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Deoxygenation of coordinated and free sulphoxides

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ABSTRACT. The deoxygenation reactions of coordinated R_2SO molecules (R = Alk, Ar) that occur with the formation of dialkyl and diaryl sulphide complexes are examined. Reduction reactions of free sulphoxides involving metal complexes and ions have been classified. It is shown using specific examples which synthetic problems can be solved with the use of different deoxygenating agents and reagent systems.

The bibliography includes 126 references.

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I. Conclusion

The considerable interest in sulphoxides is in many respects governed by the role which they have played and still play in the development of theoretical concepts in chemistry and also in resolving a number of practical problems. One of the most important properties of R_2SO molecules is their ability to undergo deoxygenation to give sulphides R_2S. The number of publications on this topic is quite considerable.[1–9] The majority of these studies are devoted to the deoxygenation of free sulphoxide molecules, whereas the reduction reactions of coordinated R_2SO molecules have been examined only briefly[7–9] or not considered at all. On taking into account the fact that deoxygenation of coordinated sulphoxides is of theoretical interest in relation to studies on the reactions of coordinated ligands and also that reduction reactions of inner-sphere R_2SO molecules can be of significance for the preparation of complexes that incorporate sulphides R_2S, we decided to compensate for this omission especially since a considerable amount of factual data on the reduction reactions of R_2SO molecules in metal complexes has appeared during the last 8–10 years.

II. Reactions involving hydrohalic acids

The first studies on the deoxygenation of free sulphoxides using HX (X = Cl, Br, I) were carried out at the beginning of the 20th century.[10–13] It was noted in a review article[5] that in general the reduction reactions of this type may be represented by the following equation:

$$R{-}S(O){-}R' + 2HX \rightarrow R{-}S{-}R' + X_2 + H_2O.$$

It was established also that the intermediate in this process is the halosulphonium salt $[R{-}\overset{+}{S}(X){-}R']X^-$, which, depending on X and also the nature of R and R', is either readily reduced to the corresponding sulphide RSR' or decomposes to form a mixture of products, amongst which RCl and RSH in particular have been identified.

Deoxygenation of dimethyl sulphoxide (DMSO) in a metal complex was carried out for the first time in 1968 [14] in a study of the reaction between $[Pt(DMSO)_2Cl_2]$ and hydrochloric acid. From IR spectroscopic data and elemental analysis, the reaction product was identified as $[Pt(DMS)_2Cl_4]$, where DMS = dimethyl sulphide. It was proposed[14] that the process takes place according to the following overall equation:

$$[Pt(DMSO)_2Cl_2] + 4HCl \rightarrow [Pt(DMS)_2Cl_4] + Cl_2 + 2H_2O.$$

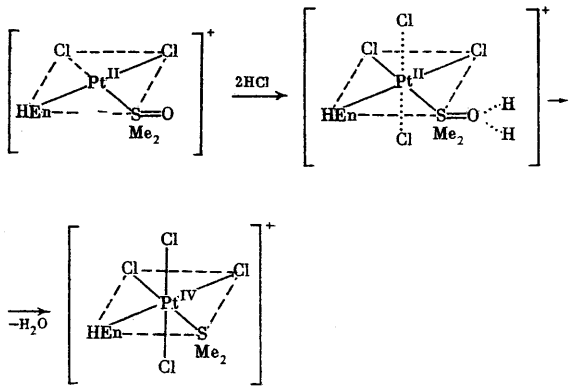
It was noted, however, that this reaction is accompanied by two side reactions and the final Pt(IV) complex is contaminated with unidentified products.

In the same year an article was published[15] in which there was a specific description of the reaction between $PdCl_2$ and tetramethylenesulphoxide (TMSO) in acetone saturated with anhydrous HCl. It was noted that the reaction of $PdCl_2$ with TMSO takes place quite rapidly and gives the complex $[Pd(C_4H_8S)_2Cl_2]$ with coordinated tetramethylenesulphide molecules. Unfortunately, Meek et al.[15] did not study or discuss the mechanism of this reaction.

In the 1970s the chemistry of sulphoxide complexes started to undergo rapid development.[7,16–19] However, only two reports appeared in the literature on the deoxygenation of R_2SO molecules in complexes. Thus, it is noted by Braddock et al.[20] that compounds of the type $[Pt(Am)_2(DMSO)Cl]Cl$ (Am = amine) in aqueous perchloric acid ($[HClO_4] > 1.0$ mol^{-1} litre^{-1}) are converted to DMS derivatives of Pt(IV), but these products were not identified or determined. In a study by Boucher and Bosnich[21] a method is given for the preparation of the complex *cis*-$[Pt(DMSO)(C_2H_4)Cl_2]$ from $K[Pt(DMSO)Cl_3]$ and ethylene in aqueous HCl. It was noted in this case that an excess of acid leads to the reduction of DMSO catalysed

by platinum. However, in this article[21] as well, no details are given on the experiment.

