DISSOLUTION OF METALLIC GOLD IN DMSO—RX SYSTEMS. THE CONCEPT OF A DONOR—ACCEPTOR ELECTRON TRANSFER SYSTEM

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UDC 546.55:542.943:547.268: 547.22:541.49:542.91

The complexing of gold during dissolution of gold powder in donor—acceptor organic and aqueous—organic Au^0 —DMSO—RX systems (where R = H or Bu, and X = Cl or Br) was studied. Ten complexes were produced, and their compositions and IR spectra in the 4000-200 cm⁻¹ range were determined. The data obtained were interpreted in terms of the concept of donor—acceptor electron transfer systems.

Keywords: metal, gold, dissolution, organic media, DMSO, RX, gold complexes, production, donor-acceptor electron transfer (DAET) systems, concept.

The application of donor—acceptor organic and aqueous—organic systems facilitates the dissolution of many transition metals, including noble metals, under mild conditions. At the same time the presence in such systems of dipole complexes (potential ligands) results in direct synthesis of various complex compounds from solid metals (powder, chips, and platelets) [1-4].

Direct synthesis and structures of the [AuBr(Me₂S)] and [AuBr₃(Me₂S] complexes, produced by dissolution of gold powder in the DMSO—HBr system, are described in [5]. The objective of the present investigation was to study the complexing of gold during its dissolution, and to establish the properties of the oxidizer and the characteristics of the reaction taking place in the Au⁰—DMSO—RX system (where R = H or Bu, and X = Cl or Br) [6].

Chemical compositions were determined and IR spectra in the 4000-200 cm⁻¹ range were investigated for the complexes [AuCl(Me₂S)] (1), [AuBr(Me₂S)] (2), [AuBr₃(Me₂S)] (3), [Me₃S][AuBr₄] (4), [Me₃S][AuBr₄(Me₂S)]·H₂O (5), [Me₃SO][AuBr₄]·H₂O (6), [Me₃S][Au₂Br₇(Me₂S)₂]·3H₂O (7), [Me₃S]₂[Au₂Br₈]·2DMSO·H₂O (8), [Me₂(Bu)SO][AuBr₄]·H₂O (9) produced here. The reaction sequence was suggested for the Au⁰—DMSO—RX system. The data obtained were analyzed according to the DAET system (donor—acceptor electron transfer system) concept [7].

EXPERIMENTAL

The gold dissolution experiments were carried out in a glass flask equipped with a magnetic stirrer and a reverse cooling system. Gold powder was produced according to a standard method of dissolving gold wire in aqua regia and reducing the tetrachloroauric acid HAuCl₄ with a hydrazine hydrochloride solution. Thermically pure DMSO, BuBr, and hydrochloric acid, and especially pure hydrobromic acid were used. Infrared spectra of the complexes were recorded with UR-20 and "Perkin—Elmer 325" spectrophotometers. The specimens for spectrometry were prepared in the form of suspensions in vaseline oil, or of tablets with KBr No noticeable reaction between KBr and other materials was detected.

Complex 1: Chloroaurate(I) Dimethylsulfide. To 0.3 g of gold powder 4 ml of DMSO and 8 ml of HCl were added. The mixture was heated at 90°C for 2 h. The gold was fully dissolved, while colorless crystals of complex 1 precipitated from the cooled solution in the form of long needles which were filtered off, washed with a mixture of pentane and ethanol, and dried on a piece of filter paper.

Complex 2: Bromoaurate(I) Dimethylsulfide and Complex 3: Tribromoaurate(III) Dimethylsulfide. The methods by which these materials were produced are described in [5].

Complex 4: Trimethylsulfonium Tetrabromoaurate(III). On addition of four volumes of water to the filtrate left after precipitation of complex 2, the wine-colored powder of complex 4 was precipitated. It was filtered off, washed with ether, and dried. We note that in [5] this complex was mistaken for complex 3, for which the authors want to apologize. The error occurred because the IR spectra of complexes 3 and 4 are similar in the 4000-400 cm⁻¹ range. Further analysis of their low-frequency IR spectra (400-200 cm⁻¹) revealed that error.

