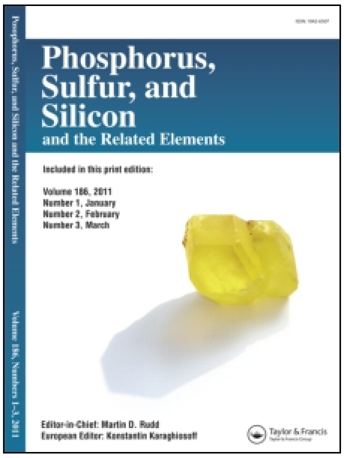

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# Pt(II) ASSISTED DEOXYGENATION OF COORDINATED SULFOXIDES BY HYDROCHLORIC- OR HYDROBROMIC ACID

Vadim Yu. Kukushkin[a]; Elena A. Aleksandrova[b]; Boris V. Zhadanov[c]
[a] Chemical Department, Leningrad State University, Petergof, USSR [b] Chair of General and Inorganic Chemistry, Lensovet Technological Institute, Leningrad, USSR [c] NPO IREA, Moscow, USSR

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## *Communication*

# Pt(II) ASSISTED DEOXYGENATION OF COORDINATED SULFOXIDES BY HYDROCHLORIC- OR HYDROBROMIC ACID

VADIM YU. KUKUSHKIN,[a]† ELENA A. ALEKSANDROVA[b]
and BORIS V. ZHADANOV[c]

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The interaction of the complexes $(Et_4N)[Pt(R_2SO)X_3]$ (R = Me, Et, $CH_2Ph$, X = Cl; R = Me, X = Br) and cis-$[Pt(Me_2SO)_2Cl_2]$ with concentrated HX (X = Cl, Br) results in the reduction of the coordinated sulfoxides and oxidation of Pt(II) to Pt(IV). As a result $[Pt(R_2S)X_5]^-$ and $[Pt(R_2S)_2X_4]$ are formed. Ligands $R_2S$ can be removed from the complexes and isolated in a free state.

*Key words:* Dibenzyl sulfoxide; deoxygenation of sulfoxides; synthesis of sulfides; Pt(II) sulfoxide complexes; Pt(IV) sulfide complexes; cis-trans isomerization.

It is well known that concentrated HX (X = Cl, Br) can deoxygenate free $R_2SO$ sulfoxides to form $R_2S$ sulfides.[1–6] However, this process is not always directed only towards the formation of $R_2S$. For example, by the interaction of $(PhCH_2)_2SO$ with HCl deoxygenation is attended by a number of side-reactions leading to the formation of products among which PhCHO (14.5%), $PhCH_2Cl$ (29.6%), $(PhCH_2)_2S_2O_2$ (12%), $(PhCH_2)_2S_2$ (35%) and $(PhCH_2)_2S$ (9%) were identified[7] (the yields are given in parenthesis).

It has been established that the interaction of the coordinated dibenzyl sulfoxide in the complex $(Et_4N)[Pt((PhCH_2)_2SO)Cl_3]$ with HCl in acetone results in $(Et_4N)[Pt((PhCH_2)_2S)Cl_5]$ isolated into a solid phase with the yield of about 65%. A different behaviour of the free and coordinated sulfoxide suggests Pt(II) assisted deoxygenation path.

The reaction of concentrated HCl with the complexes $(Et_4N)[Pt(R_2SO)Cl_3]$ (R = Me, Et, $CH_2Ph$) in acetone or acetonitrile solutions always results in the isolation of compounds of $(Et_4N)[Pt^{IV}(R_2S)Cl_5]$ type with the yields of 60–85%. The same complexes were obtained by reaction of concentrated HCl with the $(Et_4N)[Pt(R_2SO)Cl_3]$ generated in situ: a) as a result of the reaction of cis-$[Pt(R_2SO)_2Cl_2]$ (R = Me, Et) with $(Et_4N)Cl$ in MeCN or b) by reaction of $K_2[PtCl_4]$ with $R_2SO$ (R = Et, $CH_2Ph$) in the $H_2O$/MeCN mixture followed by the addition of $(Et_4N)Cl$.

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[a] Chemical Department, Leningrad State University, Universitetsky pr., 2, 198904, Stary Petergof, USSR.
[b] Chair of General and Inorganic Chemistry, Lensovet Technological Institute, Zagorodny pr., 49, 198013, Leningrad, USSR.
[c] NPO IREA, Bogorodsky val, 3, 107258, Moscow, USSR.
† The author to whom correspondence should be addressed.