Studies on the deoxygenation of inner-sphere sulphoxides have only recently started to be actively pursued. It was shown[22] that on dissolving the complex [Pt(II)(En)(DMSO)Cl]Cl (En = ethylenediamine) in a minimum solution for 2 days at 20 °C, deoxygenation of the sulphoxide ligand occurs and Pt(II) is oxidised to Pt(IV). The complex *cis*-[Pt(HEn)(DMSO)Cl_4]Cl is formed as a result. Fanizzi et al.[22] assumed that after opening of the ethylenediamine chelate ring and formation of $[Pt(HEn)(DMSO)Cl_2]^+$, the reaction takes place via a mechanism involving protonation of the inner-sphere DMSO molecule and a concerted redox conversion:



It has been established[23] that when the complex $H_2[Pt(DMSO)(\mu\text{-}O)Cl]_2$ (A) reacts with HCl in water with a molar ratio of (A) to HCl of 1:5, complex (A) is cleaved to form H[Pt(DMSO)Cl_3] and $[Pt(DMSO)(\mu\text{-}Cl)Cl]_2$. When the concentration of HCl is increased, these products are formed together with the sulphide complex *trans*-[Pt$(DMS)_2Cl_4$] (in 10–15% yield), the structure of which was established by X-ray diffraction analysis. Thus in this case also, a Pt(II) sulphoxide complex when treated with concentrated HCl is converted to a dimethyl sulphide derivatives of Pt(IV).

It was shown by Kukushkin et al.[24] that the deoxygenation of inner-sphere R_2SO molecules in platinum(II) complexes can have preparative importance. It transpired that the reaction between $(Et_4N)[Pt(II)(R_2SO)Cl_3]$ [R = Me, CH_2Ph(Bz), Ph] and HCl on heating the reaction mixture for several minutes in acetonitrile or nitromethane leads to the formation of the corresponding $(Et_4N)[Pt(IV)(R_2S)Cl_5]$ complexes, which were isolated in 80–90% yield. If HBr is used instead of HCl, the reduction of the sulphoxide and oxidation of Pt(II) is accompanied by replacement of the chloride ions in the complex by bromide ions. As a result of all these reactions, the compounds $(Et_4N)[Pt(R_2S)Br_5]$ were isolated.

It is important to note that the reaction of coordinated dibenzyl sulphoxide {in the complex $(Et_4N)[Pt(II)(Bz_2SO)Cl_3]$} with HCl takes place almost completely in favour of the deoxygenated ligand whereas reaction of free Bz_2SO with HCl is accompanied by rapid decomposition of the sulphoxide to form a mixture of products, amongst which PhCHO, BzCl, Bz_2S_2, Bz_2S, and $Bz_2S_2O_2$ have been detected.[10] Hence it follows that the reactivity of coordinated and free Bz_2SO towards HCl is substantially different. This result, so far the only one, suggests that the reduction of sulphoxides in complexes using HCl is promoted by the Pt(II) ion.

III. Conversion reactions of DMSO in systems of the type M–DMSO–RX

It was shown in a number of studies[25–35] that the reaction between the components of systems of the type M–DMSO–RX (R = H, Alk, X = Cl, Br, I) results in the deoxygenation of DMSO with the formation of DMS or secondary conversion products of DMS. The mechanism of these processes is quite complex (as is shown, for example, in four studies[31–34]). Nevertheless, it was found that an oxidisable metal promotes reaction between the components of the redox system. It may also be assumed that in the case of the reaction between metals and DMSO and HX, the resulting intermediate $Me_2\overset{+}{S}X$ is reduced by metals or metal ions formed at an intermediate stage of the process and which are oxidised and form complexes. Some of these complexes have been isolated and identified (Table 1).

IV. Reaction between inner-sphere DMSO in Pt(II) complexes and $SOCl_2$

The ability of thionyl chloride to deoxygenate free molecules of alkyl and aryl sulphoxides has been reported in the literature.[36–41] Usually these reactions take place with the formation of chloroalkyl or chloroaryl sulphides. In particular, it was established[36] that DMSO reacts with thionyl chloride at a molar ratio of 1:2 in dichloromethane to form $MeSCH_2Cl$, which was isolated in 92% yield. When diphenyl sulphoxide is reacted with $SOCl_2$, a mixture of diaryl sulphides—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.[38]

It was found[39] that coordinated DMSO reacts with $SOCl_2$ in a different way to when it is free. It transpired that the reaction of the complexes $(Et_4N)[Pt(DMSO)Cl_3]$ and *cis*-[Pt(DMSO)(DMS)Cl_2] with $SOCl_2$ at 20 °C in acetonitrile takes place for several minutes and gives DMS derivatives of Pt(IV)—$(Et_4N)[Pt(DMS)Cl_5]$ and *cis*-[Pt$(DMS)_2Cl_4$]. The reaction between the bis-sulphoxide complex *cis*-[Pt$(DMSO)_2Cl_2$] and $SOCl_2$ is interesting:

$$cis\text{-}[Pt(DMSO)_2Cl_2] + SOCl_2 \rightarrow cis\text{-}[Pt(DMS)(DMSO)Cl_4] + SO_2.$$

In this process only one coordinated DMSO molecule is reduced.

