The character of interaction of organometallic derivatives of 4-nitrophenol and 4-nitrothiophenol with anions in different media

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Interaction of R_nM-derivatives of 4-nitrophenol and thiophenol (R_nM = PhHg, PPh_3Au, Ph_3Sn, Ph_4Sb) with a set of inorganic and organic anions (Cl^-, Br^-, I^-, CN^-, $[PhOCO]^-$, $[4\text{-}NO_2C_6H_4OCO]^-$) was studied by IR and electronic spectroscopy in solvents with different polarities and coordinating properties (C_6H_6, CH_2Cl_2, DMSO). The dependence of the character of the interaction with the anions on the nature of the metal atom and heteroatom, the type of anions and the nature of the media was analyzed. Such interaction leads to ion-molecular complexes, and also to dissociation of the X—M bond (X = O, S, M = Au, Hg, Sb) with formation of the $(4\text{-}NO_2C_6H_4X)^-$ anion even in weakly polar media. Only in the case of $4\text{-}NO_2C_6H_4OSnPh_3$ does the reaction stop at the stage of complex formation. In other cases the role of complex formation with anions is less than with neutral coordinating reagents.

Key words: molecular spectroscopy, reaction of organometallic compounds.

Study of solid phase reaction of organometallic derivatives of 4-nitrophenol, 4-nitrothiophenol, and 4-nitrobenzenesulfanilide with bromides, which was performed by us previously[1], showed that this interaction results in complexes and/or anions of the $(4\text{-}NO_2C_6H_4X)^-$ type, where X = O, S, and NSO_2Ph. The role of steric hindrances was found significant in the solid phase reaction. Only few molecules localized in the near-surface layers enter into the reaction. In this connection, necessity arose to conduct the study in solvents which differ in their polarity and coordination ability. This allows one to extend the range of anions, to make quantitative estimations, and to compare the action of ionic and neutral coordination agents. Here one can also use the data obtained by us previously concerning dissociative ability of X—M (K_d) bonds and constants of complex formation with DMSO, amines, and phosphines (K_c).[2,3]

$$\mathrm{ArXM} + \mathrm{B} \overset{K_c}{\rightleftharpoons} \mathrm{ArXM...B} \overset{K_d}{\rightleftharpoons} \mathrm{ArX}^- + \mathrm{MB}^+ \qquad (1)$$

Organometallic and metal-containing derivatives of the $4\text{-}NO_2C_6H_4XMR_n$ type, where X = O and S, and R_nM = PhHg, PPh_3Au, Ph_4Sn, and Ph_4Sb, were chosen as objects of investigation. Bu_4NCl, Bu_4NBr, Bu_4NI, Bu_4NCN, $Bu_4N(PhOCO)$, and $Bu_4N(4\text{-}NO_2C_6H_4OCO)$ were used as ionic coordinating reagents. The study was performed in solvents with different polarities and coordination abilities (C_6H_6, CH_2Cl_2, DMSO) using IR and electronic spectroscopy.

Results and Discussion

We showed that interaction of the compounds studied **1** with anions in solutions can be described by an equilibrium including the formation of ion-molecular complexes **2** and anions **3**.

$$\underset{\mathbf{1}}{\mathrm{ArXM}} + \mathrm{A}^- \rightleftharpoons \underset{\mathbf{2}}{\mathrm{ArXM...A}^-} \rightleftharpoons \underset{\mathbf{3}}{\mathrm{ArX}^-} + \mathrm{MA} \qquad (2)$$

Thus, low-frequency shifts of ν_sNO_2 bands by 20—30 cm^{-1} and increases in their intensity were observed in the IR spectra of all compounds studied when they interacted with $Bu_4NCl/Bu_4NBr/Bu_4NI$ (Fig. 1). This allowed us to assume that ion-molecular complexes **2** and/or anions **3** were formed. A new band relating to the stretching vibration of the Hg—Hal bond (ν(Hg—Hal)) appeared in the low-frequency range of the IR spectrum (400—200 cm^{-1}), which suggested formation of phenylmercury halide, the second reaction product.

