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Gold Surface Modification with 2-Thiohydantoins and Their Cobalt(II) Complexes

R. B. Romashkina[a], V. D. Dolzhikova[b], E. K. Beloglazkina[a], A. G. Mazhuga[a], and N. V. Zyk[a]
[a] *Organic Chemistry Department*
[b] *Colloid Chemistry Department*
e-mail: dol@colloid.chem.msu.ru

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Abstract—Self-organized monolayers (SOMs) of 2-thiohydantoins on gold modified with lipoic acid esters were studied using contact angle measurements. The feasibility of complexing SOMs with cobalt(II) ions was demonstrated. Optimal parameters were determined for generating surface metal complexes on gold.

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Monolayers of alkanethiols and dialkyl disulfides on gold capable of self-organization and bearing various terminal functionalities, such as $–CF_3$, $–CH=CH_2$, –Cl, –Br, –CN, –OH, $–OCH_3$, $–NH_2$, $–N(CH_3)_2$, $–SO_3H$, –COOH, $–COOCH_3$, $CONH_2$, and some others, have been actively studied over the last two decades [1–5]. Such self-organized monolayers (SOMs) can be used to prepare systems with desired properties (charge transport, photochemical and biological activity, or superconductivity). Complexing of the terminal groups of alkanethiols with transition metals offers a means for manufacturing ion-selective electrodes and metal-complex surfaces for use in catalysis [6].

Notably, thiols containing donor functionalities are adsorbed on gold more firmly than their acceptor-substituted analogues. Monolayers bearing surface hydroxy and carboxy groups are very convenient for further transformations. For example, a carboxy group can be converted into amine or ester; choline groups can be used for molecular recognition of proteins and microbial cells, which can be immobilized on gold via complexing [6–8].

For adsorption of alkylmercaptans (AlkSH) on gold, the reaction can be represented as the oxidative addition of thiol to the gold surface and subsequent reductive elimination of hydrogen [9]:

$$R–S–H + Au^\circ \longrightarrow R–S^-Au^+ \cdot Au^\circ + 1/2H_2.$$

Thiolate formation on gold was proven using IR Fourier-transform spectroscopy and FTIR/mass spectrometry. A sulfur–gold bond was found to be very strong: its energy is about 40 kcal/mol [10].

It is known from [11] that the adsorption of RSSR disulfides on gold involves thiolate formation with dissociation of the S–S bond; for asymmetrical dialkyl disulfides, mixed monolayers are formed. Adsorption of RSR dialkyl sulfides on gold does not require C–S bond dissociation, as probed by secondary ion mass spectrometry [12].

The list of thiols used for gold modification is continuously increasing; various physicochemical methods (IR spectroscopy, ellipsometry, X-ray crystallography, tunnel microscopy, contact angle measurements, and others) are used to study various aspects of alkanethiol monolayer generation, such as packing, orientation, and self-organization [12–14]. Ellipsometry can serve to determine the monolayer thickness and the refractive index of the film. X-ray crystallography can determine the structure and composition of SOMs [15]. Water contact angles were measured on the gold surface modified with thiols with various terminal groups [14, 16, 17] (Table 1).

The experiments cited above were usually confined to measurements of advancing contact angles θ_a for water with inferences of how the wetting character of the modified surface differs from the initial gold surface. For studying modified surfaces, however, the potential of contact angle measurements is much greater.

(1) Measurements of advancing contact angles θ_a and receding contact angles θ_r on the same sample make it possible to determine the degree of heterogeneity of the solid surface, which is characterized by the contact angle hysteresis: $\Delta\theta = \theta_a - \theta_r$; for homogeneous surfaces, hysteresis is near zero.

(2) The molecular theory of wetting for heterogeneous surfaces makes it possible to determine the coverage of the solid surface by a modifying layer, i.e., relative adsorption.

(3) Contact angles provide data on the modifier distribution over a solid surface and the dominant orientation in the layer.

In this work, we used contact angle measurements to study SOMs of derivatives of lipoic acid (which con-

Table 1. Surface coverage (x) by a lipoic acid bromoethyl ester monolayer as a function of modification time (t)

Time, t	Contact angles, deg			X, %
	θ_a	θ_r	$\Delta\theta = \theta_a - \theta_r$	
0	80	70	10	0
10 s	72	60	12	34
1 min	71	60	11	40
5 min	70	61	9	42
10 min	67	62	5	54
15 min	64	60	4	66
30 min	63	59	4	70
1 h	63	57	6	72
5 h	62	58	4	74
10 h	61	59	2	78
15 h	60	58	2	83
20 h	58	57	1	91
24 h	56	55	1	98
48 h	56	55	1	98

tains a ring disulfide group) on gold. Monolayer self-organization brings about the dissociation of S–S bonds and generation of thiolates on the gold surface.