Thus the reaction of Pt(II) DMSO complexes with $SOCl_2$ results in the deoxygenation of DMSO and the oxidation of Pt(II) to Pt(IV); the formation of $MeSCH_2Cl$ during the reactions has not been observed. These reactions of coordinated sulphoxides have parallels in preparative organic chemistry. In particular, it was shown in three studies[39–41] that the formation of chlorinated disulphides can be avoided if the deoxygenation of R_2SO with thionyl chloride is carried out in the presence of cyclohexene[39] or sodium iodide.[41] Both of these compounds combine with chlorine. For example, the overall reaction of R_2SO with $SOCl_2$ in the presence of cyclohexene is represented by the equation

$$Ar_2SO + SOCl_2 + C_6H_{10} \rightarrow Ar_2S + SO_2 + C_6H_{10}Cl_2.$$

It may be assumed that in the reaction of Pt(II) sulphoxide complexes with $SOCl_2$, platinum(II) also acts as a chlorine-binding site. In this case Pt(IV) DMS complexes are formed.

The fact that in the reaction of the bis-sulphoxide complexes *cis*- and *trans*-[Pt$(DMSO)_2Cl_2$] with excess $SOCl_2$ only one of the DMSO ligands is reduced suggests that the processes involving reduction of DMSO and oxidation of Pt(II) are concerted.

Table 1. Initial reactants and conversion products in systems of the type metal–DMSO–RX.

Initial reactants	Products	Notes	Refs.
Pd–DMSO–n-$C_6H_{13}Br$	*trans*-[$Pd(DMS)_2Br_2$]		[25]
Rh–DMSO–n-$C_6H_{13}Br$	Rhodium(III) dimethyl sulphide complex	No information given on the structure of the rhodium and platinum complexes	[25]
Pt–DMSO–n-$C_6H_{13}Br$	Platinum(IV) dimethyl sulphide complex		
Au–DMSO–HBr	[(DMS)AuBr] and [(DMS)$AuBr_3$]	Both complexes were characterised by means of X-ray diffraction analysis	[26, 27]
M–DMSO–HX (M = Pd, Pt; X = Cl, Br)	*trans*-[$Pd(DMS)_2Cl_2$], [$Pt(DMS)_2Br_4$]	"	[28]
Noble metal–HX (X = Cl, Br)	Oxidation product of noble metal	No information given on the deoxygenation process	[29]
Ag–DMSO–HX (X = Br, I)	AgX, $(Me_3S)[AgX_2]$, $(Me_3S)[Ag_2X_3]$	$(Me_3S)[AgBr_2]$ complex was characterised by means of X-ray diffraction analysis	[30]
M–DMSO–CCl_4 (M = Fe, Co, Ni, Cu)	Metal oxidation products, DMS, CO_2, $COCl_2$, C_2Cl_6	Process takes place via the formation of dichlorocarbene	[31–34]

In concluding this section we should mention that the deoxygenation reactions of inner-sphere sulphoxides using $SOCl_2$ have parallels not only in organic but also organometallic chemistry. In particular, it has been shown[42–44] that acyl complexes can be deoxygenated with thionyl chloride or other acid halides to alkylidyne complexes

$$[M]—\overset{\overset{O}{\|}}{C}—R \rightarrow [M]\equiv C—R.$$

In these reactions also there is at least a formal reduction of the ligand and oxidation of the metal ion by the action of the acid chloride.

V. Deoxygenation of sulphoxides coordinated to Pt(II) with the reagent system PCl_5–ROH

It is known that in the reaction of phosphorus(V) pentachloride with different types of platinum(II) complexes, oxidative chlorination of the complexes occurs, giving platinum(IV) derivatives.[45–49] Fully in accordance with this are the reactions of the complexes K[$Pt(DMSO)Cl_3$] and [$Pt(R_2SO)LCl_2$] (R = Me, Et, $^1/_2C_2H_4OC_2H_4$, L = R_2SO; R = Me, L = DMS, NH_3, piperidine, pyridine, 2- and 4-methylpyridine) with PCl_5 in acetonitrile or nitromethane, resulting in the formation of the corresponding Pt(IV) compounds.[50,51]

In particular, by reacting the complex K[Pt(II)$(DMSO)Cl_3$] with PCl_5 in MeCN followed by decomposition of the excess PCl_5 with water or ethanol and addition of tetraethylammonium chloride to the mixture, (Et_4N)[Pt(IV)$(DMSO)Cl_5$] was obtained. The structure of this compound was confirmed by X-ray diffraction.[51] The reaction occurs differently if 2-propanol is used instead of water or ethanol. In this case as a result of all of the stages of the reaction, there is the formation of the DMS derivative (Et_4N)[Pt(IV)$(DMS)Cl_5$], whose structure has also been confirmed by X-ray diffraction analysis.

