Specific features of the interaction of components in the DMSO—HBr—Pd^0 system

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The products of interaction of components in the donor-acceptor electron-transport (DAET) DMSO—HBr system and their complex formation with the metallic palladium surface were studied. H_2O and Me_2S (main reaction products) and CO, CS_2, C_2H_6, MeBr, H, and CH_4 (minor reaction products) were found in the gas phase by mass spectrometry (MS). The samples of metallic palladium treated with the DAET system with a components ratio corresponding to the minimum and maximum rates of metal dissolution were studied by the methods of thermoprogrammed desorption with MS detection (TPD-MS) and XPS. According to the TPD-MS data, two forms of Me_2S are present on the metal surface, whereas the XPS method detected two complexes with the molecular compositions $Pd^{II}Br_4S_{1.26}$ and $Pd^{II}Br_{3.86}S_{1.42}$. The addition of an aqueous solution of NaOH to the system results in the formation of HCOONa, which indicates that compounds (CH_2O, HCOOH) capable of reducing the palladium complexes are present in the DAET system.

Key words: donor-acceptor electron-transport system, dimethyl sulfoxide, hydrogen bromide, palladium, complex formation, surface, metal, mass spectroscopy, XPS.

Dissolution of metals is an important stage in solvometallurgy and the synthetic chemistry of metal complexes, especially in the chemistry of noble metals. The systems that oxidize these metals can be classified depending on the role of the starting components of the liquid phase during metal dissolution as follows.

1. Molecular donor-acceptor (MDA) systems. The system contains a ligand-complex-forming agent (donor) and an oxidant (acceptor) that form molecular complexes. The metal is oxidized by a complex-bound acceptor such as molecular halogen, molecular or peroxide oxygen, quinone, and others, for example,[1,2]

$$2\,Au^0 + 4\,CN^- + 1/2\,O_2 + H_2O \longrightarrow \\ \longrightarrow 2\,[Au^I(CN)_2]^- + 2\,OH^-. \qquad (1)$$

This class also contains systems with complex ions of metals or compounds of elements in high oxidation states as oxidants[3]:

$$Au^0 + 2\,CS(NH_2)_2 + Fe^{3+} \longrightarrow \\ \longrightarrow Au[CS(NH_2)_2]_2^+ + Fe^{2+}. \qquad (2)$$

2. Donor-acceptor electron-transport (DAET) systems.[4] Unlike the MDA systems, in the DAET systems molecular complexes undergo further transformation with complete electron transfer from a donor to an acceptor. New species capable of oxidizing the metal are generated in the systems.

Inorganic DAET systems. The system contains inorganic ligand-complex-forming agents (donor) and acceptor that do not directly react with the metal. Compounds capable of metal oxidizing are formed due to the interaction of the components of the inorganic donor-acceptor system. This type of systems is exemplified by *aqua regia*, whose oxidants are nitrosyl chloride and molecular chlorine (or its hydrate) formed by the interaction of concentrated nitric and hydrochloric acids[5]:

$$Au^0 + 4\,HCl + HNO_3 \longrightarrow \\ \longrightarrow H[AuCl_4]^- + NO + 2\,H_2O. \qquad (3)$$

Organic DAET systems. The system contains an organic ligand-complex-forming agent (donor) and an organic or inorganic acceptor inert toward the metal. The DMSO—HBr system ("Chernogolovskaya Vodka")[4] studied in this work is an example of organic DAET systems. Systems of this type enable the use of a wide range of organic compounds containing various functional groups, which provides for the synthesis of metal complexes in one stage[6—8]:

$$Au^0 + 2\,BuBr + Me_2SO \longrightarrow \\ \longrightarrow Me_2SAuBr + [AuBr]_s + Bu_2O, \qquad (4)$$

$$Pt^0 + 4\,HBr + 2\,Me_2SO \longrightarrow \\ \longrightarrow [Me_2S]_2PtBr_4 + 2\,H_2O, \qquad (5)$$

$$Ag^0 + 2\,HBr + 2\,Me_2SO \longrightarrow \\ \longrightarrow [Me_3S][AgBr_2] + H_2O. \qquad (6)$$

A distinctive feature of the DMSO—HX system is the presence of several extremes on the plot of the rate

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of metal (Ag, Cu, Au, Pt, and Pd) dissolution *vs* the component ratio.[9,10] The nature of reactions occurring in these systems is yet unclear, and their investigation is still urgent.

This work is aimed at studying the products of the transformation of the components of the organic DAET system DMSO—HBr and their complex formation with metallic palladium.

Experimental

Mass spectrometry (MS), thermoprogrammed desorption with MS detection (TPD-MS), and X-ray photoelectron spectroscopy (XPS) were used. The interaction of DMSO with HBr was studied at ratios of the components corresponding to the molar fractions of DMSO $n = 0.25$ and 0.7, for which the rate of metal dissolution had extreme values.

