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Reaction of Bis[trialkyl(aryl)arsonium]-1,4-dihydronaphtalene Iodides with Mercuric Iodide in Water–Ethanol Solutions of Potassium Iodide

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Abstract — The reaction of bis[trialkyl(aryl)arsonium]-1,4-dihydronaphtalene iodides with mercuric iodide in water–alcohol solutions in the presence of excess potassium iodide gives rise to bisarsonium triiodomercurates.

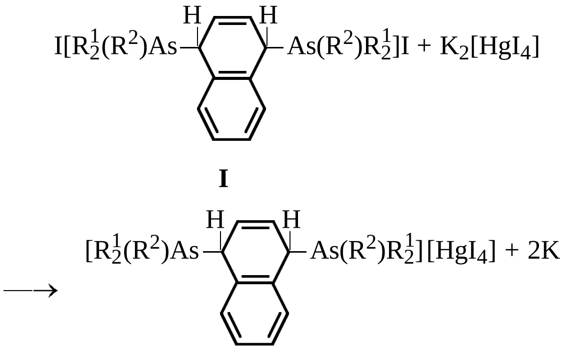
The information on the composition of acido complexes of mercury(II) in aqueous solutions and on their stability is contradictory [1–3]. In the scientific [4] and educational [5] literature the prevailing opinion is that the reaction of alkali metal iodides with mercuric iodide gives the corresponding tetraiodomercurates(II) in nearly quantitative yields. This suggests that in aqueous solutions containing both potassium iodide and mercuric iodide in a 2 : 1 molar ratio Hg(II) is present mainly as the complex anions $[HgI_4]^{2-}$. By contrast, we earlier showed [6] that tertiary arsonium iodides react with mercuric iodide in water–alcohol solutions to give, whatever the composition of the tetraalkyl(aryl)arsonium salts and the reactant molar ratio, no other products than the corresponding arsonium triiodomercurates(II).

As a continuation of our studies in the area of salts of bis[trialkyl(aryl)arsonium]-1,4-dihydronaphtalenes [6, 7] and syntheses of cation–anion acido complexes [8], in the present study we found it worthwhile to explore a hydrochemical reaction of the abovementioned bisarsonium salts with mercuric iodide in the presence of excess potassium iodide.

By analogy with the published data [4], it might be expected that the reaction would lead to tetraiodomercurates of the corresponding bis[triakyl(aryl)-arsonium]-1,4-dihydronaphtalenes as a result of consequitive reactions (1) and (2), which can be expressed by the overall equation (3).

To this end, the bisarsonium salts and mercuric iodide were taken in equimolar amounts, and a mixture of water and ethanol was used as the reaction medium (quaternary arsonium iodides are water-insoluble). Mercuric iodide was preliminarily dissolved in a solution of potassium iodide.

$$2KI + HgI_2 \longrightarrow K_2[HgI_4], \quad (1)$$



I

II

(2)

$$\mathbf{I} + HgI_2 \longrightarrow \mathbf{II}. \quad (3)$$

Mixing of alcohol solutions of bis[trialkyl(aryl)arsonium]-1,4-dihydronaphtalene iodides with aquoeus solutions of the mixture of mercuric iodide and potassium iodide results in immediate precipitation of yellowish substances. Analysis of the latter (after thorough purificaion and drying) showed that they are bis[trialkyl(aryl)arsonium]-1,4-dihydronaphtalene di(triiodomercurates), and their formation can be explained by reactions (4) and (5), or by the overall reaction (6).

It should be emphasized that changing the reaction conditions (using a two- or fourfold excess of bisarsonium iodide, altering the order of mixing the reactant solutions) had no effect on the results of the experiments: In all cases there were formed coordination compounds containing one molecule of bis[trialkyl(aryl)arsonium]-1,4-dihydronaphtalene and two molecules of the mercuric salt and having the same melting points and other physicochemical characteris-

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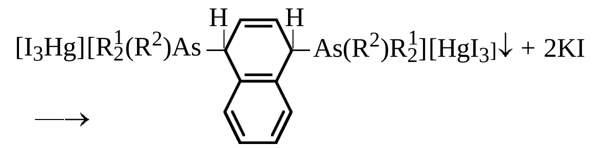
$$KI + HgI_2 \longrightarrow K[HgI_3], \qquad (4)$$

$2K[HgI_3]$ + **I**



(5)

IIIa–IIIh

R^1 = n-C_3H_7, R^2 = CH_3 (**a**); R^1 = n-C_4H_9, R^2 = CH_3 (**b**); R^1 = n-C_4H_9, R^2 = C_2H_5 (**c**); R^1 = n-C_5H_{11}, R^2 = CH_3 (**d**); R^1 = n-C_5H_{22}, R^2 = C_2H_5 (**e**); R^1 = n-C_6H_{13}, R^2 = CH_3 (**f**); R^1 = n-C_6H_{13}, R^2 = C_2H_5 (**g**); R^1 = C_6H_5, R^2 = CH_3 (**h**).