Similar reactions are typical for other Pt(II) sulphoxide derivatives, such as complexes of the type [Pt(II)$(R_2SO)LCl_2$]. The latter react with PCl_5 and with the reagent system PCl_5–ROH in different ways:

$$[Pt^{II}(R_2SO)LCl_2]— \begin{cases} \xrightarrow{PCl_5} [Pt^{IV}(R_2SO)LCl_4] \\ \xrightarrow{PCl_5/ROH} [Pt^{IV}(R_2S)LCl_4] \end{cases}$$

It should be mentioned in particular that on addition of EtOH or 2-PrOH to a mixture of [Pt(II)$(R_2SO)LCl_2$] and PCl_5, the dialkyl sulphide derivatives [Pt(IV)$(R_2S)LCl_4$] are formed in all cases. A mixture of K[$Pt(DMSO)Cl_3$] and PCl_5 reacts with alcohols in a different way. Thus, introduction of 2-propanol leads to the formation of the complex $[Pt(DMS)Cl_5]^-$, while introduction of ethanol gives a $[Pt(DMSO)Cl_5]^-$ complex. It follows from a comparison of the results obtained that in at least one case (in the reaction with K[$Pt(DMSO)Cl_3$] or with Pt[$R_2SO)LCl_2$], an inner-sphere rather than free molecule of R_2SO is deoxygenated.

It may be assumed that in the reaction of the complexes K[$Pt(DMSO)Cl_3$] and [$Pt(R_2SO)LCl_2$] with PCl_5, oxidation of the Pt(II) ion to Pt(IV) occurs and the intermediate (A) is formed:

$$\left[\begin{array}{c} O^+PCl_4 \\ \| \\ Pt^{IV}—SMe_2 \end{array}\right]$$
(A)

The subsequent addition of water leads to the hydrolysis of the sulphur-containing ligand with the formation of a Pt(IV) dialkyl sulphoxide complex, while when 2-propanol is introduced it is reduced and a Pt(IV) dialkyl sulphide derivative is formed.

It is known from the literature that the deoxygenation reactions of free R_2SO molecules using PCl_5 occur quite readily. However, there are significant differences in the form of reduction of inner-sphere and uncoordinated dialkyl sulphides. Thus, the reaction between free DMSO in PCl_5 occurs rapidly and leads to the formation of $MeSCH_2Cl$.[52,53] However, no complexes with such a

ligand were detected amongst the products from the reaction of coordinated DMSO with PCl_5.[50,51]

In the literature there are also examples of the conversion of R_2SO molecules to R_2S using PCl_5–reducing agent systems (where NaI [41] or 1-morpholino-1-cyclohexene [54] act as the reducing agent) as well as acid halide–alcohol–amine systems [where the acid halide is $SOCl_2$ and Cl(O)C–C(O)Cl].[6] In the latter case reaction of DMSO with the acid halide results in the formation of the salt $[Me\overset{+}{S}Cl]Cl^-$, which then reacts with an alcohol in the presence of NR_3 according to the scheme:[6]

$$[Me_2\overset{+}{S}Cl]\,Cl^- \xrightarrow[-NR_3\cdot HCl]{MeCH(OH)Me,\ NR_3} \rightarrow [Me_2\overset{+}{S}{-}OCHMe_2]Cl^- \xrightarrow[-NR_3\cdot HCl]{NR_3} Me_2S + Me_2CO.$$

In contrast to the reactions of free DMSO, the introduction of NR_3 is not required for the deoxygenation of inner-sphere DMSO.[39,50,51] This difference in the nature of the processes is likely to be due to the change in reactivity of the DMSO molecule as a result of coordination.

VI. Conversion of sulphoxides on treatment with metal ions in lower oxidation states

It is indicated in a review article[55] that Ti^{3+} compounds are mild and quite specific reducing agents as a result of titanium having a high affinity for oxygen. It is this factor that determines the reactivity of Ti^{3+} in reduction processes. Thus, $TiCl_3$ is an excellent reducing agent for nitro and nitroso compounds, aromatic and aliphatic *N*-oxides, and also azoxy compounds and oximes.[55] The ability of Ti^{3+} to extract an oxygen atom has also been extended to deoxygenation reactions of sulphoxides.[56,57]

It was shown[58] that the reaction of R_2SO with $TiCl_3$ can be used for the synthesis of R_2S. Different aryl and alkyl sulphides were obtained by this method. Reduction takes place for 2–4 h on boiling the reactants in a methanol–dichloromethane solvent mixture. The respective sulphides were isolated in 70–90% yield. Ho and Wong[58] assumed that the reaction takes place according to the following scheme:

$$R_2S{=}O + Ti^{3+} \longrightarrow R_2\overset{+}{S}{-}O{-}Ti^{\cdot\cdot\cdot}\ (Cl^-) \longrightarrow R_2S + Ti{=}O^{2+}.$$

The proposed synthetic method[58] was subsequently adapted for the deoxygenation of other sulphoxides.[59,60]

The reducing power of Ti^{2+} is known to be greater than that of Ti^{3+}.[55] It has also been established that Ti^{2+} salts do not exist in aqueous solution as they are oxidised 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. Ti^{2+} derivatives obtained by this method were used[61] for the reduction of R_2SO (R = Alk, Bz, Ph) to R_2S. The process was carried out in an ether–dichloromethane solvent mixture at 20 °C and was complete after not more than 1 min. In another study[62] when $TiCl_4$ was reacted with LiH in THF (with a 1 : 4 molar ratio of reactants), "low-valent titanium complexes" were obtained. On boiling alkyl or aryl sulphides with these compounds in THF for 10 h, the corresponding sulphides are formed. The prolonged time and relatively high temperature of the synthesis should be noted here.

