On the Redox Chemistry of Ge^I Bromide

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First results on the redox chemistry of Ge^I bromide are reported herein. During the attempt to solubilize Ge^IBr, which is synthesized in preparative scale using a co-condensation technique of the high-temperature molecule Ge^IBr, a redox reaction with the solvent acetone occurs. During this unexpected redox reaction Ge^I is oxidized to Ge^{IV} and acetone is reductively coupled to 1,1-dimethyl-3-oxobutan-1-yl.

Introduction

Ge^IBr is a good starting material for the synthesis of germanium cluster compounds with "naked" germanium atoms,[1] which represent a new class of cluster compounds in germanium chemistry.[2] Ge^IBr can be synthesized by a preparative co-condensation technique, in which the high-temperature molecule Ge^IBr, synthesized at 1600 °C, is condensed together with a solvent at –196 °C.[3] When toluene is used as the solvent during the co-condensation reaction, Ge^IBr is isolated as an orange solid. Sadly, this solid Ge^IBr is insoluble in inert solvents such as THF, Et_2O, or $C_2H_4Cl_2$ and therefore it cannot be used for the synthesis of molecular cluster compounds of germanium, which is our main goal. To get Ge^IBr in a soluble form we performed in the following co-condensation reactions where we used a mixture of toluene and a donor molecule as the solvent. During these experiments, it turned out that donor molecules such as THF, Et_2O, NEt_3, or CH_3CN, which worked quite well in the case of subvalent group 13 halides such as Ga^IBr or Al^IBr,[4] are not capable to solubilize Ge^IBr, and thus we always obtained the solid Ge^IBr. However, the use of amines with long alkyl chains such as $NnPr_3$ or $NnBu_3$ led to a different result.

When a mixture of toluene/$NnPr_3$ is used as the solvent during the co-condensation reaction, an emulsion of a dark-red oil in a pale yellow solution is obtained after heating the co-condensate to –78 °C. This means, if either $NnPr_3$ or $NnBu_3$ are used as the donor component during the co-condensation reaction, Ge^IBr is obtained in the form of a dark-red oil which can be used for subsequent reactions. Using this emulsion as the starting material, we synthesized the cluster compounds $Ge_8[N(SiMe_3)_2]_6$[5] and $\{Ge_9[Si(SiMe_3)_3]_3\}^-$[6] by the reaction with $Li[N(SiMe_3)_2]$ and $Li[Si(SiMe_3)_3]$, respectively.

These reactions are carried out inside the co-condensation apparatus, because isolation of the emulsion leads to a great loss in yield of Ge^IBr, as the dark-red oil remains almost quantitatively inside the apparatus. Since the performance of these reactions inside the co-condensation apparatus are very complex – e.g. it is difficult to observe and to monitor the reaction process – it is desirable to obtain Ge^IBr solutions, which might then be isolated and used outside the apparatus for subsequent reactions. Thus, we expect to obtain better control of the reaction conditions (temperature, stoichiometry etc.) and we will be able to observe the color gradient during the reaction, which, for technical reasons, is not possible inside the co-condensation apparatus. Therefore, we had to find a solvent or a mixture of solvents for the co-condensation reaction which would lead to Ge^IBr solutions. Herein we report on the attempt to obtain such Ge^IBr solutions.

Results and Discussion

Ge^IBr appears to be soluble in acetone, since while cleaning the co-condensation apparatus with acetone, we observed that the remaining Ge^IBr gave initially a dark-red solution. Consequently, we conducted a co-condensation experiment of Ge^IBr with dry acetone as the solvent. After allowing the temperature of the co-condensate to increase from –196 to –78 °C, a dark-red solution was obtained and no residue remained inside the apparatus. This means that Ge^IBr was quantitatively dissolved. Unfortunately, it turned out that Ge^IBr is not stable in acetone, as the dark red color of the solution vanishes on warming to room temperature leading to a pale yellow solution. On concentrating this solution, we were able to isolate a product of the reaction in the form of colorless crystals. X-ray crystal structure analysis of these crystals reveals that the compound

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$Br_3GeC_6H_{11}O$ (**1**), whose molecular structure is shown in Figure 1, was formed in 30% yield.