For the mass spectrometric determination of gaseous reaction products, experiments were carried out in an evacuated (1.3 N m^{-2}) thermostatted glass reactor at 60 °C. To determine the products of deep conversion of the components of the system at maxima of the metal dissolution rate, the reaction mixture was heated for 2 h at 100 °C. For the TPD-MS analysis of the products adsorbed on the palladium surface, the metal powder was exposed to the reaction mixture for 2 h at 60 °C. The setup and TPD-MS analysis have been described in detail in the previous work.[11] The TPD spectra were obtained by linear heating at the rate $\beta = 3$ deg min^{-1}. The activation energy of desorption $E(D)$ was found by a known procedure.[12] To determine the oxidation state of the elements on the palladium surface by XPS, the metallic foil was treated with a DMSO—HBr solution under conditions similar to those of the TPD analysis of the products. X-ray photoelectron spectra were recorded on a Varian IEE-15 spectrometer with induced electron emission (USA).

Results and Discussion

To reveal the nature of the final products of the interaction of DMSO with HBr in the absence of the metal, the gas phase was analyzed by MS at different initial ratios of the components. In both cases ($n = 0.25$ and 0.7), the MS analysis of the gaseous reaction products showed water and dimethyl sulfide. CO, CS_2, C_2H_6, MeBr, H_2, and CH_4 were found as admixtures. In addition, H_2S, HBr, Me_2S_2, Me_2SO, SO_2, COS, and CO_2 were found in amounts an order of magnitude lower than the previous admixtures.

In another experimental series, metallic palladium was treated with a DMSO—HBr solution at the same ratio of the components. The TPD-MS data showed that the metal surface contains two adsorbed forms of dimethyl sulfide with an effective activation energy of desorption $E'(D) = 116.7$ kJ mol^{-1} (at 90 °C) and $E''(D) = 113$ kJ mol^{-1} (at 140 °C) (Fig. 1). It can be assumed that the adsorbed species Me_2S and $Me_2S \cdot Br_2$ can be sources of two forms of dimethyl sulfide desorbed from the metal surface. The desorption of two forms of Me_2S is not a result of the decomposition of the palladium complex on the surface. The thermogravimetric study[13] of the $(Me_2S)_2PdBr_2$ complex isolated from the reaction mixture showed that its thermal decomposition starts at 235 °C and proceeds with the elimination of methylmercaptan and dimethyl disulfide (products of dimethyl sulfide decomposition) followed by the evolution of ethyl bromide and ethane. Palladium sulfide PdS is the final decomposition product. The XPS study of the metallic palladium samples treated with the DAET system at component ratios corresponding to the minimum and maximum rates of metal dissolution (molar fraction of DMSO $n = 0.25$ and 0.7, respectively) gave the results presented in Table 1.

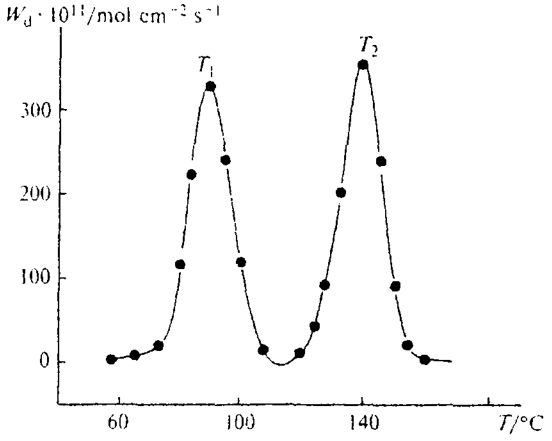


Fig. 1. Thermodesorption spectra of dimethyl sulfide from the palladium surface. $E_{d1} = 116.7$ kJ mol^{-1} (T_1), $E_{d2} =$ 113 kJ mol^{-1} (T_2).

The bond energy for palladium corresponds to Pd^{2+}, and the atomic ratio of palladium, bromine, and sulfur at the minimum point of the dissolution rate corresponds to the composition $PdBr_4S_{1.26}$, and that at the maximum point corresponds to $PdBr_{3.86}S_{1.42}$. Sulfur has a broadened peak and, most probably, exists in the oxidation state (IV) rather than (II). Bromine remains negatively charged, but its electron density is lowered. Based on the obtained data, we may assume that the adsorbed complexes $(Me_2S)_xPdBr_2$ and compounds whose compositions are close to $Me_2S(OH)Br$ and $Me_2S \cdot Br_2$ are present on the metal surface. The liquid phase contains, most likely, several complexes, whose compositions depend on the ratio of the components. However, only $(Me_2S)_2PdBr_2$ has been isolated in the solid state.[13]

