Electrochemical activation of the alkylation of GeI_2 by *n*-butyl bromide and methylcobalt(III) bisdimethylglyoximate

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The mechanism of the alkylation of GeI_2 by *n*-butyl bromide and methylcobalt(III) bisdimethylglyoximate in acetonitrile was studied using cyclic voltammetry. The reaction with the methylcobalt complex occurs *via* anodic activation (oxidation of the methylcobalt complex), while the reaction with *n*-butyl bromide is initiated by cathodic activation (reduction of GeI_2).

Key words: methylcobalt dimethylglyoximate, *n*-butyl bromide, germanium diiodide, alkylation, electrochemical activation.

Germanium compounds containing one or two methyl groups were found in natural water. These compounds are assumed[1] to be formed from GeO_2 and methylcobalamine ($Me-CoB_{12}$) *via* a free radical mechanism. Nevertheless, attempts to methylate GeO_2 by $Me-CoB_{12}$ under conditions for methylation of inorganic mercury or platinum compounds were unsuccessful.

Unlike $Me-CoB_{12}$, which is capable of transferring the methyl group in the form of a carbanion, radical, or carbocation, such methylating reagents as MeI, *S*-adenosyl methionine, or betaine are only donors of the methyl cation.[2] These compounds alkylate metals in a low degree of oxidation, for example, Sn^{II} and Pb^{II}, *via* the mechanism of oxidative addition.[3] It has been recently shown that GeI_2 in micromolar concentrations can also react with MeI and $Me-CoB_{12}$ in aqueous solutions at different pH to form only the monomethyl product.[4] The methylation by $Me-CoB_{12}$ occurs at pH 1 (yield 1.3%) and does not occur at pH 7. Unlike this reaction, the methylation by MeI occurs best of all at pH 7.6 (aqueous solution modeling sea water, yield 6%), and the yield decreases as pH decreases (1.6% at pH 1).

In this work, the possibility of the anodic and cathodic electrochemical activation of the alkylation of GeI_2 was studied to elucidate the mechanism of these reactions. *n*-Butyl bromide (Bu^nBr) and the methylcobalt(III) dimethylglyoximate complex $(dmgH)_2CoMe$ (**1**), which has been previously used for the alkylation of inorganic mercury compounds,[5] were used as the alkylating reagents.

Experimental

GeI_2 was obtained by a known procedure.[6] Cobalt complexes $(dmgH)_2Co$ [7] and $(dmgH)_2CoMe$ [8] were synthesized by procedures described previously.

Acetonitrile was purified by successive treatment with CaH_2, $H_2SO_4 + KNO_3$, and P_2O_5.

^1H NMR spectra were recorded on a Bruker AC 200P instrument.

GLC-MS studies were carried out on a MAT INCOS 50 instrument (RSL column, 30 m × 0.25 mm).

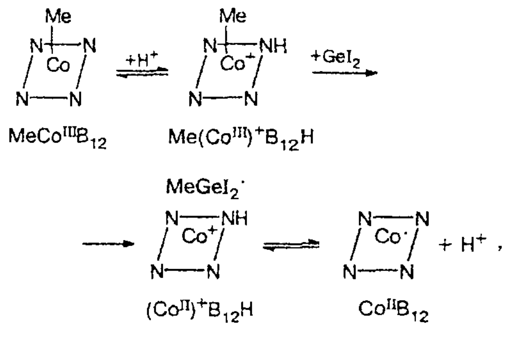
A PI-50-1.1 potentiostat was used for electrochemical studies. A platinum plate (diameter 3.5 mm) was used as the working electrode, 0.05 *M* Bu_4NBF_4 served as the supporting electrolyte, and Ag/AgCl/KCl (sat.) was the reference electrolyte. All measurements were performed in an argon atmosphere.

The PM3 method[9] included in the HyperChem Release 4 program was used for semiempirical calculations.

Results and Discussion

The free radical mechanism (Eqs. (1)—(3)) was suggested for the reaction of $Me-CoB_{12}$ with Ge^{II}, and the mechanism of oxidative addition (Eqs. (4)—(6)) was suggested for the methylation by methyl iodide.