The strongly bonded surface films of thiols and disulfides on gold can later be chemically modified at their terminal groups, for example, for manufacturing compact transition metal catalysts. For this purpose, in particular, for preparing cobalt complexes (potential metal-complex catalysts), in this work we modified the gold surface in three stages, which were as follows:

(1) Adsorption of lipoic acid bromoethyl ester on gold (first layer).

(2) Modification of this layer by thiohydantoin—trisubstituted imidazoline, which is a good complex former for cobalt ions (second layer).

(3) Complexing of surface groups of the second layer with cobalt ions (third layer).

Figure 1 illustrates the sequence of monolayer generation stages on gold. Lipoic acid bromoethyl ester and thiohydantoin were synthesized as in [18, 19].

The layer-by-layer modified gold surface was studied by contact angle measurements. Advancing (θ_a) and receding (θ_r) contact angles of water were measured, contact angle hysteresis ($\Delta\theta = \theta_a - \theta_r$) was estimated as a function of layer generation time, and the gold surface coverage by an adsorbate layer was calculated using wetting theory for heterogeneous surfaces [20].

Let θ_0 be the water advancing angle on the unmodified gold surface and θ_m be the advancing angle on the surface completely covered with modifier molecules. In the progress of adsorption on the unmodified surface, regions occupied by modifier molecules appear; the surface coverage increases with adsorption time. If x is the fraction of the initial surface occupied by regions of one type (modified), then $(1 - x)$ is the relative fraction of the unmodified surface area, and the equilibrium angle θ on this surface is determined from the Rebinder, Cassie, and Baxter equation [20]:

$$\cos\theta = x\cos\theta_m + (1 - x)\cos\theta_0. \qquad (1)$$

Then, the surface coverage x can be calculated from

$$x = \frac{\cos\theta - \cos\theta_0}{\cos\theta_m - \cos\theta_0} = \frac{\Gamma}{\Gamma_m}. \qquad (2)$$

Thus, advancing contact angle measurements on a modified surface help to ascertain the relative adsorption of the modifier on a solid.

An MG horizontal microscope equipped with a goniometer unit was used to measure advancing and receding contact angles (θ_a and θ_r). The measurement accuracy was ±1°. Water advancing angles on gold were measured with applying drops 0.01–0.02 mL onto a solid surface. For each case, contact angles of three to five drops were measured on the same substrate. These measurements were carried out in a closed chamber (to inhibit vaporization) 3–5 min after applying a drop. The contact angles determined in this way were close to equilibrium values, being invariable with time: the contact angle remained unchanged for 30 min after measurements. Contact angles θ_r were measured with an air bubble 0.01–0.03 mL in volume brought to the surface of a sample in water. These measurements were carried out at 20°C 3–5 min after the bubble was anchored. The root-mean square deviation for contact angle measurements was ±2°. We used germanium plates (5 × 5 mm) coated with a vacuum-sputtered gold layer (50 × 10 nm thick); $\theta_a = 80°$; $\theta_r = 70°$.

Modification was carried out as follows: To generate a bromoethyl ester monolayer on gold, plates were exposed to 10^{-3} M solution of the compound in ethanol for various periods of times (varying from 10 s to 48 h), followed by repeated washing with ethanol and drying in air.

To generate the second modifier layer, disulfide-modified samples were exposed to a 10^{-2} M thiohydantoin solution and acetonitrile (the exposure time was varied from 10 min to 24 h), followed by repeated washing with the solvent and drying in air.

Then, the resulting surface layer was exposed to a 10^{-3} M $CoCl_2$ solution in acetonitrile to complex it with cobalt.

The lipoic acid bromoethyl ester monolayer on gold was completely formed in 24 h; contact angles had fixed values; the contact angle hysteresis was practically zero (Table 1).