Institute of Structural Macrokinetics, Russian Academy of Sciences, Chernogolovka 142432, Moscow District. Translated from Izvestiya Akademii Nauk, Seriya Khimicheskaya, No. 3, pp. 498-506, March, 1992. Original article submitted March 21, 1991.

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Com-	1 1 1				round/calc	ulated, %		
plex	Empirical formula	System	Color	υ	н	x	s	Au
	[AuCl(Me ₂ S)] (C ₂ H ₆ ClSAu)	Au" – DMSO – HCl	Colorless	8.4	1.9 2.04	12.0 12.05	10.3 10.87	65.9 66.89
21	[AuBr(Me ₂ S)] (C ₂ H ₆ BrSAu)	Au ⁶ - DMSO - HBr	Colorless	7.8	2.0	23, 1 23, 1	9.2	58.0 58.11
en	[AuBr ₃ (Me ₂ S)] (C ₂ H ₆ Br ₃ SAu)	Au ⁰ DMSO HBr	Wine-colored	5.0 4.81	1.3	48.9 48.10	6.6 6.41	38.3 39.48
æ	[Me ₃ S][AuBr ₄] (C ₃ H ₆ Br ₄ SAu)	Au ⁿ – DMSO – HBr	Wine-colored	6.8 6.06	1.6	52.1 53.87	4.6	33.9 33.16
ŝ	[Me ₃ S][AuBr ₄ (Me ₂ S)]·H ₂ O (C ₅ H ₁ ,Br ₄ OS ₂ Au)	Au ⁿ – DMSO – HBr	Dark-red	8.1 8.90	2.2	<u>48.1</u> 47.48	9.0 9.50	29.6 29.23
9	[Me ₃ SO][AuBr ₄]·H ₂ () (C ₃ H ₁₁ Br ₄ O ₂ SAu)	Au ^o – DMSO – HBr	Dark-wine	6.2 5.73	1.9	51.0 50.95	5.3 5.10	32.2
7	[Me ₃ S][Au ₂ Br ₇ (Me ₂ S) ₂]·3H ₂ O (C ₇ H ₂₇ Br ₇ O ₃ S ₃ Au ₂)	Au ⁰ – DMSO – HBr	Wine-colored	6.4 6.95	1.5	47.1	7.0	33.4 32.59
æ	[Me ₃ S] ₂ [Au ₂ Br ₈].2DMSO·H ₂ O (C ₁₀ H ₃₂ Br ₈ O ₃ S ₄ Au ₂)	Au ⁶ - DMSO - HBr	Wine-colored	7.9 8.81	2.0	47.1	9.9 9.40	28.93
6	[M ₀₄ (Bu)SO][AuBr ₄]·H ₂ O (C ₆ H ₁₇ Br ₄ O ₂ SAu)	Au ^e – DMSO – BuBr	Violet	9.9 10.74	2.5	<u>48.0</u>	5.2 4.78	29.7 29.40
10	[Me ₃ S]Br (C ₃ H ₉ BrS)	DMSO BuBr	Colorless	23.1 22.92	5.73	<u>49.3</u> 50.97	20.1 20.38	1