The possibility of reducing sulphoxides with tin(II) chloride in the presence of HCl was first demonstrated in 1947.[64] This method was subsequently improved.[64] The reaction is carried out by boiling a solution of dialkyl sulphoxide and $SnCl_2.H_2O$ in methanol with added HCl for 2–3 h.

Tin(II) chloride has been used[65–67] for the reduction of coordinated DMSO. It was shown that the reaction of the complex *cis*-$[Pt(II)(DMSO)_2Cl_2]$ or a mixture of $K_2[Pt(II)Cl_4]$ and DMSO in hydrochloric acid with $SnCl_2.H_2O$ for 5–7 min with heating (70–90 °C) gives *cis*- and *trans*-$[Pt(IV)(DMS)_2Cl_4]$ respectively. Pt(IV) complexes with diethyl and dipropyl sulphide ligands were obtained in a similar manner. Kukushkin et al.[65–67] assume that the reactions for formation of $[Pt(R_2S)Cl_4]$ complexes can occur in both the inner and outer sphere of the coordination compounds.

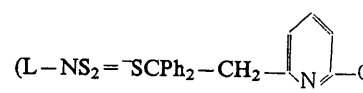
In concluding this section we should note that deoxygenation of sulphoxides can also be achieved using chromium,[68] vanadium,[69] molybdenum,[69,70] and tungsten[70,71] compounds in lower oxidation states.

VII. Reactions of sulphoxides with Mo(IV) complexes

The enzyme molybdenum oxotransferase is known to catalyse the two-electron oxidation or reduction of substrates of the type X/XO in a process which can formally be represented by the equation:

$$X + H_2O \rightleftarrows XO + 2H^+ + 2e.$$

It was demonstrated in a number of studies by Hold et al.[72–78] that $MoO(L{-}NS_2)(DMF)$ and $MoO_2(L{-}NS_2)$ complexes



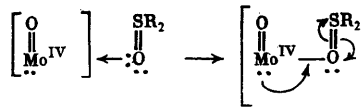
are convenient model compounds for the study of biological oxygen transfer processes. In particular, it was shown[74] that the compound $MoO(L{-}NS_2)(DMF)$ can effectively deoxygenate different alkyl and aryl sulphoxides. The process occurs in two stages. At the first stage the inner-sphere DMF is replaced by an R_2SO molecule:†

$$MoO(L{-}NS_2)(DMF) + R_2SO \rightleftarrows MoO(L{-}NS_2)(O\text{-}R_2SO) + DMF,$$

and deoxygenation takes place at the second stage:

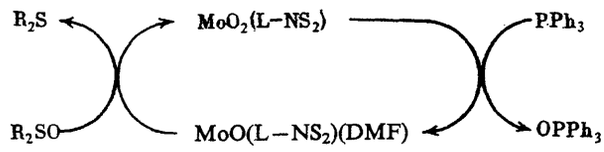
$$MoO\,(L{-}NS_2)\,(O\text{-}R_2SO) \rightarrow MoO_2\,(L{-}NS_2) + R_2S.$$

On the basis of the studies carried out,[74–78] the following reaction scheme was put forward:



† Inner-sphere *O*-coordinated sulphoxides will here and subsequently be denoted as *O*-R_2SO, while *S*-coordinated sulphoxides will be indicated as *S*-R_2SO.

It was shown in one of these studies[74] that the dioxomolybdenum complex $MoO_2(L-NS_2)$ oxidises triphenylphosphine to triphenylphosphine oxide. The following catalytic cycle was also established



It was shown in a number of studies[79–88] that certain other Mo(IV) complexes can effectively deoxygenate dialkyl sulphoxide molecules to give the corresponding sulphides. However, these processes have not been studied in detail.