As was shown by us previously,[2,3] the formation of anions (**3**) and molecular complexes can be distinguished by the position of long-wave bands in the elec-

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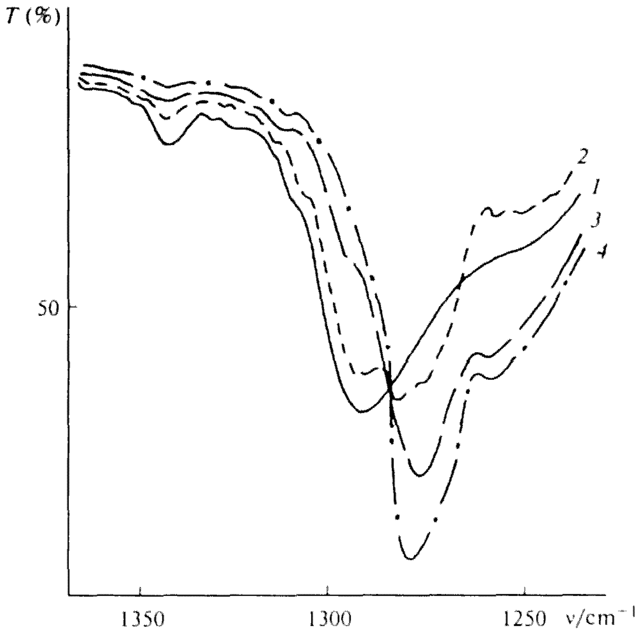

Fig. 1. The IR spectra in CH_2Cl_2 of $4\text{-}NO_2C_6H_4OAuPPh_3$ (*1*) and of the products of its reactions with Bu_4NI (*2*), Bu_4NBr (*3*), Bu_4NCl (*4*).

tronic spectra. For this reason our further studies were mainly based on the analysis of elecronic spectra.

We considered the following factors governing the form of equilibrium (2): the nature of the metal atom and the heteroatom, the type of anion, and the polarity and coordinating properties of the medium.

The influence of the nature of the metal atom on the equilibrium processes investigated manifests itself when one compares the character of the interactions with the anions of different 4-nitrophenol derivatives. The interaction of Bu_4NBr/Bu_4NCl with the PPh_3Au derivative, which has a high dissociation constant in DMSO (K_d = $2.5 \cdot 10^{-4}$ mol L^{-1}) and a small constant of complex formation with neutral coordinating reagents (K_c = 1.45 L mol^{-1}),[3] leads to cleavage of the O—Au bond and transport of the $(PPh_3Au)^+$ cation. Thus, λ_{max} of the long-wave band of the elecronic spectrum is 428—434 nm for different solvents (Table 1), which coincides with the position of the band of the nitrophenoxide anion.[2] The value of $\Delta\lambda_{max}$ is equal to 56—58 nm (Table 1), as in the case of interaction with neutral coordinating reagents. However, no formation of an intermediate ion-molecular complex was detected in solutions in either C_6H_6, CH_2Cl_2, or DMSO, though a molecular complex is formed during the reaction with neutral coordinating reagents.[3] With the PhHg derivative[2] the decrease in K_d in DMSO by one order of magnitude (K_d = 10^{-5} mol L^{-1}), while the constant of complex formation remains unchanged, leads to a change in the character of the equilibrium, namely, to formation of both the anion (λ_{max} is 408—434 nm, $\Delta\lambda_{max}$ is 71—97 nm) and the ion-molecular complex (λ_{max} is 385—400 nm, $\Delta\lambda_{max}$ is 48—61 nm) (Table 1). The absorption band of the ion-molecular complex is shifted bathochromically (by 28 nm) from that of the molecular complex that forms when this compound interacts with a neutral coordinating reagent.[3] The even lower ability of the Ph_3Sn derivative[2] to dissociate (K_d = $7 \cdot 10^{-6}$ mol L^{-1}), accompanied by its significantly greater ability to form complexes (K_c = 140 L mol^{-1}), leads to formation of only the ion-molecular complex (λ_{max} is 394 nm in C_6H_6, $\Delta\lambda_{max}$ is 81 nm) under the action of Bu_4NHal (Table 1). The Ph_4Sb derivative as well as the PPh_3Au derivative has a high ability to dissociate (K_d = 10^{-4} mol L^{-1}) and the least ability to form complexes (K_c = 0.5 L mol^{-1}).[2] However, only a single ion-molecular complex band was observed in the elecronic spectrum in interactions with equimolar amounts of Bu_4NBr or Bu_4NCl in a solution of C_6H_6 due to considerable steric hindrances. The anion band appears only in a great excess of Bu_4NHal, and its intensity increases as the salt concentration increases.