TABLE 1. Elemental Analysis of Complexes 1-10

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Com-	Climan B and Lincold M		Maxiu	ma of	absorp	tion baı	nds, cm ⁻¹					
plex	Molecular Iormula	4 OH (HO 0H)	V CH ₃		δc	H ₃	vso	ρCE	l ₃	ρH _z O	SV	5 ⁸
-	[AuCh(Me2S)]	I	3003 m 29 2920 w 29	93, m 110w	1435/m 1410 s 1320 m	1420 s 1385w 1300 w	i	1035 s 960 m	998-s	1	725 m	675 m
29	[AuBr(Me ₂ S)]	3	3000, w 29 2920, w 29	90 m 110 m	1435 m 1410 s	1420 sh	1	1035 s 960 w	995 s	i	725 W 625 W	675 w
3	[AuBr ₃ (Me ₂ S)]	1	3010 w 29 2910	m.060	1425 m 1390 w 1300 w	1405 m 1325 m	I	1050 m 940 s	1035 s 910 m	ĩ	720 ^{-m} 645 w	680 w
4	[Me _s S][AuBr ₄]	i	3005 s 29	120 s	1427 s 1350 s	1410 S 1315 w	ł	1040 s	940 m	Ţ	730 w 620 w	653 m
ŝ	[Me ₃ S][AuBr, (Me ₂ S)]·H ₂ O	3420 br (1635 m)	3010 w 29 2910 m	ш06	1425.s 1390.m 1305.w	1407 [,] s 1325 s	Ę	1050 w. 945 s	1030s 910 m	815 [.] m	730 w 675 m	715 m 647 w
ø	[Me ₃ SO][AuBr ₄].H ₂ O	3420 br (1635 w)	3000 m. 29	m 810	1423 s 1385 w 1315 w	1408 s 1350 s	1205 m	1040 s 935 m	м 066	785 w	740 w 655m	720 w
r-	[Me ₃ S][Au ₂ Br ₇ (Me ₂ S) ₂].3H ₂ O	3420br (1630 w)	3020.w 29 2915 m	95 m	1420 S 1400 S 1310 m	1415¢m 1325·s	i	1045s 990s 970 m	1040.sh 980.s 960 m	815w	735 w 675 w	725 w 645 w
æ	[Me ₃ S] ₂ [Au ₂ Hr ₈]-2 DMSO-H ₂ ()	3420 br (1630 m)	3010 m 29 2910 m	195m	1420 s 1390 w 1305 w	1400 m 1325 s	1055 s	940 m 1030 s 910 s	940/s	815w	745 w 675 w	715 w 640 w
o,	[Me _z (Bu)SO][AuBr,]·H _z O	3425 br (1640 m)	3000 m 29)20 m	1425 ^{(S} 1350(s	1410 s 1310 w	1260 w 1200 s	1040 s 935 m	M-026	790 m	725 w	650, m
10	[Me ₃ S]Br	1	2990.s 29)10 s	1433.s 1370 w 1300 m	1420 s 1330 m	1	1070 sh 943 s	1048 s	I	725 m	645.m

TABLE 2. Maxima of Absorption Bands and Assignment of Frequencies in the IR Spectra of Complexes 1-10 (4000-400 cm⁻¹)

TABLE 3. IR Sp	pectra (400-200 cm ⁻¹) of Complexes 1-9
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Com-	Molocular formula		v	max. cm ⁻¹	
plex	Milecular rorman	SC2	MS	MX·	•
1 2 3 4	[AuCl(Me ₂ S)] [AuBr(Me ₂ S)] [AuBr ₃ (Me ₃ S)] [Me ₃ S][AuBr ₄]	285w 273br 290br 292w 284w 270	323 m 328 w 325 w	343 m 227 s 256 s 232 w 247 s	355. m 204 w 240 w 215 w 208 w
5 6	[Me ₃ S][AuBr ₄ (Me ₂ S)]·H ₂ O [Me ₃ SO][AuBr ₄]·H ₂ O	284 s 290 w 285 w	319 m -	247 S 247 S	358 s 244. sh
7	$[Me_3S][Au_2Br_7(Me_2S)_2]\cdot 3H_2O$	285 m	325. W	256s 252 s 247s 231 w	357 w 215 m
8	$[Me_{3}S]_{2}[Au_{2}Br_{8}] \cdot 2DMSO \cdot H_{2}O$	285/W	-	254m 247s 230w	355 w 221 w 215 m
9	[Me ₂ (Bu)SO][AuBr ₄]·H ₂ O	2 85 ₩	-	247s	216 w 208 w

*Unassigned frequencies.