At pH = 1:



(1)

$$Me{\cdot}GeI_2 + O_2 \longrightarrow Me(Ge^{IV})^+I_2 + O_2^{\cdot-}, \qquad (2)$$

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$$Co^{II}B_{12} + H_2O + O_2 \longrightarrow H_2O(Co^{III})^+B_{12} + O_2^{\cdot -}. \quad (3)$$

At pH = 7.6:

$$GeI_2 + MeI \longrightarrow GeI_2^{\cdot +} + Me^{\cdot} + I^-, \quad (4)$$

$$GeI_2^{\cdot +} + I^- \longrightarrow GeI_3^{\cdot}, \quad (5)$$

$$GeI_3^{\cdot} + Me^{\cdot} \longrightarrow MeGeI_3. \quad (6)$$

The fact that reaction (1) occurs at low pH values indicates that the ligand can be protonated, and the bond between the Co atom and the protonated N atom can be cleaved; the protonated form $Me(Co^{III})^+B_{12}H$ is likely the source of methyl radicals. The formation of an active source of free radicals by protonation—decoordination has been previously established for the alkylcobalt(III) complexes containing the tridentate ligand.[10]

The previously proposed[4] mechanism of the alkylation of GeI_2 by MeI suggests that at the first key stage of the process (Eq. (4)) an electron is transferred from GeI_2 to MeI. However, a different mechanism is also possible (Eqs. (7)—(9)), which includes the reverse electron transfer, from MeI to GeI_2.

$$GeI_2 + MeI \longrightarrow GeI_2^{\cdot -} + Me^+ + 1/2\ I_2 \quad (7)$$

$$GeI_2^- + Me^+ \longrightarrow MeGeI_2 \quad (8)$$

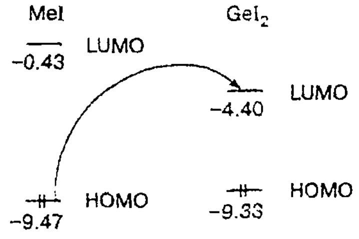
$$MeGeI_2 + 1/2\ I_2 \longrightarrow MeGeI_3 \quad (9)$$

Previously,[11] based on the electrochemical behavior of Ge^{II} halides in acetonitrile and DMF, it has been established that the transfer of an electron from the GeI_2 molecule is difficult in the absence of nucleophilic ligands, such as dioxane, triphenylphosphine, and pyridine (oxidation peaks are absent at a potential less than 2.5 eV). By contrast, GeI_2 is reduced rather readily (reversible process at E_r^{Red} −0.80 V). Based on these results, we assume that reactions (7)—(9) are more probable than reactions (4)—(6), *i.e.*, GeI_2 acts as the electron acceptor.

The electrochemical data confirm the results of the semiempirical calculations by the PM3 method of the MeI and GeI_2 molecules and their radical anions. According to the calculations, the MeI molecule has a tetrahedral configuration with the C—I bond length of 2.02 Å (the literature value[8] for sp^3-C—I is 2.16 Å). When the radical anion is formed, the C—I bond elongates to 2.86 Å, which corresponds to the dissociative reduction mechanism ($MeI + e^- \longrightarrow Me^{\cdot} + I^-$). The GeI_2 molecule has an angular structure (I—Ge—I angle 115°; Ge—I bond length 2.53 Å), and the corresponding radical anion has a linear structure (I—Ge—I angle 179°; Ge—I bond length 2.44 Å). A slight change in the Ge—I bond length indicates the nondissociative reduction mechanism ($GeI_2 + e^- \longrightarrow GeI_2^{\cdot -}$), which agrees with the observed reversibility of the reduction[11] and indicates that the radical anion is fairly stable.

The calculated energies of the boundary orbitals shown in Scheme 1 indicate that the transfer of an electron from MeI to GeI (Eq. (7)) is more probable than the back electron transfer (Eq. (4)).

Scheme 1



We assumed that the anodic activation is more efficient in the alkylation of GeI_2 by complex **1**, since this complex alkylates GeI_2 at low pH values. In the acidic medium, the protonated cation of the cobalt complex is generated (Eq. (1)); similarly, the cation of complex **1**, which can be an active source of radicals like the protonated cation, is formed in the oxidation.

The cathodic activation leads to the generation of the $GeI_2^{\cdot -}$ radical anions, which, according to our assumption, participate in the reaction of GeI_2 with RI. Therefore, it could be expected that the cathodic activation is efficient when GeI_2 is alkylated by alkyl halides.

The voltammograms of the $(dmgH)_2Co^{III}$—Me complex (curve *1*) and its equimolar mixture with GeI_2 (curve *2*) in acetonitrile are presented in Fig. 1. The peaks of the quasi-reversible $(dmgH)_2CoMe/(dmgH)_2Co^+Me$ pair (E_p^{Ox} = 0.97 V; E_p^{Red} = 0.88 V) are observed on curve *1*. A multiple potential scan in the range from 1.8 to −1.0 V results in the appearance of two new peaks on the voltammetric curves (curve *2*): anodic (peak *A*; E_p^{Ox} = 1.45 V) and cathodic (peak *B*; E_p^{Red} = −0.98 V). The cathodic peak in potential corresponds to the reduction of $(dmgH)_2Co$ (**2**). It can be assumed that peak *A* corresponds to the oxidation of the methyl derivative of trivalent germanium $MeGeI_2$ (see Eq. (1)) or dimer $(MeGeI_2)_2$ (see below).

