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Novel Bioactive Hybrid Composites Based on Coordination Compounds of Some Tertiary Arsines with Mercury(II) Halides†

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The novel arsenic-containing coordination compounds with the bridge structure were synthesized and studied. Antibiocorrosion covers based on synthesized compounds have created. Some of the mechanical and exploatative characteristics have been determined.

Key Words: Coordination compounds, Arsenic, Mercury helides, Antibiocorrosive.

INTRODUCTION

There are more than hundred aggressive microorganisms which can destruct the various natural, synthetic and artificial materials. Losses caused by biodestruction of such materials reach enormous amounts and constitute annually millions of dollars. One of the ways to protect the synthetic materials from the action of microorganisms is a creation of novel polymer covers with high bioactivity by modification of various polyfunctional adhesive polymer matrices with bioactive compounds[1].

The present work refers to the synthesis of new compounds as bioactive components for antibiocorrosive covers of natural, synthetic and artificial materials.

EXPERIMENTAL

The reactions of the synthesis of asymmetric tertiary arsines complexes type of $Ar_2AsR\cdot HgCl_2$ and $Ar_3As\cdot HgX_2$ were carried out in various organic solvents, by interaction of mercury(II) chlorides or bromide with aryl(alkyl) arsines at different concentrations, ratio of initial reagents and different temperatures. Coordination compounds were precipitated under the action of saturated ether-solution of mercury(II) halides with corresponding tertiary arsines in molar ratio 1:1 and isolated as oil-like compounds after prolonged leaving of the reaction mixture (20-30 days).

RESULTS AND DISCUSSION

Antibiocorrosive covers contain two components-biologically active compound and polymer matrix, where the biologically active compound is dropped. As the bioactive compounds we have synthesiszed novel arsenic-containing complexes (Table-1). We have synthesized two types of coordination compounds: $Ar_2AsR\cdot HgCl_2$ and $Ar_3As\cdot HgX_2$ (X = Cl, Br). Asymmetry tertiary arsines complexes type of $Ar_2AsR\cdot HgCl_2$ (where Ar is aryl and R-alkyl) were formed according to the following reaction scheme:

$$Ar_2AsR + HgCl_2 \longrightarrow Ar_2(As)R\cdot HgCl_2$$

TABLE-1

No.	Coordination compound	log (Δ_F)	$T_{melt.}$ (°C)
I	$(CH_3C_6H_4)_2AsC_2H_5\cdot HgCl_2$	3.35	137
II	$(CH_3C_6H_4)_2AsC_4H_9\cdot HgCl_2$	3.62	143
III	$(CH_3C_6H_4)_3As\cdot HgCl_2$	3.81	173
IV	$(CH_3C_6H_4)_2AsC_2H_5\cdot HgBr_2$	3.35	131
V	$(CH_3C_6H_4)_2AsC_4H_9\cdot HgBr_2$	3.62	145
VI	$(CH_3C_6H_4)_3As\cdot HgBr_2$	3.81	164
Correlation coefficient r = 0.921519			

It was shown that symmetric trialkyl arsines could not form crystalline compounds with mercury(II) chlorides:

$$R_3As + HgCl_2 \not\longrightarrow R_3As\cdot HgCl_2$$

where R = n-C_3H_7, iso-C_5H_{11} or C_7H_{15}.

Symmetric triaryl arsines have formed with mercury(II) halides crystalline products:

$$Ar_3As + HgX_2 \rightarrow Ar_3As\cdot HgX_2$$

where Ar = C_6H_5 or m-CH_3-C_6H_4, X = Cl or Br.

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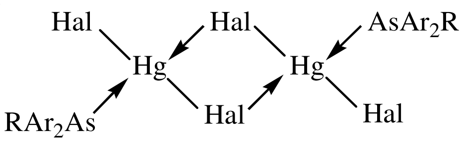
It was established that the change of the ratio of initial reagents (in wide limits) did not influence on the chemical composition of the products-it was always equal to 1:1. The assumption that the obtained products are identical was confirmed by the fact that their melting point did not change. Thus based on numerous experiments optimal conditions for this process were elaborated. All synthesized products are white crystalline, stable compound. It was established that the yield in case of triarylarsines is far less than in case of diaryl(alkyl)-arsines. The rate of formation of adducts of triphenylarsine with mercury(II) chloride and bromide prevails over the rate of formation of the product of addition of tri-*m*-tolylarsines. This fact can be explained by the spatial factor and by electronegativity of β-substituent. It must be noted, that $(m\text{-}CH_3\text{-}C_6H_4)_3As\cdot HgCl_2$ is more coarse crystalline than other synthesized compounds. In aqueous solution (all the more in organic solvents) mercury(II) halides are weakly ionized and the concentration of Hg^{2+} ions, for example, in extracted solution of sublimate is not more than 10^{-8}. It means that it is non-electrolyte ($\alpha_{HgCl_2} < \alpha_{H_2O}$) and when $HgCl_2$ undergoes dissociation it will stop at the first stage:

$$HgCl_2 \leftrightarrow HgCl^+ + Cl^-$$

The addition of triaryl- and diarylalkyl arsines to mercury(II) halides can be considered as nucleophilic process:

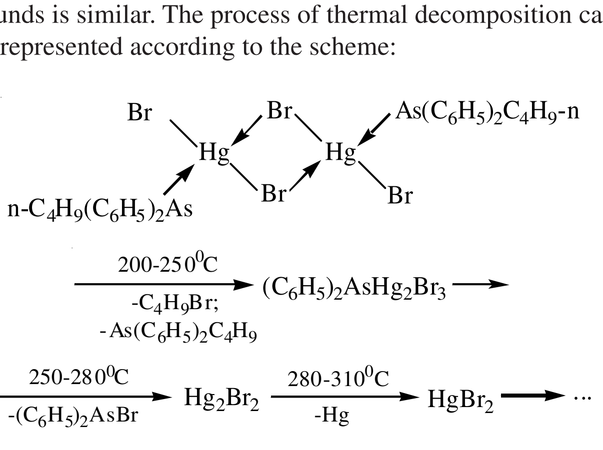
$$Ar_3As + HgHal_2 \xrightarrow{\times} [Ar_3As \rightarrow HgHal]Hal$$

The molecular electroconductivity of the obtained compounds was determined in dimethylformamide. The data of the molecular electroconductivity (less then 30 om^{-1} cm^2) confirmed that these compounds are non-electrolytes. IR spectra of the obtained compounds showed that the absorption band in the region 580-560 cm^{-1} (corresponding to $As\text{-}C_{alk.}$), disappears, thus, the absorption band at 620 cm^{-1} appears which is characteristic to $As\text{-}C_{alk.}$, when As is in sp^3 hybridization state. Based on the data of molar electro-conductivity and IR spectra we can propose that the compound is dimmer bridge complex:



, (Hal = Cl or Br)

We carried out the thermographic analysis of the synthesized compounds. The thermolysis of each synthesized compounds is similar. The process of thermal decomposition can be represented according to the scheme:



We have elaborated the method of the algebraic-chemical characterization of typical structures (main characterizing structure) of synthesized compounds - R_2AsR, where R = $m\text{-}CH_3C_6H_5$; R' = $m\text{-}CH_3C_6H_5$; *iso*-C_4H_9; C_2H_5. For creation of the bank of data for these chemical structures we have used the fragmentation matrix (F-matrix) method. We constracted the F-matrices for our systems and use log (Δ_F) (F called as fragmentation matrix)-effective topologic index for construction and investigation of fragmentation "structure-properties" type correlation equations. As the synthesized compounds are crystalline, we have constructed the correlation equation and it has the form:

$$T_{melt} = 78 \log(\Delta_F)\text{-}123 \text{ (A)}; \quad T_{melt.} = 72 \log(\Delta_F)\text{-}110 \text{ (B)}$$

where A: for the complex of $HgCl_2$, B: for the complex of $HgBr_2$.

The values of the $T_{melt.}$ and log (Δ_F) for these compounds are presented in the Table-1.

We have carried out the preliminary virtual (theoretical) bioscreening of obtained structures (using the characterizing mentioned above arsenic-containing fragments) by using of internet-system program PASS C & T[2]. The estimation of probability of activity of compounds was carried out *via* determination of parameters P_a (active) and P_i (inactive). Based on virtual bioscreening the synthesized compounds (**I-VI**), with experimentally high probability (P_a = 0.55-0.80), showed virtually antibacterial, antifungal, anthelmintic, antiviral and anticarcinogenic activity. Preliminary microbiologically study of the investigated compounds confirmed the virtual concepts (anticarcinogenic activity was not tested).

By using of synthesized bioactive compounds (1, 3, 5 %) and selected polymer matrix (polyurethanes and polyester urethanes non-modified and modified by siliconorganic oligomers) we prepared novel inorganic-organic antibiocorrosive covers[3]. We studied tribological properties[4] of polymer matrices and antibiocorrosive covers based on them. It was established that the friction of polyurethane and polyester urethane matrices modified by siliconorganic oligomers and antibiocorrosive covers, is higher for non-modified polyurethanes. So, the modification can be used for improvement of tribological properties of antibiocorrosive covers. By using of gravimetric method the water absorption ability of obtained antibiocorrosive covers was determined. It was established that during 720 h their water absorption ability was 0.01-0.03 %. Their testing on photochemical and thermal stability (in air, isothermal aging at 40 and 60 ºC), on action (on definite time) of "light-weather" (complex action of moisture and of air oxygen, of ultra-violet eradiation of sun or of "scattered" sunlight, CO_2) showed, that during 1200 h the initial expression, colour, optical transparency and mechanical properties (homogeneity of the surface without formation of splits) of antibiocorrosive covers has not deteriorated.

Conclusion

Novel antibiocorrosive covers based on bioactive arsenic-containing compounds and polyurethanes modified by siliconorganic oligomers have created and studied.

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