Our results agree with the concepts on the equilibrium[14] interaction of DMSO and HBr, whose final products are H_2O, Me_2S, and molecular or complex-

Table 1. Bond energies (±0.2 eV) for the measured XP lines

n_{DMSO}	t/min	Br/Pd	S/Pd	$E_{Br(3d)}$[b]	$E_{Pd(3d(5/2))}$[b]	$E_{S(2p)}$[b]
0.25	15	4.0	1.26	69.7	338.1	164.2
0.7	15	3.38	1.42	69.7	338.3	164.8

bound Br_2, and the intermediates $Me_2S(OH)Br$ and $Me_2S\cdot Br_2$ are responsible, most likely, for metal oxidation. The formation of these substances can be presented as the following scheme:

$$\underset{\mathbf{L}}{Me_2S{=}O} + HBr \rightleftharpoons \underset{(MC)}{[Me_2S{=}O\cdot HBr]} \rightleftharpoons \underset{\mathbf{1}}{Me_2S(OH)Br} \tag{7}$$

$$Me_2S(OH)Br + HBr \rightleftharpoons \underset{\mathbf{2}}{Me_2SBr_2\cdot H_2O} \tag{8}$$

$$Me_2SBr_2\cdot H_2O \rightleftharpoons \underset{\mathbf{3}}{Me_2S\cdot Br_2} + H_2O \tag{9}$$

$$Me_2S\cdot Br_2 \rightleftharpoons \underset{\mathbf{L'}}{Me_2S} + \underset{\mathbf{4}}{Br_2} \tag{10}$$

The total reaction is

$$Me_2SO + 2\,HBr \rightleftharpoons Me_2S + Br_2 + H_2O. \tag{11}$$

The calculated free energy of reaction (11), ignoring complex formation, is -23.4 kJ mol^{-1}.[16]

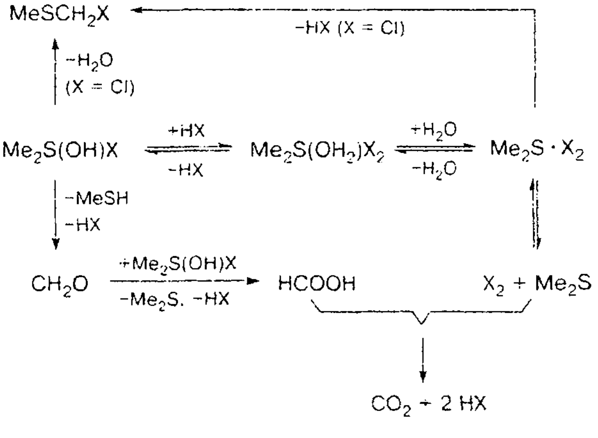
In the presence of the ligand-complex-forming agents, dimethyl sulfoxide (**L**) and dimethyl sulfide (**L′**), halogen-containing compounds **1**—**4** can serve as oxidants.

To reveal the nature of the oxidant formed by the reaction of Me_2SO and HBr, an aqueous solution of NaOH was introduced into the system at reactant ratios corresponding to the lowest and highest rates of metal dissolution.[9]

Sodium formate, except for Me_2S, was the only product. This indicates that species capable of reducing the metal complexes that form in the liquid phase are generated in the system under some conditions. These reducing agents and possible products of their transformation (CH_2O, CO, and CO_2) have previously been found in the composition of the coordination compounds.[5,15]

The reaction of Me_2SO with HX (taking into account reaction (7)) can proceed according to Scheme 1.

Scheme 1



The compounds formed in the system can exist in different forms, for example, as resonance forms ($Me_2S^{II}\cdot Br_2 \longleftrightarrow Me_2S^{IV}Br_2$) or tautomers ($[Me_2SOH]Br \rightleftharpoons [Me_2SH][OBr]$). In the DMSO—HX system, the interaction of the reactants can proceed *via* two pathways: generation of oxidants (halogen-containing compounds **1**—**4**) and reducing agents (CH_2O and HCOOH). The predominant formation of oxidants or reducing agents depends on the DMSO to HX ratio and temperature of the process (at >100 °C the evolution of CH_2O from the reaction mixture is accelerated). The formation and evolution of the reducing agents can be described by the following reactions:

$$\underset{D}{Me_2SO} + \underset{A}{HX} \rightleftharpoons \underset{D\cdot A}{\{Me_2SO\cdot HX\}} \rightleftharpoons Me_2S(OH)X, \tag{12}$$