VIII. Processes involving metal ion–reducing agent systems

In the previous section we considered deoxygenation reactions of sulphoxides using metal ions in low oxidation states that act simultaneously as electrophilic activators and reducing agents. However, metal ions in relatively high oxidation states can be used to deoxygenate R_2SO, but in this case chlorinated products are formed. Thus, in a study of the reactions of DMSO with $NbQX_4$ compounds (Q = X = Cl; Q = X = Br; Q = Me, X = Cl), XCH_2SMe products were obtained in all cases.[89–92] The authors of all four studies conclude that the process consists of two stages. At the first stage oxygen is transferred to give an oxocomplex and sulphonium salt:

$$NbQX_4 + 3Me_2SO \rightarrow NbOQX_2 \cdot 2Me_2SO + [Me_2\overset{+}{S}X]\,X^-,$$

At the second stage the sulphonium salt is converted to a haloalkyl sulphide:

$$[Me_2\overset{+}{S}X]\,X^- \rightarrow XCH_2SMe + HX.$$

The formation of XCH_2SMe can be avoided if the deoxygenation process is carried out using systems of the metal ion–reducing agent type. Complex hydrides of boron and aluminium are most frequently used as reducing agents.[93] This type of reduction of sulphoxides was first carried out in 1971.[94] In accordance with the recommended procedure stated in two studies,[94,95] the reduction was carried out by adding $NaBH_4$ slowly to a solution of R_2SO and $CoCl_2.6H_2O$ in 95% ethanol. Water was then added, heating was applied briefly, and the sulphides were extracted with ether. After removal of the ether the corresponding sulphides R_2S were isolated in good yield. The reduction of sulphoxides was also carried out using mixtures of $TiCl_4-NaBH_4$,[96,97] $TiCl_4-LiAl_4$,[98] $FeCl_3-NaBH_4$,[99] and Fe(III)LCl–$NaBH_4$ (L = tetraphenylporphyrinate).[100] The authors of all these studies[94–100] naturally assume that the process includes a stage involving *O*-coordination of R_2SO with the metal ion, resulting in electrophilic activation of the sulphoxide ligand and the sulphur atom becomes more sensitive to nucleophilic attack by hydride. It is important to note that the proposed mechanism has parallels in organic chemistry. In particular, reductions of alkoxysulphonium salts with complex boron hydrides have been reported.[101,102] An experiment carried out by Johnson and Phillips[102] demonstrated that the following conversion route occurs:

$$Ph-\overset{+}{S}(OMe)-Me \xrightarrow{[BH_4]^-} Ph-\overset{+}{S}(H)-Me \xrightarrow{-H^+} Ph-S-Me.$$

The reduction of sulphoxides with the reagent systems $BF_3.OEt_2-NaI$,[103] BF_3-NaI,[104] and $B(OPh)_3-NaBH_4$ [105] takes place via the same route.

In concluding this section we should report the results of one study[106] in which the conversions of dibutyl, dibenzyl, and diphenyl sulphoxides to the sulphides using aluminium(III) iodide in acetonitrile are recorded. It would appear that in these reactions the aluminium ion functions as the electrophilic activator and the I^- ions reduce the coordinated sulphoxides.

IX. Reduction of sulphoxides with carbonyl or carbene ligands in complexes

It is well known that the reactivity of carbon monoxide changes significantly when it is coordinated.[19] In a number of cases nucleophilic oxidation processes are made possible as a result of the electrophilic activation of CO molecules. According to studies that have been conducted, the mechanism of these types of reactions can be represented by the following scheme:

$$[M-CO] + \overline{O}-\overset{+}{A} \rightarrow \left\{M-C(=O)-O-\overset{+}{A}\right\} \xrightarrow{-CO_2} [MA].$$

Amine oxides, nitro- and nitroso-arenes, and iodosobenzene[107–109] have been widely used as oxygen donors in order to carry out these processes. It has been reported in a review article[108] that dialkyl sulphoxides can also act as this type of organic donor.

The reduction of sulphoxides by carbonyl complexes was first reported by Alper and Keung.[110] It was established that the reaction of various sulphoxides with $Fe(CO)_5$ at 130–135 °C in diglyme or di-n-butyl ether leads to the deoxygenation of R_2SO with the formation of the corresponding R_2S compounds and oxidation of an inner-sphere molecule of CO to CO_2. The nucleophilic oxygenation of the carbonyl ligand in the complex $[CpFe(CO)_3](PF_6)$ by DMSO and trimethylamine oxide has been studied.[111] Unfortunately, no information was given about the reduction products of dimethyl sulphoxide.[111]

It has been shown[112,113] that molybdenum hexacarbonyl is quite an effective agent for the deoxygenation of alkyl and aryl sulphoxides. The complex $Mo(CO)_6$ reduces sulphoxides on heating in solutions of dimethoxyethane[112] or acetic acid.[113]

Judging by the frequencies of the ν(CO) stretching vibrations in platinum(II) complexes, a CO ligand has high electrophilic activity.[107,108] The synthesis of the complex *cis*-$[Pt(DMSO)(CO)Cl_2]$ [ν(CO) = 2138 cm^{-1}] has been reported.[114] It has also been shown that heating this compound gives a mixture of products, amongst which CO_2 and CH_3Cl were identified. In the IR spectra of the solid products of thermolysis, the absorption bands characteristic of inner-sphere DMSO had disappeared. Pakhomova et al.[114] regard these results as an indication of the redox nature of the interaction between the coordination DMSO and CO ligands.