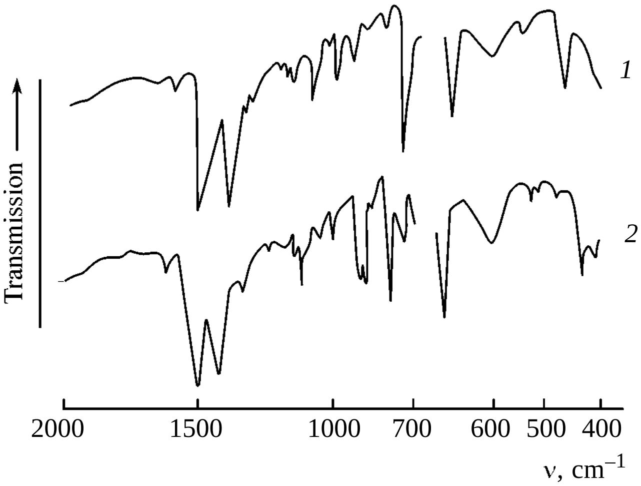
$$HgI_2 + \mathbf{I} \longrightarrow \mathbf{III} + 2KI. \qquad (6)$$

tics. The reaction pathway, too, was unaffected by the presence of excess potassium iodide in the reaction mixture, even though potassium tetraiodomercurate can, in essence, be regarded as the result of reaction (7):

$$KI + K[HgI_3] \rightleftarrows K_2[HgI_4]. \qquad (7)$$

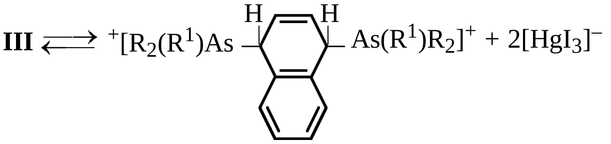
The obtained compounds are finely crystalline substances insoluble in water, ethanol, ether, benzene, and other nonpolar organic solvents but fairly readily soluble in acetone and dimethylformamide.

The composition and structure of the products were confirmed by the elemental analyses and IR spectra. The IR spectra (see figure) in their main features are similar to the spectra of the starting bis[trialkyl(aryl)arsonium]-1,4-dihydronaphtalene iodides [6, 7]. The presence in the cation of arsenic in the sp^3 state and thus the ionic character of the synthesized compounds are in general sustained by the observation of absorption bands in the region of 600 and 625 cm^{-1} due to As–C_{alk} and As–C_{arom} absorption, respectively [9].



IR spectra of (*1*) bis(methyldibutylarsonium)-1,4-dihydronaphtalene triiodomercurate(II) and (*2*) bis(methyldiphenylarsonium)-1,4-dihydronaphtalene triiodomercurate(II).

The coordination formulas of the synthesized compounds were also confirmed by their molar electrical conductivities (μ) in dilute solutions. Since the samples are water-insoluble, the μ values were obtained in dimethylformamide solutions. The results are summarized in the table, from which it follows that the molar electrical conductivities of the synthesized compounds vary from 139 to 154 Ω^{-1} cm^2 mol^{-1}, which is indicative of their three-ion composition [10].



Thus, our studies confirm the ability of Hg(II)

Yields, melting points, electrical conductivity (μ), and elemental analyses of bis[trialkyl(aryl)arsonium]-1,4-dihydronaphtalenes triiodomercurates(II)

Comp. no.	Yield, %	mp, °C	μ, Ω^{-1} cm^2 mol^{-1}	Found, %		Formula	Calculated, %	
				As	I		As	I
IIIa	87	80–81	139	9.08	46.23	$C_{24}H_{42}As_2Hg_2I_6$	9.13	46.40
IIIb	78	96–97	142	8.63	44.68	$C_{28}H_{50}As_2Hg_2I_6$	8.82	44.82
IIIc	76	102–103	143	8.52	43.91	$C_{30}H_{54}As_2Hg_2I_6$	8.68	44.09
IIId	83	117–118	148	8.28	42.82	$C_{32}H_{58}As_2Hg_2I_6$	8.54	43.39
IIIe	75	120–121	149	7.92	42.34	$C_{34}H_{60}As_2Hg_2I_6$	8.40	42.71
IIIf	81	132–133	153	7.83	41.82	$C_{36}H_{66}As_2Hg_2I_6$	8.27	42.05
IIIg	74	137–138	154	7.49	40.92	$C_{38}H_{70}As_2Hg_2I_6$	8.15	41.41
IIIh	72	151–152	145	8.13	42.39	$C_{36}H_{34}As_2Hg_2I_6$	8.42	42.80

to react in aqueous solutions of alkali metal iodides with some cations, yielding triiodomercurate(II) salts.

EXPERIMENTAL

The IR spectra were recorded in the range 400–4000 cm^{-1} on a UR-20 spectrometer as suspensions in Vaseline oil placed between KBr plates.

The solvents (ethanol, dimethylformamide) were purified and dried prior to use by the procedures described in [11]. Chemically pure grade mercuric and potassium iodides were used. The working solutions for quantitative determination of iodide anion were prepared by the procedure described in [12]. Arsenic was determined by the Evins method [13], and iodine, by the procedure in [14].

The specific electrical conductivities were measured in DMF solutions at 25°C on an Impuls conductometer with the accuracy rating of ±1.5% The molar electrical conductivities were calculated by the following formula:

$$\mu = \chi \frac{1000}{c}.$$

Here χ and c are the specific electical conductivity and the concentration of the solution, respectively.

Bis(methyldipropylarsonium)-1,4-dihydronaphtalene triiodomercurate(II) (IIIa). To a dilute solution of a mixture of 1.1 g of mercuric iodide and 0.9 g of potassium iodide, a dilute ethanolic solution of 1.8 g of bis(methyldipropylarsonium)-1,4-dihydronaphtalene diiodide was added. The immediately formed precipitate was left in the flask overnight at room temperature to complete crystallization. The precipitate was filtered off, washed several times with twice distilled water, and dried in a vacuum dessicator to constant weight over phosphorus pentoxide and paraffin wax to obtain 3.52 g (87%) of a finely crystalline yellowish substance, mp 80–81°C.

Complexes **IIIb**–**IIIh** were prepared by the same procedure.

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