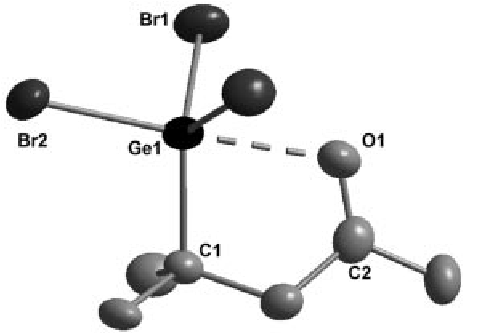


Figure 1. Molecular structure of $C_6H_{11}Br_3GeO$ (**1**) (hydrogen atoms are ommited). Selected bond lengths [pm] and angles (°): Ge1–Br1: 230.6(1), Ge1–Br2: 238.9(1); Ge1–C1: 198.3(8), Ge1–O1: 242.4(1); C2–O1: 120.8(1); Br1–Ge1–C1: 120.4(3); Br2–Ge1–C1: 104.2(1).

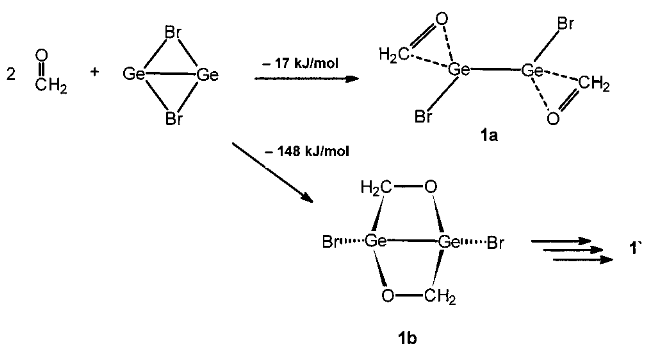
Clearly compound **1** contains germanium in the oxidation state +4. The central germanium atom is surrounded tetrahedrally by three bromine atoms and a carbon atom of the organic ligand 1,1-dimethyl-3-oxobutan-1-yl.

The organic ligand in **1** is oriented in such a way that an additional Ge–O contact is formed (dashed bond in Figure 1). Because of this Ge–O contact, the Ge–Br bond length to the oppositely-bound bromine atom is elongated by 9 pm (239 pm) with respect to the other Ge–Br bond lengths (230 pm), which are as long as those found in other $RGeBr_3$ compounds.[7] Therefore, a 4+1 coordination of the Ge atom is found, which leads to a strong distortion of the tetrahedral surrounding of the Ge atom towards a trigonal-bipyramidal surrounding.

The organic ligand in **1** originates from the solvent acetone, as acetone was the only organic compound present during the reaction. The ligand is built up from two molecules of acetone, in which the carbonyl function of one molecule is completely reduced.

This means that Ge^IBr reacts with acetone in a redox reaction in which Ge^I is oxidized to Ge^{IV} and acetone is reductively coupled to 1,1-dimethyl-3-oxobutan-1-yl in which the former carbonyl carbon atom (formal oxidation state +2) is bonded directly to the germanium atom (formal oxidation state –1). Such a redox reaction is not known for Ge^{II} halides, which indicates that the redox potential of Ge^{II} halides is too small to reduce acetone which has a reduction potential of –2.84 V.[8] As the redox reaction works with Ge^I bromide, the minimum redox potential for the oxidation of Ge^I bromide in this reaction is –2.84 V and is therefore in the range of the alkali metals (Na = –2.71 V; K = –2.93 V[8]), showing that Ge^I bromide is a strong reducing agent.

To get a first insight into the reaction mechanism of this redox reaction, we performed DFT calculations[9] for the initial step of the reaction on the model system GeBr and H_2CO, taking into account the reaction sequence outlined in Scheme 1.[10]



Scheme 1. Possible first step for the model redox reaction of GeBr and H_2CO.

The calculations show that the formation of three-membered Ge–C–O rings (**1a**) is energetically favored by only 17 kJ mol^{-1}, which can therefore be regarded as a weak complex in which H_2CO is only coordinated to the germanium center leading to a small elongation of the C–O bond length to 128 pm, with respect to uncoordinated H_2CO where the C–O bond length is 121 pm. The formation of four-membered C–O–Ge–Ge rings (**1b**) is energetically favored by 148 kJ mol^{-1}, which can therefore be regarded as a possible first product in the redox reaction, where the C–O bond length is now considerably elongated to 139 pm.