$$Me_2S(OH)X \longrightarrow CH_2O + MeSH + HX, \tag{13}$$

$$CH_2O + Me_2SO \longrightarrow HCOOH + Me_2S, \tag{14}$$

$$CH_2O + Me_2S(OH)X \longrightarrow HCOOH + Me_2S + HX, \tag{15}$$

$$Me_2S(OH)X + HX \longrightarrow Me_2S(H_2O)X_2 \xrightarrow{-H_2O} Me_2S\cdot X_2 \longrightarrow X_2 + Me_2S, \tag{16}$$

$$HCOOH + X_2 \longrightarrow CO_2 + 2\,HX, \tag{17}$$

$$HCOOH + Me_2S\cdot X_2 \longrightarrow CO_2 + 2\,HX + Me_2S, \tag{18}$$

$$HCOOH + Me_2S(OH)X \longrightarrow CO_2 + HX + H_2O + Me_2S. \tag{19}$$

Here D is the donor, and A is the acceptor.

In conclusion note that the organic DAET systems (including DMSO—HBr) differ from their inorganic analogs by the manifestation of both oxidative and reductive properties. This creates prerequisites for the formation of systems with controlled direct one-stage synthesis of coordination compounds and directed transfer of the metal phase in condensed complex-forming media.

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References

1. I. N. Plaksin, *Metallurgiya blagorodnykh metallov* [*Metallurgy of Noble Metals*], Metallurgizdat, Moscow, 1958 (in Russian).

2. I. L. Lavrent'ev and M. L. Khidekel', *Usp. Khim.*, 1983, **52**, 607 [*Russ. Chem. Rev.*, 1983, **52** (Engl. Transl.)].
3. G. G. Mineev and A. F. Panchenko, *Rastvoriteli zolota i serebra v gidrometallurgii* [*Solvents of Gold and Silver in Hydrometallurgy*], Metallurgiya, Moscow, 1994, p. 105 (in Russian).
4. E. T. Epel'baum, V. I. Ponomarev, and I. P. Lavrent'ev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 1325 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 1167 (Engl. Transl.)].
5. B. V. Nekrasov, *Osnovy obshchei khimii* [*Foundations of General Chemistry*], Khimiya, Moscow, 1965, **1**, 410 (in Russian).
6. G. A. Nifontova and I. P. Lavrent'ev, *Trans. Met. Chem.*, 1993, **18**, 2730.
7. L. A. Atovmyan, O. N. Krasochka, V. I. Ponomarev, and O. I. Filipenko, *Tez. dokl. XII Vsesoyuz. Chugaevsk. soveshch. po khimii kompleksnykh soedinenii* [*Abstrs. XII All-Union Chugaev Meeting on Chemistry of Complex Compounds*], Novosibirsk, 1975, 239 (in Russian).
8. L. V. Shirshova, I. P. Lavrent'ev, and V. I. Ponomarev, *Koord. Khim.*, 1989, **15**, 1048 [*Sov. J. Coord. Chem.*, 1989, **15**, 616 (Engl. Transl.)].
9. L. V. Shirshova and I. P. Lavrent'ev, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 1929 [*Russ. Chem. Bull.*, 1992, **41**, 1513 (Engl. Transl.)].
10. G. A. Nifontova, Yu. B. Sikorenko, D. A. Osipchuk, S. G. Kokoreva, and I. P. Lavrent'ev, *Zh. Fiz. Khim.*, 1998, **72**, 1179 [*Russ. J. Phys. Chem.*, 1998 (Engl. Transl.)].
11. N. V. Kir'yakov, E. A. Grigoryan, and G. P. Sikharulidze, *SFKhT*, 1990, **3**, 1120 (in Russian).
12. M. A. Frish, F. Holtzberg, and D. L. Kaiser, *Chemistry of Oxide-Superconductors*, Ed. C. N. R. Rao, Blackwell Sci. Publ., 1988, 85.
13. C. G. Kokoreva, G. A. Nifontova, L. G. Korableva, and Yu. B. Sikorenko, *Zh. Neorg. Khim.*, 1995, **40**, 1320 [*Russ. J. Inorg. Chem.*, 1995, **40** (Engl. Transl.)].
14. C. G. Kokoreva, G. A. Nifontova, and I. P. Lavrent'ev, *Tez. dokl. "XVII Vseros. simp. molodykh uchenykh po khimicheskoi kinetike" (Klyaz'ma, February 1—5, 1999)* [*Abstrs. "XVII All-Russ. Symp. of Young Scientists on Chemical Kinetics"*], Klyaz'ma, 1999, 21 (in Russian).
15. G. A. Nifontova, Ph. D. (Chem.) Thesis, Institute of Structural Macrokinetics, Academy of Sciences of the USSR, Chernogolovka, 1988, 86 pp. (in Russian).
16. L. V. Shirshova, Ph. D. (Chem.) Thesis, Institute of Structural Macrokinetics, Academy of Sciences of the USSR, Chernogolovka, 1990, 113 pp. (in Russian).

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