When the solution of $(Et_4N)[Pt(Ph_2SO)Cl_3]$ in acetonitrile is saturated by gaseous HCl the deoxygenation of $Ph_2SO$, oxidation of Pt(II) and S-ligand substitution take place. As a result of the processes operating together free $Ph_2S$ and $(Et_4N)_2[PtCl_6]$ are formed.

Treatment of $(Et_4N)[Pt(Me_2SO)Br_3]$ with concentrated HBr in acetone gives $(Et_4N)[Pt(Me_2S)Br_5]$ whereas boiling of reagents in water leads to release of the solid *trans*-$[Pt(Me_2S)_2Br_4]$ and the formation of $(Et_4N)_2[PtBr_6]$ in the solution.

The reaction between *cis*-$[Pt(Me_2SO)_2Cl_2]$ and concentrated HCl in MeCN, $MeNO_2$ and in acetone-$d_6$ was monitored by means of TLC and $^1$H-nmr methods. It has been established that *cis*-$[Pt(Me_2S)(Me_2SO)Cl_4]$ is formed first and gradually disappears. Later, *cis*-$[Pt(Me_2S)_2Cl_4]$ appears in the mixture, this complex is completely isomerized to the trans-isomer. The direction of *cis* → *trans* isomerization is consistent with the conclusion made in Ref. 8. The reaction of *cis*-$[Pt(Me_2SO)_2Cl_2]$ with HBr produces deoxygenation, oxidation of Pt(II) and substitution of $Cl^-$ for $Br^-$ with the formation of *trans*-$[Pt(Me_2S)_2Br_4]$.

The reaction path of Pt(II) sulfoxide complexes with HX probably incorporates the formation of the $\{R_2(X)\overset{+}{S}—Pt(II)]X^-$ intermediate. The platinum ion is a halogen-trapping center assisting the conversion of $\{R_2(X)\overset{+}{S}—Pt(II)\}X^-$ into $[R_2S—Pt(IV)X_2]$.[9,10]

The deoxygenation reaction of coordinated sulfoxides can be used in the preparative organic chemistry to obtain $R_2S$. Sulfides are removed from the inner sphere of the complexes of Pt(IV) by $SCN^-$ substitution in water (in case of the dibenzyl sulfide complex, $PhCH_2NCS$ was found in addition to free dibenzyl sulfide) or by the reduction of complexes $(Pt(IV) \rightarrow Pt(O))$ via $N_2H_4$ in water–alkaline medium. The released $R_2S$ is extracted into $CHCl_3$ or $CH_2Cl_2$ and therefore is separated from other products of synthesis.

Deoxygenation of the dibenzyl sulfoxide in $(Et_4N)[Pt((PhCH_2)_2SO)Cl_3]$:HCl (3 ml; $\rho = 1.18\ g\ cm^{-3}$) was added to the solution of $(Et_4N)[Pt((PhCH_2)_2SO)Cl_3]$ (1.01 g, 1.52 mmol) in acetone (40 ml) and boiled to evaporation of about 30 ml within 15 min then the resultant product was precipitated by addition of hexane (50 ml). After solvent decantation, the precipitate was washed with hot (60°C) toluene (10 × 3 ml), filtered and washed on a filter with hot toluene (2 × 3 ml) and hexane (3 × 3 ml), dried in air at 20°C. Yield of $(Et_4N)[Pt((PhCH_2)_2S)Cl_5] =$ 0.68 g, 63% based on Pt. For $C_{22}H_{30}Cl_5NPtS$ Calc. % Cl = 24.72, % Pt = 27.21. Found % Cl 24.4, % Pt 27.3. M.P. = 214°C (Kofler tables). IR (KBr pellet), $cm^{-1}$: $\nu_{PtCl}$ 335 s, 316 m. Molar conductivity is $64\ Ohm^{-1}\ cm^2\ mol^{-1}$ (DMF). The identification of the $(PhCH_2)_2S$ ligand was carried out by means of the TLC and $^1$H-nmr methods after substitution by $SCN^-$ in water followed by extraction of the free $(PhCH_2)_2S$ into $CDCl_3$.

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