Deoxygenation of R_2SO molecules also occurs in processes involving another platinum(II) carbonyl compound—the complex $(Ph_3PBz)[Pt(CO)Cl_3]$ [ν(CO) = 2081 cm^{-1}]. Thus it was shown[115] that reaction of this complex with sulphoxides R_2SO (R = Me, Et,

n-Pr, Bz) in a nitromethane–acetic acid solvent mixture for several hours leads to the formation of $(Ph_3PBz)[Pt(R_2SO)Cl_3]$. On maintaining the complex $(Ph_3PBz)[Pt(CO)Cl_3]$ and the respective sulphoxide in an atmosphere of CO (1 atm, 20 °C, 5–7 days) in $MeNO_2$–$MeCO_2H$, deoxygenation of R_2SO molecules occurs and sulphides R_2S are formed. The reduction of sulphoxides by carbon monoxide does not occur in the absence of $(Ph_3PBz)[Pt(CO)Cl_3]$.

It was also shown in the same study[115] that reaction of $(Ph_3PBz)[Pt(R_2SO)Cl_3]$ complexes with CO under the conditions described above gives R_2S and $(Ph_3PBz)[Pt(CO)Cl_3]$ as the main products of synthesis. The reaction of $(Ph_3PBz)[Pt(Ph_2SO)Cl_3]$ with CO gives Ph_2S and a mixture of unidentified platinum-containing products. Preliminary results[115] suggest that the deoxygenation of R_2SO using CO in the presence of $(Ph_3PBz)[Pt(CO)Cl_3]$ is catalytic in nature.

The carbon atom that is bound to the central atom in carbene complexes is known to be activated as an electrophile. In the same way as for metal carbonyls, nucleophilic oxygenation reactions are typical for such compounds. Fairly recently Fisher et al.[116] obtained results indicating that DMSO can be deoxygenated by $(OC)_5W[C(R)Ph]$ complexes (R = H, Ph, OMe]. As a result of a redox reaction, the tungsten DMS complex $(OC)_5W(SMe_2)$ and O=C(R)Ph are formed.

X. Processes that occur in sulphoxide phosphine complexes

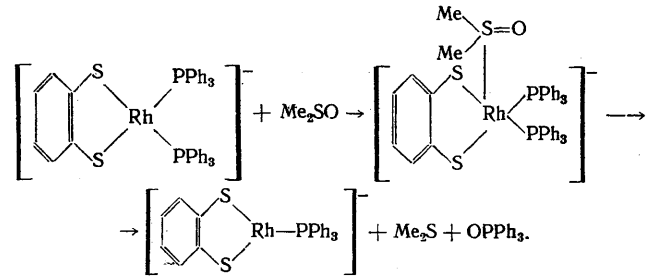
Bryan et al.[117] have reported the deoxygenation of DMSO that occurs to the following equation

$$[ReO(PPh_3)_2Cl_3] + 2Me_2SO \xrightarrow[C_6H_6]{HCl} \rightarrow [ReO(Me_2S)(OPPh_3)Cl_3] + Me_2S + OPPh_3.$$

The synthesis of $[ReO(Me_2S)(OPPh_3)Cl_3]$ takes place in the presence of hydrogen chloride, which is itself a reagent capable of deoxygenating DMSO. However, the process can also occur in the absence of HCl, but in this case the yield of DMS complex is reduced slightly (75% instead of 95%). It was also noted that $[ReO(Me_2S)(OPPh_3)Cl_3]$ is not formed when $[ReO(PPh_3)_2Cl_3]$ is treated with DMS or $OPPh_3$. It is thought[117] that the reaction mechanism includes a stage involving *O*-coordination of the DMSO molecule. The metal ion in this case functions as an electrophile activator, increasing the partial positive charge on sulphur and weakening the S–O bond. Subsequently there is a reaction with triphenylphosphine, which deoxygenates the DMSO molecule. It should be mentioned in connection with this study[117] that a process similar to that described in it had previously been reported.[118] It was established[117,118] that HCl catalyses the deoxygenation of DMSO by triphenylphosphine. This process also includes a stage involving electrophilic activation of DMSO by protonation of sulphinic oxygen.

On keeping $[M(Dppe)(O\text{-}DMSO)Cl]ClO_4$ complexes [M = Pt, Pd; Dppe = 1,2-bis(diphenylphosphino)ethane] in a mixture of dichloromethane and DMSO for a month (M = Pt) or 3 h (M = Pd), DMSO is deoxygenated to give the DMS derivatives $[M(Dppe)(DMS)Cl]ClO_4$. The latter are unstable and dimerise, giving $[\{M(Dppe)Cl\}_2](ClO_4)_2$ and DMS.[119] Unfortunately, Davies et al.[119] give no information about the oxidation product or about the presence of phosphine oxide in the mixture after completion of the reaction.