The formation of a similar four-membered M_2CO ring is also known for the adsorption of acetone on a (2×1)-reconstructed Si(001) surface, where the surface-lattice structure undergoes a reconstruction in which adjacent silicon dimers pair together and form dimers through a σ bond and a π bond.[11] In this system the carbonyl function reacts with silicon dimers in a similar way to a [2+2] cycloaddition reaction.[12] Such a [2+2] cycloaddition is also possible for the redox reaction discussed here, as the bond between the germanium atoms in BrGeGeBr can formally be seen as a "triple" bond (Br–Ge≡Ge–Br). Therefore, it seems plausible that the first step of the discussed redox reaction is a [2+2] cycloaddition of the carbonyl function to $(GeBr)_2$, which is also suggested by the results of the quantum chemical calculations.

The oxygen atom that originates from this redox reaction is found in a second compound, which can also be isolated in the form of colorless crystals on further concentration of the reaction solution. Crystal structure analysis of these crystals shows that **2** is a cationic germanium oxocluster compound $[Ge_6O_8R_6{\cdot}2H_2O]^{2+}$ (R = $C_6H_{11}O$) which crystallizes together with two $GeBr_3^-$ anions. The molecular structure of **2** is shown in Figure 2.

The Ge–O backbone of **2** consists of a central Ge_4O_4 eight-membered ring in chair conformation. Two planar Ge_3O_3 six-membered rings are condensed on opposite sides of the eight-membered ring. Structurally, **2** can be compared with $Ge_6O_8R_6Cl_2$ (R = *t*Bu) (**3**) which was synthesized by Puff et al. by careful hydrolysis of $tBuGeCl_3$.[13] The major difference between **2** and **3** is the fact that **2** is a cationic species while **3** is neutral. As **2** is a cationic compound, two different Ge sites are found inside the cluster

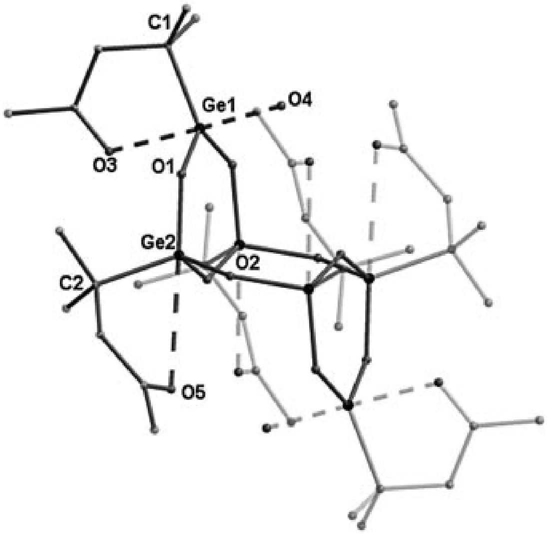


Figure 2. Molecular structure of $[Ge_6O_8(C_6H_{11}O)_6{\cdot}2H_2O]^{2+}$ (**2**) (hydrogen atoms are ommited for clarity and two five-membered GeC_3O rings are highlighted). Selected bond lengths [pm] and angles (°): Ge1–O1: 174.3(3); Ge1–O3: 222.5(3); Ge1–O4: 199.8(3); Ge1–C1: 196.3(4); Ge2–O1: 178.3(3); Ge2–O2: 175.8(3); Ge2–O5: 282.4(4); Ge2–C2: 197.3(4); O1–Ge1–C1: 119.91(18); O3–Ge1–O4: 178.17(13); O1–Ge2–O2: 104.80(13); Ge1–O1–Ge2: 126.51(16).

core. Four germanium atoms are tetrahedrally coordinated by three oxygen atoms (Ge–O: 177 pm) and the carbon atom of the organic ligand (Ge–C: 197 pm). Two germanium atoms have a trigonal-planar geometry and are surrounded (sum of angles: 358.5°) by two oxygen atoms (Ge–O: 174 pm) and a carbon atom of the organic ligand (Ge–C: 196 pm). Additionally, two further germanium oxygen contacts are found: one to the oxygen atom of the keto group of the organic ligand (Ge–O: 222 pm) and one to the oxygen atom of a water molecule (Ge–O: 200 pm). Therefore, the coordination number is 3+2. The reason why **2** is isolated as a cationic species might be the fact that the carbonyl function of the organic ligand is able to stabilize the cationic center, forming a five-membered GeC_3O ring. On the other hand, the presence of the Br^- acceptor $GeBr_2$ is necessary. The formation of a five-membered ring is also found in the case of the tetrahedrally coordinated germanium atoms, although in this case the germanium–oxygen contact between the germanium atom and the oxygen atom of the carbonyl function is much longer (282 pm), but is still significantly shorter than the sum of the van der Waals radii (ca. 310 pm).