Complex 5: Trimethylsulfonium Tetrabromoaurate(III) Dimethylsulfide Monohydrate. Complex 6: Trimethylsussulfonium Tetrabromoaurate(III) Monohydrate. Complex 7: Trimethylsulfonium Heptabromo-bis-Diaurate(III) Dimethylsulfide Trihydrate and Complex 8: bis-Trimethylsulfonium Octobromodiaurate(III) Monohydrate, Solvated with DMSO. Gold powders were kept in mixtures containing equal volumes of DMSO and HBr (the synthesis conditions of complex 6 being DMSO:HBr = 1:10) until complete dissolution of the metal. Thus, for complex 5 the mixture was held for a long time in air at $\sim 20^{\circ}$ C, and for complex 6, for 1 week at $\sim 20^{\circ}$ C, with subsequent heating at 80°C for 2 h. The heating conditions for complex 7 were 75°C for 3 h, while for complex 8 they were 90°C for 4 h. The reacting mixtures were left at $\sim 20^{\circ}$ C for a long time in order to crystallize the gold complexes, which were then separated by filtration.

Complex 9: Butyldimethyloxosulfonium Tetrabromoaurate(III) Monohydrate. To 0.2 g of gold powder 3 ml of DMSO and 6 ml of BuBr were added. The mixture was heated for 4 h at 90°C until complete dissolution of the gold. During the heating a white deposit (polyformaldehyde) formed on the wall of the flask, above the liquid level. After the gold had dissolved, the mixture separated; a darker layer of the compound dissolved in DMSO was at the bottom. Filtration after a long period of holding separated black-violet crystals of compound 9, with opaque, reflecting facets, from the solution.

Complex 10: Trimethylsulfonium Bromide. Mixtures of DMSO and BuBr (mole ratios 2:1, 1:1, or 1:2) were held for a long time at $\sim 20^{\circ}$ C. With time, the solutions changed color first to yellow, then to orange. After a long time, colorless crystals of complex 10 formed in the shape of platelets which were separated from the solution by filtration.

RESULTS AND DISCUSSION

In the DMSO-HCl system, Au⁰ oxidizes to a univalent state, producing complex 1, stable in air. In the DMSO-HBr system, at ~20°C or with slight heating, a similar bromide complex 2 forms, while heating at higher temperatures and for longer periods results in the oxidation of Au(I) to its trivalent state, forming complex 3: [AuBr₃(Me₂S)] [5]. Addition of water to the filtrate remaining after the precipitation of complex 2 starts the precipitation of anionic complex 4: [Me₃S][AuBr₄]. Complexes 5-8, with ions such as the anions [AuBr₄]⁻, [Au₂Br₇]⁻, and [Au₂Br₈]²⁻, and the cations [Me₃S]⁺ and [Me₂SO]⁺ were apparently formed as products of exchange reactions between complex 3, components of the system, and the products of their reactions during holding of the reaction mixture for a long time.

In the DMSO-BuBr system, the butyldimethyloxosulfonium salt $[Me_2(Bu)SO]^+[AuBr_4]^-H_2O$ (complex 9) and trimethylsulfonium bromide $[Me_3S]Br$ (complex 10) were produced.

The complexes produced were identified from the results of elemental analysis (Table 1) and IR spectrometry (Tables 2 and 3). The gold dimethylsulfide complexes 1-3, previously produced by some other methods, were known. The structures of complexes 2 and 3 were described in [5]. According to the x-ray structural analysis by O. S. Filipenko, complex 1 is isostructural to its bromide analog 2. Complexes 4-9 are anionic complexes of Au(III): trimethylsulfonium or trialkyloxosulfonium salts. The frequency of symmetrical stretching vibrations ν C—S[Me₃S]⁺ (650 cm⁻¹) is lower than that for Me₂S (675 cm⁻¹) [8-11].