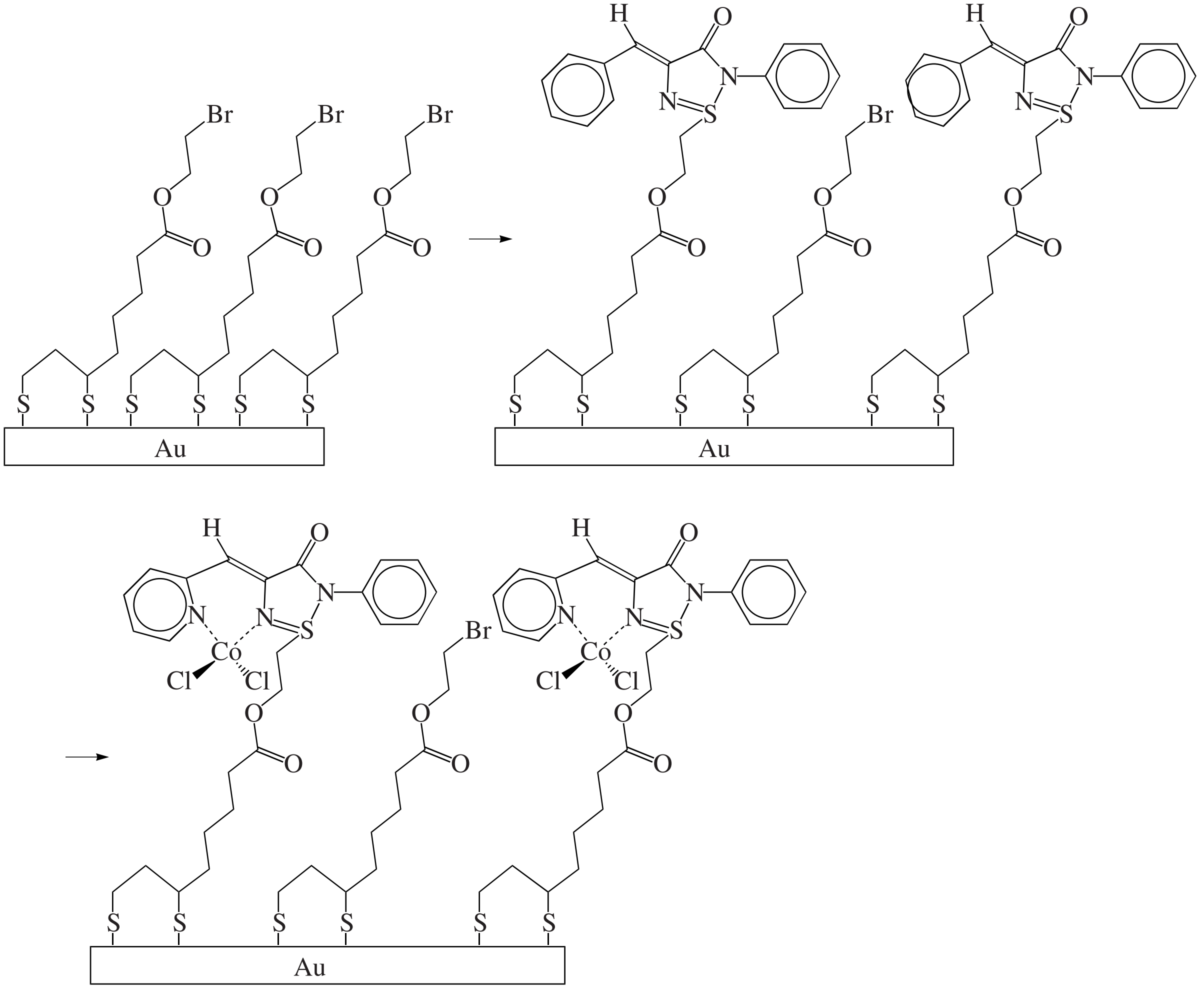

Fig. 1. Scheme of layer-by-layer modification of the gold surface with lipoic acid bromoethyl ester, 2-thiohydantoin, and cobalt(II).

When a disulfide monolayer is formed on gold, the surface becomes hydrophilic even for the maximal surface coverage $\theta_0 = 55°$. This value agrees with water contact angles for thiol layers bearing Br as a terminal group: for a close-packed monolayer, $\theta_m = 55°$ [21].

Table 1 displays the results of calculations of the monolayer surface coverage by the lipoic acid bromoethyl ester modifier, x, as a function of modification time. The maximal surface coverage is 98%, signifying the practically complete surface coverage by the disulfide monolayer.

In the progress of surface coverage with the adsorbate layer (with increasing modification time), the contact angle hysteresis $\Delta\theta = \theta_a - \theta_r$ decreases to become virtually zero for the modification time $t = 24$ h. This is evidence of a sufficient homogeneity of the monolayer.

