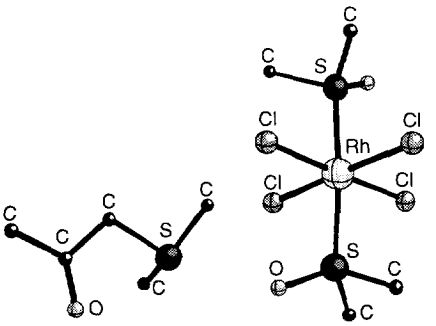


Scheme 26.

The subsequent reaction pathway involved protonation of the sulfinyl oxygen atom of the ligand followed by elimination of water molecules and Me_2S from the coordination sphere of the intermediate.

Calligaris and Faleschini [178] observed an unexpected deoxygenation of

dimethyl sulfoxide coordinated to rhodium(III). The authors prepared needle-like crystals of $[(Me_2SO)H][RhCl_4(S\text{-}Me_2SO)_2]$ from an acetone solution. The X-ray structure of the latter showed a severe disorder around Rh, which has been interpreted in terms of the presence of both the *cis*- and *trans*-isomers, in approximately a 3:1 molar ratio. Other broad and low-intensity peaks displayed in the electron density map are probably due to some solvent of crystallization. After approximately 1 year in a small closed vessel in the light, the needles transformed in part into prisms, which again were the subject of an X-ray diffraction study. The newly formed compound was found to be $[Me_2SCH_2C(O)Me][trans\text{-}RhCl_4(S\text{-}Me_2SO)_2]$:

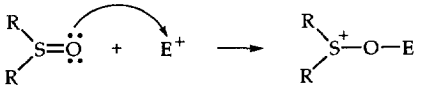


indicating that deoxygenation had occurred. The NMR spectrum of a solution of the prismatic crystals was in agreement with the presence of the sulfonium cation. The mechanism for the above transformation is unknown and under current investigation [178].

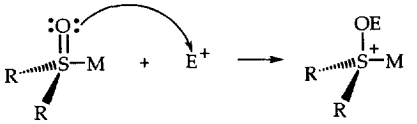
12. CONCLUSIONS

The discussion presented above illustrates that a number of methods for the metal-ion mediated deoxygenation of sulfoxides are now available. Most of these reactions are believed to involve initial activation of the sulfinyl group of R_2SO by an electrophilic reagent E^+, Scheme 27. The electrophilic reagent binds to the oxygen atom, which is normally the most basic site in a sulfoxide, increases the partial positive charge on the sulfur atom, and thus facilitates the reduction.

The current level of understanding of the deoxygenation reactions discussed in this review is far from complete. Despite developments in the reduction of *O*-bound sulfoxides, future work on the deoxygenation reactions of *S*-coordinated sulfoxides will certainly give rise to interesting results. Future research could well be aimed at improving our understanding of the mechanistic pathways involved in these processes. Kinetic studies would not only provide valuable fundamental information, but also give further impetus for the development of new synthetic methods for the deoxygenation of sulfoxides and the preparation of R_2S-containing complexes.



E^+ : hard metal ions, electrophilically activated ligands, Lewis and Brønsted acids



E^+: strong Lewis and Brønsted acids

Scheme 27.

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