Conclusions

The results presented here show that it is possible to get Ge^IBr solutions. Ge^IBr is hereby, as expected, more reactive than the corresponding $Ge^{II}Br_2$ for which no comparable redox reactions are known. In the case of acetone, this reactivity is too high to apply acetone as a solvent. However, this redox capability might be of great interest for redox reactions and C–C coupling reactions in organic chemistry. In the case of our planned chemistry where we would like to use the disproportionation reaction of Ge^IBr to get to cluster compounds, such a redox reaction has to be ruled out. Therefore, we had to search for other solvents which would be able to solubilize Ge^IBr and which would be stable enough towards reduction to act only as a solvent. Another suitable method might be the introduction of donor molecules to lower the reactivity of the Ge^I halide. These investigations are the subject of current experiments.

Experimental Section

Liquid germanium was treated with HBr under high vacuum at 1550 °C, and the resulting gaseous products (ca. 15 mmol GeBr) were condensed together with acetone (150 mL) at a surface at –196 °C. After the co-condensate was allowed to warm to –78 °C a dark-red solution was obtained. The solution was heated to room temperature. During the heating process the color of the solution changed from dark red to pale yellow. The solution was concentrated and stored at –28 °C, whereby colorless crystals of Br_3Ge-$C_6H_{11}O$ (**1**) formed (600 mg, 30%). Unfortunately, for technical reasons (hydrolyses or oxidation of the microcrystalline samples) it proved impossible to obtain a satisfactory elemental analysis.

The solution was filtered and further concentrated to yield colorless crystals containing $[Ge_6O_6(C_6H_{11}O)_6{\cdot}2H_2O]^{2+}$ (**2**) (20 mg, 0.6%).

Compound 1: ^1H NMR (250 MHz, C_6D_6): δ = 1.03 (s, 6 H, CH_3), 1.42 (s, 3 H, CH_3), 2.90 (s, 2 H, CH_2) ppm. ^{13}C NMR (63 MHz, C_6D_6): δ = 23.9 (CH_3), 30.3 (CH_3), 46.2 (C), 51.7 (CH_2), 205.8 (C=O) ppm.

Crystal Structure Data of $Br_3GeC_6H_{11}O$: M_r = 411.47 g mol^{-1}, monoclinic, *P*2(1), *a* = 7.2981(15), *b* = 12.119(2), *c* = 20.085(4) Å, β = 97.40(3), *V* = 1761.6(6) Å^3, *Z* = 6, $\rho_{calcd.}$ = 2.327 g cm^{-3}, μ_{Mo} = 12.768 mm^{-1}, $2\theta_{max}$ = 52.10°, 13708 measured reflections, 6338 independent reflections [*R*(int.) = 0.0550], numerical absorption correction (min./max. transmission 0.0402/0.1019), R_1 = 0.0360, wR_2 = 0.0856. Stoe IPDS-diffractometer (Mo-K_α radiation, λ = 0.71073 Å, 200 K).

Crystal Structure Data of $C_{36}H_{70}Br_6Ge_8O_{16}$: M_r = 1819.1 g mol^{-1}, triclinic, *P*-1, *a* = 10.5934(16), *b* = 12.2614(16), *c* = 13.5835(19) Å, α = 63.462(15), β = 76.452(17), γ = 81.486(17)°, *V* = 1532.6(4) Å^3, *Z* = 1, $\rho_{calcd.}$ = 1.971 g cm^{-3}, μ_{Mo} = 7.831 mm^{-1}, $2\theta_{max}$ = 52.10°, 11842 measured reflections, 5509 independent reflections [*R*(int.) = 0.0594], numerical absorption correction (min./max. transmission 0.0784/0.1378), R_1 = 0.0370, wR_2 = 0.0978. Stoe IPDS-diffractometer (Mo-K_α radiation, λ = 0.71073 Å, 200 K). CCDC-245799 (for **1**) and -245800 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[10] As no structural information was available about Ge^IBr in solution, we had to assume an initial structure for the calculations. Here we assumed, that the monomeric Ge^IBr radical which was trapped in the matrix of solvent molecules during the co-condensation dimerizes first to give Ge_2Br_2. This process is energetically favored by 238 $kJ\,mol^{-1}$ according to quantum chemical calculations (ref.[9]). This dimer (Ge_2Br_2) is then used as starting point for the calculations.

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