The second modifier layer is formed on the disulfide monolayer as a result of thiohydantoin chemisorption. The maximal modification time (24 h) corresponds to the completion of the thiohydantoin monolayer on the lipoic acid bromoethyl ester surface. For the maximal surface coverage ($x = 76\%$), the contact angle is 30° (Table 2). In calculating the degree of thiohydantoin surface modification, we used $\theta_m = 15°$ [14].

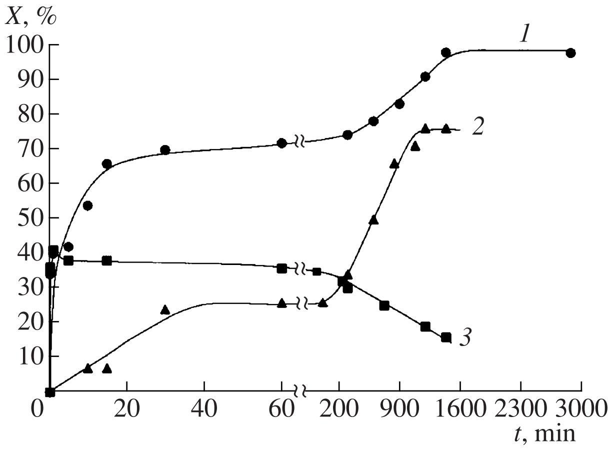

Fig. 2. Degree of gold modification (X) vs. time (t) for layer-by-layer coverage with (*1*) lipoic acid bromoethyl ester, (*2*) 2-thiohydantoin, and (*3*) cobalt(II).

Table 2. Degree of thiohydantoin modification of the lipoic acid bromoethyl ester SOM (*X*) as a function of modification time (*t*)

Time, *t*	Contact angles, deg			X_2, %
	θ_a	θ_r	$\Delta\theta = \theta_a - \theta_r$	
10 min	53	48	6	7
15 min	52	46	6	8
30 min	49	41	7	24
1 h	48	40	8	26
5 h	45	35	10	34
10 h	40	30	10	50
14 h	34	20	14	66
18 h	32	20	12	71
20 h	30	20	10	76
24 h	30	20	10	76

Table 3. Fillage of thiohydantoin SOM with cobalt(II) ions (*X*, %) as a function of complexing time (*t*)

Time, *t*	Contact angles, deg			X_3, %
	θ_a	θ_r	$\Delta\theta = \theta_a - \theta_r$	
10 s	50	45	7	36
1 min	52	46	6	41
5 min	51	47	4	38
15 min	51	47	4	38
1 h	50	47	3	36
2 h	50	48	2	36
4 h	48	44	4	32
6 h	47	40	7	30
12 h	45	42	3	25
20 h	41	38	3	19
24 h	40	37	3	16

The value of the contact angle hysteresis $\Delta\theta = \theta_a - \theta_r$ signifies an increased heterogeneity of this modifier layer compared to the disulfide monolayer; this increase can be explained by the fact that some disulfide molecules on the gold surface are bound to thiohydantoin molecules and some are not. The generation of a homogeneous layer can also be sterically hindered by such a bulky substituent as thiohydantoin.

When a surface complex with $CoCl_2$ is formed, the contact angle is an extreme function of modification time: while $t \leq 1$ min, contact angles θ_a abruptly increase, then decreasing monotonically; when the modification time is 20 h, θ_a = const = 40° (Table 3, Fig. 2). For a monolayer whose terminal groups contain metal ions, $\theta_m = 76°$ [14]. At the maximum point, $\theta_0 = 52°$; the surface coverage is 40%. With increasing complexing time, the surface coverage drops to 16%. Probably, structuring and ordering of the outer modifier layer have ended by this moment. This nontrivial structural alteration of the layer can be due to complexes with various compositions generated on the surface because of the existence of various donor atoms (N, S, and O) in molecules in the monolayer. Molecules of the monolayer can acquire conformations differing from their initial orientation in the monolayer. As a result, the contact angle changes. Our data indicate that there is some optimal time for complexing with the transition metal, providing the maximal amount of cobalt in the surface layer of the complex former.

In summary, using contact angle measurements in tandem with the molecular theory of wetting of heterogeneous surfaces, we demonstrated the feasibility of complex formation between thiohydantoins immobilized on gold and cobalt(II) ions and the generation of metal-complex surfaces.

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