The IR spectra of complexes 5, 7, and 8 contain both types of bands (Table 2) because these complexes have $[Me_3S]^+$ and Me_2S or DMSO molecules in their composition.

A special characteristic of IR spectra of trialkyloxosulfonium salts is the displacement of ν SO into a higher frequency region in comparison with the ν SO in DMSO. For [Me₃SO]I, ν SO is 1230 cm⁻¹, while for [Me₃SO][HgI₃] it is 1235 and 1220 cm⁻¹ [12]. In the IR spectra of complexes 6 and 9 there is a band in the 1200 cm⁻¹ region (Table 2) which was absent in the spectra of the other complexes studied. This suggests that complexes 6 and 9 contain the [R₃SO]⁺ cations.

Vibrations of the Au—X and Au—S bonds appear in the IR spectra below 400 cm⁻¹ [10, 13]. Data for the low-frequency IR spectra of the complexes produced are presented in Table 3. On the basis of comparison of the x-ray structural data [5] and the IR spectrometric data for complexes 1-3, the frequencies 323, 328, and 325 cm⁻¹, respectively, were assigned to vibrations of the Au—S bonds. On this basis, the absorption in this region for complexes 5 (319 cm⁻¹) and 7 (325 cm⁻¹) was also assigned to vibrations of that type, which suggests that complexes 5 and 7 contain coordinated Me₂S molecules in their composition.

The 247 cm⁻¹ band, characteristic for absorption of the $[AuBr_4]^-$ anion [13], was assigned to vibrations of the Au-Br bonds in complexes 4-6 and 9. In the spectrum of the $[AuBr_3(Me_2S)]$ complex (complex 3) there is a clearly defined band at 256 cm⁻¹ and a weak absorption at 232 cm⁻¹. In the spectra of complexes 7 and 8, the bands related to the vibrations of Au-Br bonds have a more complex structure, which can be explained by the presence in them of bridging Br atoms.

The compositions of the complexes produced show that various reaction products of the original mixture components take part in the complexing. This gives some idea about reactions in DMSO–RX systems during oxidation of metals.

On the basis of analysis of numerous experimental data on dissolution of transition metals in donor—acceptor media, a concept of donor—acceptor electron transfer systems (DAET systems) was formulated [7]. According to this concept, the components of such a system, i.e., a donor (usually a dipolar, aprotic compound) and an acceptor (for instance a halide-containing organic or inorganic compounds), react reversibly to form some molecular complexes (MC) which later, in solution or under the influence of the polarizing effect of a metal surface, undergo some intramolecular redox transformations, producing some components which can act as metal oxidizers. The DAET system concept suggests that the oxidizer forming in the system should contain both the donor (required for the coordination with metal) and the acceptor centers, either located side by side in the molecule or interconnected through a system of conjugate bonds. In this case, on coordination of the donor center (or the donor functional group) with the atoms of the metal surface, an electron transfer bridge is formed through which the electron is transferred from the metal surface to the acceptor center.

Formation of MC or associates in such systems was established by a spectrophotometric investigation of the DMSO $-CCl_4$ and DMF $-CCl_4$ systems [14]. Reaction between the components of these systems is indicated by a nonlinear dependence of the optical density of the CCl₄ solution in DMSO or DMF on the CCl₄ concentration, as well as by long-wave displacement of CCl₄ absorption maxima in DMSO and DMF (261 and 268 nm, respectively) in comparison with the CCl₄ spectrum in nonpolar heptane (221 nm).