The rhodium(I) complex—$(Me_4N)[Rh(PPh_3)_2(S_2C_6H_4)]$—reacts with DMSO in DMF-d_6 and catalyses the transfer of oxygen from DMSO to triphenylphosphine.[120] Sellman et al.[120] propose that the reaction scheme includes a stage involving coordination of DMSO with the rhodium(I) ion, activation of the ligand, and formation of DMS, triphenylphosphine oxide and a tricoordinate Rh complex stabilised by the solvent:

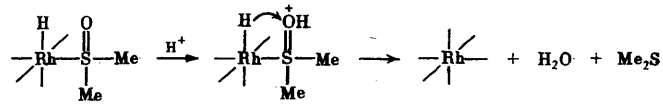


It should be noted that the conclusion, unsupported by experimental evidence, about *S*-coordination of the sulphoxide to the Rh(I) ion bound to other "mild" ligands raises certain doubts. As a rule in this situation DMSO is coordinated by its oxygen atom rather than by sulphur.[16–19] If our assumption is subsequently proved right, it may be possible to indicate more definitely that there is a similarity between the processes described in the three studies.[117,119,120]

XI. Other deoxygenation reactions of sulphoxides

The reduction of inner-sphere DMSO can occur when thermolysis of complex compounds in the solid state is carried out. Thus, it has been reported[121] that heating of the complexes $[Os(S\text{-}DMSO)_4Cl_2]$ and $[Os(S\text{-}DMSO)_3(O\text{-}DMSO)Cl_2]$ at 150 °C causes the disproportionation of dimethyl sulphoxide to give dimethyl sulphone and the complexes $[Os_2(\mu\text{-}SMe)_2(Me_2S)_2Cl_4]$ and $[Os(\mu\text{-}SMe)_2(Me_2S)(O\text{-}Me_2SO)Cl_4]$ respectively. The thermolysis of zirconium and hafnium compounds of the type $MCl_4.9DMSO$ has been described.[122] It was shown that heating these compounds in the solid state results in the formation of the hydroxo complexes $[M(OH)_2Cl_2(DMSO)_2]$ at an initial stage through a reaction with atmospheric moisture. When the temperature is increased further, conversion of the DMSO molecules occurs. Me_2S, HCl, and $Me_3S^+Cl^-$ were identified amongst the reaction products. Arsenin et al.[122] believe that the formation of DMS occurs in the inner sphere with the participation of HCl.

The deoxygenation of dialkyl sulphoxides using rhodium complexes was reported as early as 1969.[123] Thus it was shown that DMSO in the presence of $RhCl_3.3H_2O$ or *cis*-$[Rh(Et_2S)_3Cl_3]$ can be reduced with H_2 under mild conditions. By studying the kinetics of these reactions, it was possible to deduce that reaction of the initial compounds, DMSO and H_2 leads to the formation of sulphoxide hydride derivatives:



The subsequent reaction route involves protonation of the sulphinyl oxygen atom of the ligand followed by elimination of water molecules and DMS from the inner sphere of the complex.

XII. Conclusion

It is well known that sulphoxides exhibit weak oxidising properties. For example, in water (pH 7) the redox potential of the Me_2SO/Me_2S pair is only 0.16 V [124]

$$Me_2SO + 2H^+ + 2e \rightleftarrows Me_2S + H_2O.$$

However, the reactivity of R_2SO molecules when coordinated changes significantly.

An analysis of data on the deoxygenation of sulphoxides with complexes and metal ions shows that in the vast majority of cases the first stage of the reaction consists of *O*-coordination of R_2SO molecules with an M^+ ion:

$$R_2SO + M^+ \rightarrow [R_2S{=}OM^+ \longleftrightarrow R_2\overset{+}{S}{-}OM].$$

Here the metal ion functions as an electrophilic activator which increases the partial positive charge on sulphur and makes the ligand more sensitive towards reaction with a reducing agent. In fact, analysis of a number of X-ray diffraction studies (for example, those of Cotton[125] and Elding[126]) demonstrates that there is a significant elongation of the S–O bond in complexes with *O*-coordinated R_2SO molecules in comparison with free molecules. This in turn suggests that there is a significant contribution of the structure $R_2\overset{+}{S}-OM$ in the mesomeric hybrid of the molecule. It should be noted here that electron-acceptor substituents R on the sulphur atom also assist this type of electrophilic activation.

When *S*-coordination of R_2SO molecules occurs, the contribution of a bipolar structure to the mesomeric hybrid of the molecule decreases.

$$\begin{array}{ccc} :\ddot{O}:^- & & :O: \\ | & & \| \\ Me_2S^+ : \rightarrow [M] & \longleftrightarrow & Me_2\underset{\cdot\cdot}{S} : \rightarrow [M]. \end{array}$$

This is suggested by the X-ray diffraction data on S–O bond lengths for free and *S*-bonded R_2SO molecules (see, for example, the study of Davies).[7] This all signifies that the susceptibility of the oxygen atom of the inner-sphere R_2SO molecule to electrophilic attack will decrease. However, if acylation nevertheless occurs (particularly when active reagents such as PCl_5 or $SOCl_2$ are used), the coordinated sulphoxide becomes "doubly activated"—by the acyl residue on the oxygen atom and the metal ion on the sulphur atom. This type of species should evidently have a higher oxidising potential than an R_2SO molecule that is merely *O*-bonded. This may possibly account for the ease of the deoxygenation reaction of *S*-coordinated sulphoxides on treatment with hydrogen halides.

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