The influence of the nature of the heteroatom on the character of the interaction with anions has been shown for PhHg derivatives (X = O, S). Thus, the derivative with an S—Hg bond, which, in contrast to the derivative with an O—Hg bond, does not dissociate in DMSO,[2] does not form the $(4\text{-}NO_2C_6H_4S)^-$ ion while interacting

Table 1. The electronic spectra of $4\text{-}NO_2C_6H_4XMR_n$ in different solvents, λ_{max}/nm

XMR_n	C_6H_6			CH_2Cl_2			DMSO		
	Additive	λ_{max}	$\Delta\lambda_{max}$	Additive	λ_{max}	$\Delta\lambda_{max}$	Additive	λ_{max}	$\Delta\lambda_{max}$
$OAuPPh_3$				—	370 s		—	378 s	
				Bu_4NBr	428 s	58	Bu_4NBr	434 s	56
OHgPh	—	337 s		—	339 s		—	368 s	
	Bu_4NBr	385 s, 408 s	48, 71	Bu_4NBr	400 s, 427 s	61, 89	Bu_4NBr	434 s	66
$OSnPh_3$	—	313 s		—	315 s		—	321 s	
	Bu_4NBr	394 s	81	Bu_4NBr	397 s	82	Bu_4NBr	403 s	82
$OSbPh_4$	—	360 s							
	Bu_4NBr	368 s, 435 sh	8, 75						
SHgPh	—	345 s							
	Bu_4NBr	408 s, 500 sh	63, 155						

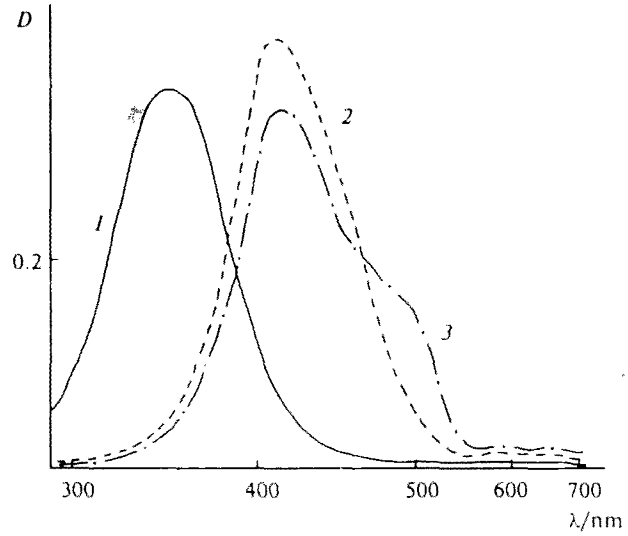

Fig. 2. The electronic spectra in C_6H_6 of $4\text{-}NO_2C_6H_4SHgPh$ (*1*) and of the products of its reaction with Bu_4NBr (*2, 3*):
2, $[4\text{-}NO_2C_6H_4SHgPh] : [Bu_4NBr] = 1 : 2$;
3, $[4\text{-}NO_2C_6H_4SHgPh] : [Bu_4NBr] = 1 : 5$.