The previous investigation [15] of a gold surface treated with the DMSO—BuBr mixture, using x-ray fluorescence spectrometry, also confirmed the reaction between components of the DMSO system and BuBr. Analysis of the location of x-ray fluorescence lines indicated that neither DMSO nor BuBr could be detected on the gold surface after the treatment. For instance, the value $E_{\rm fr}S2p$ corresponds not to the original DMSO but to sulfur compounds with a degree of oxidation of 6⁺ (for instance [R₃SO]⁺ which is included in complex 9). A new line appears in the C1s spectra, corresponding to C atoms with a considerable positive charge. This can be explained by the presence of carbonyl compounds. Thus, formation of polyformaldehyde is observed during the synthesis of complex 9.

Let us analyze the results obtained in this investigation in terms of the DAET system concept. In the DMSO—HCl system, gold oxidizes to Au(I). In the Au⁰—DMSO—HBr system, the Au(I) complex also forms at $\sim 20^{\circ}$ C or after brief heating. Later on, Au(I) oxidizes to Au(II). Above 70°C the oxidation progresses rapidly, which makes separation of the Au(I) complex impossible, although its formation is detected (complex 2 is insoluble in the reaction mixture). The fact that gold oxidizes via the Au(I) stage suggests that this process has a one-electron nature, i.e., that the oxidizer forming in the system is apparently a one-electron acceptor.

The following reaction sequence in the Au⁰-DMSO-RX systems can be suggested on the basis of published data on the chemistry of sulfoxides and the results of investigation of the oxidation of transition metals in donor-acceptor organic and aqueous-organic media:

N

For DMSO-HX:

$$|Me_2^+S-OH|X^- \xrightarrow{-H_2O} | \xrightarrow{(X=Cl)} MeSCH_2Cl$$
(2)

$$\frac{\left|\begin{array}{c}+HBr\\(X=Br)\end{array}\right|}{(X=Br)} \left[Me_2^{+}-Br\right]Br^{-}$$
(3)

$$\xrightarrow{H} 2Au^{\bullet} 2AuBr + Me_2S$$
(5)

$$[Me_2 \dot{S} - Br]Br - - - - - - - - + AuBr - + Me_2 S$$
(6)

$$\longrightarrow Me_2 S \cdot Br_2 \rightleftharpoons Me_2 S + Br_2 \tag{7}$$

$$2Me_{2}S + HX \longrightarrow [Me_{3}S]^{+}X^{-} + MeSH$$
(8)

$$\longrightarrow MeSH + CH_2O + HX$$
(9)

$$[Me_2\bar{S}-OH]X^- - \left[\underbrace{Me_2\bar{S}}_{+Me_2\bar{S}} [Me_3\bar{S}=O]X^- + MeSH \right]$$
(10)

$$[Me_3\tilde{S}=O]X^- + Au^0 \longrightarrow [Me_3\tilde{S}=O \longrightarrow Au^0]X^- \longrightarrow AuX + Me_2SO + \frac{1}{2}Me - Me$$
(11)

For DMSO-BuBr:

$$Me_{2}SO + BuBr \rightleftharpoons [Me_{2}SO \cdot BuBr] \rightleftharpoons [Me_{2}\dot{S} - O - Bu]Br^{-} \rightleftharpoons [Me_{2}(Bu)\dot{S} = O]X^{-}$$

$$(MC) \qquad (Ox''') \qquad (Ox'')$$

$$(12)$$

$$\longrightarrow Me_2S + C_3H_7 - CHO + HBr$$
(13)

$$[Me_2 \dot{S} - O - Bu]Br^{-} \longrightarrow MeSBu + CH_2O + HBr$$
(14)

$$\begin{array}{c} & Bu \\ & & \downarrow \\ & +Au^{9} & \downarrow \\ & & \downarrow \\ & & \downarrow \\ & & & \downarrow \\ &$$

