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ELECTROCHEMICAL SYMMETRIZATION OF CARBORANYLMERCURY SALTS

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Summary

Preparative electrochemical symmetrization of *C*- and *B*-carboranylmercury salts was carried out. The mechanism of the electrochemical reaction is discussed.

Introduction

One of the well known reactions in organomercury chemistry is symmetrization of organomercury salts RHgX into fully substituted mercury derivatives R_2Hg. The choice of the symmetrization agents (KI, NaI, KCN, $Na_2S_2O_3$, NH_3, Cd, Zn, Na/Hg, K/Hg, metal hydrides, etc. [1]) depends greatly on their radical nature. Earlier Reutov et al. [2] have shown the principle method for the electrochemical symmetrization of alkylmercury salts by application of the polarographic technique. This fact was later verified by preparative electrochemical symmetrization of decylmercury salts [3]. Symmetrization of *C*- and *B*-carboranylmercury salts does not occur under the action of complexing agents, and it can be carried out only by such reducing agents as naphthalene anion radical [4], cadmium amalgam [5] or lithium aluminium hydride [6]. The principal method of electrochemical symmetrization of carboranylmercury salts has been shown by the polarographic technique [7].

The aim of the present work is to find a preparative electrochemical way for symmetrization of *C*- and *B*-carboranylmercury salts.

Experimental

General technique for electrochemical symmetrization

All the electrolysis processes were run in a galvanostatic regime (300 mA, 50–150 V) in a 50 ml volume glass cell without separating the cathode and anode spaces. Cathode and anode materials, electrical currents, solvents and supporting electrolytes are given in Table 1 for each experiment. In all experiments with the exception

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TABLE 1

ELECTROCHEMICAL SYMMETRIZATION OF CARBORANYLMERCURY SALTS RHgX

R	X	Yields (%) based on		Current (mA)	Solvent	Supporting electrolyte	Cathode	Anode
		substance	current					
C_6H_5-*o*-$CB_{10}H_{10}C$	Br	80	86	50	Acetone	Bu_4NBr	Pt	Mg
m-$H_2C_2B_{10}H_9$	Cl	78	76	100	Acetone	Et_4NCl	Cu/Hg	Mg
m-$H_2C_2B_{10}H_9$	CF_3COO	70	68	100	Acetone	CF_3COOK	Cu/Hg	Pt
$(CH_3)_2$-*m*-$C_2B_{10}H_9$	Cl	65	28 [a]	200	CH_3CN	$NaClO_4$	Pt	Mg
$(CH_3)_2$-*m*-$C_2B_{10}H_9$	CF_3COO	75	78	100	CH_3CN	CF_3COOK	Pt	Pt
o-$H_2C_2B_{10}H_9$	Cl	70	77	100	CH_3CN	Et_4NCl	Pt	Mg
o-$H_2C_2B_{10}H_9$	CF_3COO	74	87	100	Acetone	CF_3COOK	Pt	Mg
m-$H_2C_2B_{10}H_9$	Cl	32	68 [b]	100	CH_3CN	Et_4NCl	Pt	Mg

[a] 240% of electricity, based on the one-electron process, was passed. Besides the main product 7% of carborane and 8% of bis(carboranyl) were detected. [b] 50% of electricity, based on the one-electron process, was passed. Besides the main product 15% of carborane and 15% of bis(carboranyl) (from GLC data) were detected.

of those indicated, 120% of electricity, based on the one-electron process, was passed. After the end of electrolysis the reaction solution was evaporated to dryness in vacuo. The residue was treated with hot benzene (2 × 50 ml), the benzene solution was then filtered and was passed through a short (~ 5 cm) silicagel column. The column was washed with benzene, the benzene extracts were dried, and the residue was recrystallized from benzene/hexane mixtures. The yields and some of the characteristics of the products obtained are summarized in Table 1.

Electrolysis of bis(m-carboran-9-yl)mercury

50 ml acetonitrile solution, 1.22 g (2.5 mmol) of bis(*m*-carboran-9-yl)mercury and 0.25 g (2.0 mmol) of $NaClO_4$ were electrolysed in a galvanostatic regime (300 mA, 150–200 V). After 100% electricity, based on the one electron process, was transferred the reaction mixture was dried. The residue was treated with ether and the ether extract filtered and analyzed by GLC and GC/MS techniques. The GLC and GC/MS analysis showed that the main substance in the reaction mixture was initially bis(*m*-carboran-9-yl)mercury (~ 80%). *m*-Carborane and bis(*m*-carboranyl) were formed in relatively small yields of 7 and 8%, respectively. Apart from the product indicated the residue consisted of 5% unidentified by-products, not containing the carborane moiety.

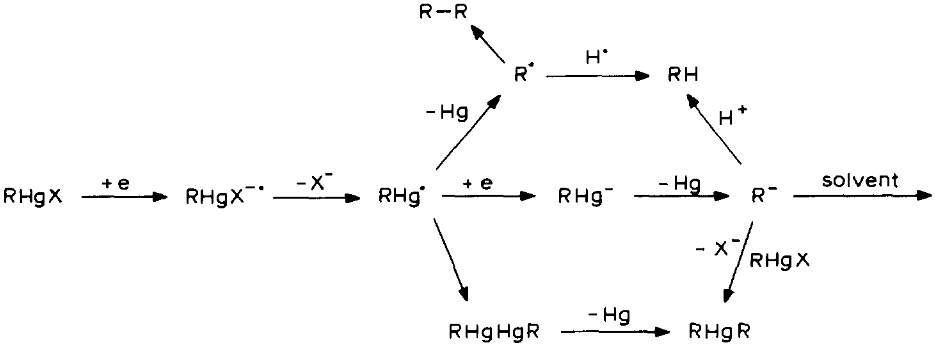
GLC and GC/MS analysis

A packed glass column filled with Chromosorb W (100–120 mesh)/2% by weight of Dexil 200, F.I. Detector, and helium as gas carrier at a rate of 30 ml/min were used for GLC analysis. The column temperature was rised from 80 to 300°C at a rate of 8°C/min.