No formation of methylgermanium compounds was observed in the absence of anodic activation. This is indicated by the ^1H NMR spectra of an equimolar mixture of complex **1** and GeI_2 in CD_3CN. The spectra of the reaction mixture do not contain the signal of protons of the methyl group bound to germanium (in CD_3CN δ 2.80 for $MeGeI_3$; 1.90 for Me_2GeI_2; 1.033 for Me_3GeI [13]). The GLC-MS data also indicate that MeGe derivatives are absent (the absence of molecular ions and the products of fragmentation at the Ge—Me bond). It is the anodic activation at the oxidation potential of the methylcobalt complex which is necessary for the reaction between complex **1** and GeI_2. When a cathodic rather than anodic potential scan is performed from 0 to

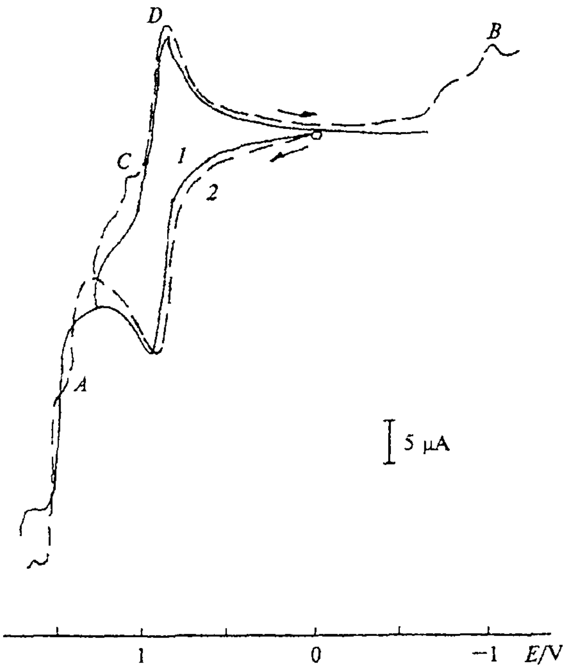


Fig. 1. Cyclic voltammograms recorded against the background of a 0.05 *M* solution of Bu_4NBF_4 in MeCN (v = 0.2 V s^{-1}): *1*, $1 \cdot 10^{-3}$ mol L^{-1} $(dmgH)_2Co^{III}$—Me; *2*, $1 \cdot 10^{-3}$ mol L^{-1} $(dmgH)_2Co^{III}$—Me; $1 \cdot 10^{-3}$ mol L^{-1} GeI_2.

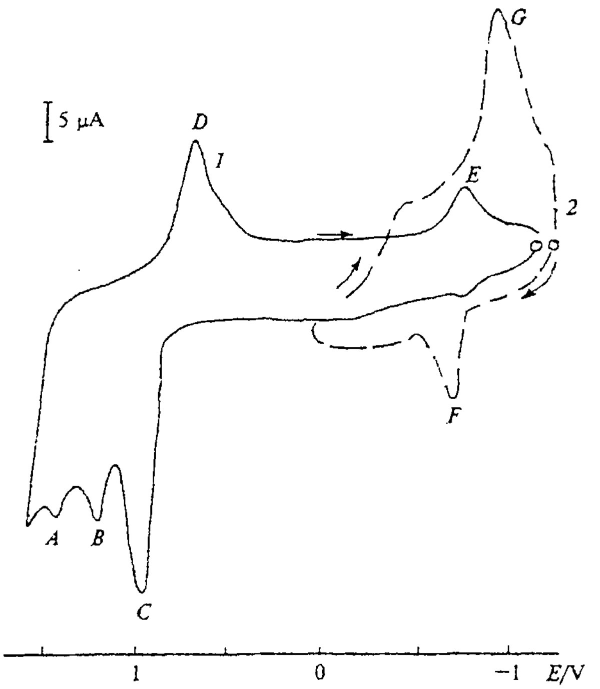


Fig. 2. Cyclic voltammograms recorded against the background of a 0.05 *M* solution of Bu_4NBF_4 in MeCN (v = 0.2 V s^{-1}): *1*, $1 \cdot 10^{-3}$ mol L^{-1} GeI_2; $5 \cdot 10^{-3}$ mol L^{-1} Bu^nBr (after electrolysis at −1.20 V); *2*, $1 \cdot 10^{-3}$ mol L^{-1} $(dmgH)_2Co$; $1 \cdot 10^{-3}$ mol L^{-1} GeI_2; $5 \cdot 10^{-3}$ mol L^{-1} Bu^nBr (after electrolysis at −1.20 V).