with small additions of Bu_4NBr/Bu_4NCl (ratio of $C_{4NO_2C_6H_4SHgPh}$ to C_{Bu_4NHal} is 1 : 2). Under these conditions a band of the ion-molecular complex (λ_{max} 408 nm in C_6H_6, $\Delta\lambda_{max}$ 63 nm) appears in the electronic spectrum (Table 1). It should be noted that this band is shifted batochromically (by 12 nm) from the band of the molecular complex with DMSO. When rather considerable amounts of Bu_4NHal were added (ratio of $C_{4NO_2C_6H_4SHgPh}$ to C_{Bu_4NHal} was 1 : 5), we registered the partial transfer of the organometallic cation $PhHg^+$. A long-wave shoulder, corresponding to the absorption of the thiophenoxide ion, appears in the spectrum in the 500 nm range (Fig. 2).

The dependence of the complex formation reactions and the transfer of the metal-containing cation on the nature of the anion (Cl^-, Br^-, I^-, CN^-, $[PhOCO]^-$, $[4\text{-}NO_2C_6H_4OCO]^-$) was considered for PhHg and PPh_3Au nitrophenoxides. It was revealed that under the same conditions the concentration of the $(4\text{-}NO_2C_6H_4O)^-$ ion formed decreases in the series: $Cl^- > Br^- > I^- > (PhOCO)^- > (4\text{-}NO_2C_6H_4OCO)^- > CN^-$ (Fig. 3).

Quantitative calculations were performed in the study of the interaction of PPh_3Au derivatives of 4-nitrophenol with halide anions (Cl^-, Br^-, I^-) and with the $(4\text{-}NO_2C_6H_4OCO)^-$ anion, and the constants of the equilibrium of the transfer of the metal-containing cation were determined for them. (Table 2).

The analysis of the results given in Table 2 shows that the principle of hard and soft acids and bases is not decisive in this case. The constants change in the following series: $Cl^- > Br^- > I^- > (4\text{-}NO_2C_6H_4OCO)^-$. The basicity of the anions A^- and the strength of the M—A bond formed (R_nM—Hal and $R_nM—OCOC_6H_4NO_2$-4) seem to be factors acting oppositely. Thus, the basicity of halide ions decreases in the series $Cl^- > Br^- > I^-$.[4] The strength of R_nMHal compounds (M = Hg, Pb, Sn), according to thermochemical data,[5] also decreases when passing from Cl^- to Br^- and I^-. The Cl^- anion contributes to the transfer of the metal-containing cation to a greater extent than the Br^- and I^- anions.

Table 2. The constants of the equilibrium of the transfer of the PPh_3Au^+ cation under the action of the anions in CH_2Cl_2

A^-	$K \cdot 10^{-3}$/mol L^{-1}
Cl^-	1.36
Br^-	0.74
I^-	0.70
$[4\text{-}NO_2C_6H_4OCO]^-$	0.21

The dependence of the character of this interaction on the medium was analyzed. In contrast to the solid phase reaction of the Ph_4SbO derivative with Hal^- ions, where owing to the steric hindrances only a complex with Hal^- (λ_{max} 390 nm)[1] was formed, in a benzene solution the transfer of the organometallic anion (λ_{max} 435 nm) was observed in addition to the ion-molecular complex. We demonstrated with the HgPh-derivative that the character of the interaction changes under the action of DMSO which serves as a coordinating and ionizing solvent. We observed in it, in contrast to C_6H_6 and CH_2Cl_2, only the transfer of the organometallic cation without intermediate complex formation. This is evidenced by the absence of the absorption band of the complex as well as the presence of an isobestic point between the bands of the starting compound and the