$$[\operatorname{Me}_{2}(\operatorname{Bu})S^{+1} \to \operatorname{Me}_{2}(\operatorname{Bu})S^{+} \to \operatorname{Au}^{0}]\operatorname{Br}^{-} \to \operatorname{Au}^{0}]\operatorname{Br}^{-} \to \operatorname{Au}^{0}\operatorname{Br}^{-} \to \operatorname{Au}^{0}\operatorname{Bu}^{-} \to \operatorname{Au}^{0}\operatorname{Bu}^{-}$$

$$\underset{(Ox)}{\operatorname{Me_2SO}} \xrightarrow{+\operatorname{HBr}} [\operatorname{Me_2\overset{+}{S}} -\operatorname{OH}] \operatorname{Br}^{-} \xrightarrow{+\operatorname{HBr}} [\operatorname{Me_2\overset{+}{S}} -\operatorname{Br}] \operatorname{Br}^{-} + \operatorname{H_2O}$$
(17)

$$[Me_2\dot{S} - Br]Br^- + AuBr \longrightarrow AuBr_3 + Me_2S$$
(18)

Equilibrium transformations (reactions 1, 12, and 17) produce the $[Me_2\dot{S} - OY]X^-$ components, the likely oxidizers (Ox, Ox'''). Their further redox transformations produce either a halogen molecule, polarized by solvation (Ox', reactions 3 and 17) or a trialkyloxosulfonium salt (Ox'', reactions 10 and 12). The oxidizers formed in the system react with metal (reactions 4-6, 11, 15, 16, and 18), forming halides of Au(I) and Au(III). Reaction of the latter two with transformation products of the original components of the system generates either neutral (complexes 1-3) or anionic (complexes 4-9) gold complexes. In the DMSO--HCl system, the polarized halogen molecule is not generated because the methyl group is immediately chlorinated (reaction 2). Therefore, the DMSO--HCl system oxidizes gold only to Au(I) (complex 1).

As can be seen from the above reaction sequence, oxygen-containing components (Ox, Ox'', Ox''') as one-electron acceptors (reactions 4, 11, 15, and 16). However, we cannot rule out the possibility that $[Me_2S - OH]X^-$ (Ox) in an acid environment is, like $[Me_2S Br]Br^-$, a two-electron acceptor:

$$[Me_2 \overset{+}{S} - OH]X^- + 2Au^0 \xrightarrow{+Hx} 2AuX + Me_2S + H_2O.$$
⁽¹⁹⁾

We emphasize that the above sequences do not exhaust all reactions in the system but only demonstrate some possible routes to the formation of components detected in the complexes produced. This suggests that the results obtained here do not contradict the DAET system concept and fit quite well into its framework.

Note that Épel'baum et al. [16], based on the DAET system concept, studied the reactivity of the onium compounds $[Me_2(Et)S = O]BF_4^-$, $[Me_2N = CH - OEt]BF_4^-$, $[Me_2S = O]I^-$ (similar to the oxidizers in the above reactions) modeling the DAET system, in relation to metallic Cu. It was shown that these compounds can oxidize metal and are one-electron acceptors.

The concept of DAET systems can be extended to such classic inorganic systems as HCl—HNO₃. In this case, the intermediate molecular associate dissociates, forming two types of oxidizers: nitrosyl (a one-electron acceptor) and hydrated molecular chlorine (a potential two-electron acceptor):

$$HNO_3 + 3HCl \rightleftharpoons [HNO_3 \cdot 3HCl] \longrightarrow [N=0]Cl^- + Cl_2 + H_2O$$
(MC) (Ox) (Ox')

Note that when comparing the HNO_3 —HX (aqua regio) and DMSO—HX ("Aqua Chernogolovka"), one can detect a certain functional similarity. Both systems are characterized by the formation of intermediate components which can act as one-electron acceptors, and of a two-electron acceptor, a solvated molecular halogen. Therefore, these systems dissolve noble metals easily [1].

The results obtained suggest that the DAET system concept is promising and useful for the selection of systems when there is a need to solve a problem related to oxidation of transition metals.

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