−1.2 V in an acetonitrile solution of a mixture of these reagents, the reduction peak of $(dmgH)_2Co^{II}$ (see Fig. 1, curve *2*, peak *B*) is absent. It appears only at the primary anodic potential scan (after the oxidation of methylcobalt and transfer of the methyl group to GeI_2). The anodic current-catalyzed methylation of GeI_2 by complex **1** can probably be described by the following equation:

$$GeI_2 + [(dmgH)_2Co^{III}\text{—}Me - e] \longrightarrow [MeGeI_2] + (dmgH)_2(Co^{III})^+. \qquad (10)$$

Along with the appearance of peaks *A* and *B*, the fact that in the presence of GeI_2, as can be seen from curve *2*, the reduction peak of the $(dmgH)_2(Co^{III})^+$ complex (peak *C*; E_p^{Red} = 1.25 V) appears on the reverse (after the anodic scan) cathodic branch of the oxidation of complex **1** indicates that reaction (10) does occur, and the value of the reduction current of the $[(dmgH)_2CoMe]^{\cdot+}$ radical cation decreases by the value of the current of this peak (see Fig. 1, peak *D*).

The data of ^1H NMR spectroscopy and the redox curves of an acetonitrile solution of an equimolar mixture of GeI_2 and Bu^nBr indicate that the methylation of GeI_2 by butyl bromide is slow. The ^1H NMR spectrum (CD_3CN, δ) consists only of signals of protons of the Bu^n group (CH_2Br, 3.5; CH_2CBr, 1.85; CH_2C, 1.5; CMe, 1.0). Only the reduction peak of GeI_2 (−0.80 V) is observed on the voltammograms. Based on our previous data[11] on the electrochemical reduction of GeI_2, we verified the possibility of the reduction activation of the alkylation of GeI_2 by butyl bromide. For this purpose, the electrolysis of an acetonitrile solution of the Bu^nBr—GeI_2 (1 : 1) mixture was performed at −1.2 V followed by the voltammetric analysis of the reaction mixture. Peaks *A*, *B*, and *C* on the anodic branch of curve *1* (Fig. 2) are evidence that the alkylation occurs. The potential of peak *A* coincides with the potential of peak *A* in Fig. 1 (1.45 V), and peaks *B* and *C* correspond to the two-stage oxidation of Br^- [14] (peak *D* corresponds to the reduction of Br_2, peak *E* corresponds to the reduction of the remaining GeI_2). Thus, reaction (11) occurs in the cathodic activation.

$$\begin{array}{ccccc} GeI_2 + e^- + Bu^nBr & \longrightarrow & Bu^nGeI_2 & + & Br^- \qquad (11) \\ & & \text{Peak } A \big\downarrow -e^- & & -e^- \big\downarrow \text{Peaks } B \text{ and } C \\ & & \text{Product} & & Br_2 \end{array}$$

The voltammetric curve obtained after the electrolysis at the same potential (−1.2 V) of an equimolar mixture of GeI_2, $(dmgH)_2Co^{II}$, and Bu^nBr in acetonitrile is designated by number *2* in Fig. 2. The anodic part of the voltammogram reproduces exactly the anodic part of the voltammogram obtained after the electrolysis of a mixture of GeI_2 and Bu^nBr (see Fig. 2, curve *1*). The cathodic part indicates that the $[(dmgH)_2Co^I]^{\cdot-}$

radical anion is accumulated during the electrolysis (peaks *G* and *F*). Reactions (11) and (12) can occur during the electrolysis on the cathode.

$$\begin{tikzcd}
(dmgH)_2Co^{II} + e^- \arrow[r, shift left, harpoon] & (dmgH)_2(Co)^{I\cdot-} \arrow[l, shift left, harpoon] \arrow[r, "BuBr"] \arrow[d, shift left, "\text{Peak } F"] & (dmgH)_2Co^{III}Bu \quad (12) \\
& (dmgH)_2Co^{II} \arrow[u, shift left, "\text{Peak } G"] &
\end{tikzcd}$$

The fact that the $((dmgH)_2Co^I)^-$ radical anion is accumulated in the near-electrode layer indicates that reaction (11) mainly occurs, and reaction (12) is almost absent.

Thus, the results obtained are evidence that the methylation of GeI_2 requires the redox activation (anodic or cathodic, depending on the alkylating agent). Both the anodic reaction with complex **1** and the cathodic reaction with Bu^nBr result in the same product (peak *A* in Figs. 1 and 2). The $RGe \cdot I_2$ structure (or dimeric structure) suggested previously[4] can be assigned to this product. However, unlike the published results,[4] the mechanism of alkylation by alkyl halides includes not the $GeI_2^{\cdot+}$ radical cations, but the $GeI_2^{\cdot-}$ radical anions.

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