The same column and the same temperature conditions in a LKB-9000 GC-mass-spectrometer were applied.

Results and discussion

The results of the present work prove that symmetrization of *C*- and *B*-carboranylmercury salts could be carried out with high yields by the electrochemical method. Use of aprotonic solvents for this reaction allows the use of platinum, copper, or mercury cathodes. When a copper cathode is used the amalgamation of

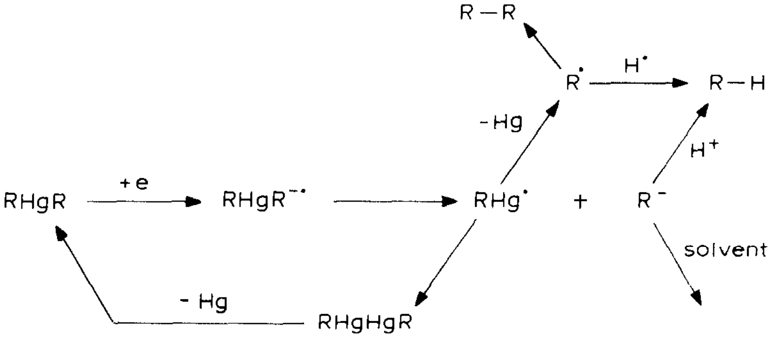


SCHEME 1

the electrode took place first and the further reduction proceeded with the mercury cathode. The distribution of the products obtained allows us to propose Scheme 1 of electrochemical reactions.

According to this scheme bis(carboranyl) can be formed only as a result of a single electron transfer reaction. All the other products, such as carborane and bis(carboranyl)mercury, can be formed by either one or two electron transfer steps. Since bis(carboranyl) was detected as a by-product in the reaction mixture then single electron transfer reduction seems to occur. However, as electrosynthesis was carried out without potential control the possibility of some contribution of the double-electron transfer process could not be excluded.

The use of different cathode materials slightly influences the main electrochemical reaction pathway and, much more significantly, the distribution of the by-products. Thus, the use of a Cu/Hg cathode results exclusively in bis(carboranyl)mercury, whereas the use of a Pt cathode leads to the formation of other reaction products: carborane and bis(carboranyl), in low yields. The following explanation for this phenomenon is proposed: the adsorbtion energy of the carboranylmercury radical on the Pt cathode is probably less than it is on the Cu/Hg electrode; thus such a radical is more capable for desorbtion from the electrode, which is followed by demercuration and the formation of the carboranyl radical. The second possibility for carborane and bis(carboranyl) formation is a result of a symmetrization reaction. In order to examine such a possibility the solution of bis(carboranyl)mercury was electrolysed. After 100% of electricity based on the one-electron process was passed, 20% of initial bis(carboranyl)mercury was decomposed giving carborane and bis(carboranyl). Reaction scheme 2 can be proposed.



SCHEME 2

Scheme 2 actually describes the further transformation of bis(carboranyl)mercury obtained by reduction of RHgX given in Scheme 1. Both Schemes 1 and 2 conform closely with the results of a polarographic study of carboranylmercury compounds [7].

However, it must be noted that the formation of carborane and bis(carboranyl) according to Scheme 2 does not rule out their formation in accordance to Scheme 1. Thus, while 50% of electricity, based on the one-electron reduction of *m*-carboranylmercury chloride was passed the products consisting of 70% of bis(carboranyl)mercury, 15% of carborane and 15% of bis(carboranyl) were detected along with unreacted initial chloride. In the latter case the formation of bis(carboranyl) and carborane can proceed only by the reactions shown in Scheme 1 since, according to polarographic data [7], the reduction potential of initial *m*-carboranylmercury chloride is ca. 2 V less negative than it is for bis(carboranyl)-mercury (0.66 and 2.5 V, respectively).

At the same time the maximum yields of symmetrical products were obtained when 120% of electricity, based on the one-electron process, was passed. Yields of the symmetrization products decreased to 65% (exp. 4) based on substances and 28% based on current when 240% of electricity, based on the one-electron reduction, was passed. In this case 7% of carborane and 8% of bis(carboranyl) were detected.

It is known that *B*-carboranylmercury salts and their symmetrical derivatives react with halogens [5]. For this reason to avoid anode halogen evolution an Mg anode was used. In this case the halide anion formed by the cathode reaction is bound by the magnesium ion. When carboranylmercury trifluoroacetates were used and anodic decomposition of carboxylates to CO_2 by the Kolbe reaction occurred, an inert platinum anode was used.

The nature of the solvent and supporting electrolyte little influences the yields of the final products.

The results obtained indicate that electrochemical symmetrization of carboranylmercury salts goes smoothly and with high yields depending slightly on the reaction conditions. On the other hand the application of the Cu/Hg cathode is more preferable since the amalgamation of the copper electrode during the reaction avoids contamination of the reaction products by the mercury metal.

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