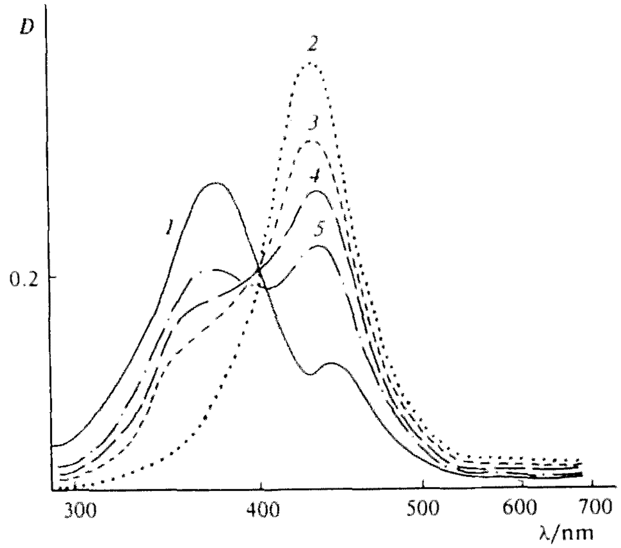

Fig. 3. The electronic spectra in DMSO of $4\text{-}NO_2C_6H_4OAuPPh_3$ (*1*) and of the products of its reactions with Cl^- (*2*), I^- (*3*), $[PhOCO]^-$ (*4*), $[4\text{-}NO_2C_6H_4OCO]^-$ (*5*).

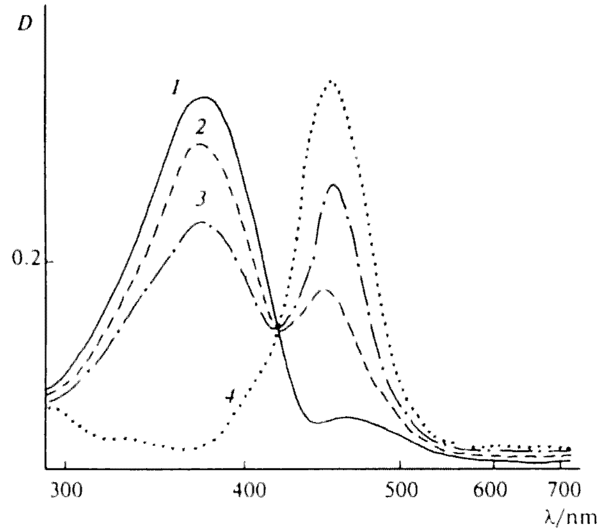

Fig. 4. The electronic spectra in DMSO of 4-$NO_2C_6H_4OHgPh$ (*1*) and of the products of its reactions with Bu_4NBr (*2—4*):
2, [4-$NO_2C_6H_4OHgPh$] : [Bu_4NBr] = 1 : 0.4;
3, [4-$NO_2C_6H_4OHgPh$] : [Bu_4NBr] = 1 : 0.7;
4, [4-$NO_2C_6H_4OHgPh$] : [Bu_4NBr] = 1 : 1.

anion formed (Fig. 4). DMSO, which forms a complex with mercury nitrophenoxide and makes it partially dissociate, seems not to contribute to the formation of the ion-molecular complex with Hal^-.

Thus, consideration of the interaction of the ArXM compounds studied with the anions in the solution allowed us to establish some features of the operating processes. As in the case of interaction with neutral coordinating agents, the character of interaction with the anions depends above all on the ability of the M—X bonds to dissociate and on the ability of ArXM to form complexes. The interaction of ArXM with the anions results in the formation of ion-molecular complexes accompanied by cleavage of the X—M bonds resulting in the formation of $(4\text{-}NO_2C_6H_4X)^-$ anions. In contrast to neutral coordinating reagents, when interaction with the anions takes place, dissociation of the X—M bond and transfer of the R_nM cation are observed even in nonpolar and slightly polar media in all cases except that of the Ph_3SnO derivative. The role of complex formation processes during interactions with the anions is much smaller than for the neutral coordinating agents, and no complexes form with the anions in the case of the PPh_3AuO derivative.

Experimental

The IR spectra were measured on a Specord M-80 instrument in Nujol and in solution (in CaF_2 cells, d = 0.0068—0.0620 cm; low-frequency IR spectra were recorded in polyethylene cells and on plates).

The electronic spectra were obtained with a Specord M-40 spectrophotometer in solution (in CaF_2 cells, d = 0.0068—0.0620 cm and in quartz cells, d = 0.1—1.0 cm) and in the solid state (using a support of incomplete internal reflection).

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