

A comparison of boron hydride- and hydrocarbon-based thiol derivatives assembled on gold surfaces.

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ABSTRACT

The elements carbon and boron uniquely form extensive series of compounds with hydrogen; hydrocarbons and boron hydrides. In comparison to carbon, which forms various chain- or ring-like structures, boron, an electron deficient element, forms *quasi*-aromatic clusters architecturally derivable from a twelve-vertex icosahedral unit. Herein, we focus on a comparison of hydrocarbon and boron hydride based systems anchored to a gold surface via one or more thiol groups. This study includes the aspects of bonding, electrochemistry, and thermal, radiation and oxidation stabilities.

Keywords: gold, boron hydride, carborane, hydrocarbon, thiol

1 INTRODUCTION

Hydrocarbon chemistry plays an important role in our everyday life. It is a chapter of chemistry that is well understood, and many books, articles and reports have been addressed to its principles and applications [1]. Boron hydrides do not occur naturally and therefore its chemistry is a product of human curiosity and scientific investigation. The structures formed by boron hydrides are dominated by the fact that atoms of boron have one electron less than do atoms of carbon whilst having the same number of electronic orbitals. This fact has led to boron being sometimes referred to as electron deficient [2]. The electron-precise nature of carbon and the electron-deficient character of boron is responsible for most of the structural differences between their respective hydride series. For example, the bonds between sp^3 -hybridised carbon atoms in an alkane chain can rotate freely and thus give the molecule a relatively high degree of flexibility for adopting various conformations. In an attempt to share electron density boron hydrides form clusters, based on triangular 3-centre, 2-electron bonds, which lead to generally more rigid structures. Such clusters can be assigned to three basic classes according to the rules of Wade and Williams [3]. The comparison of the selected thiolated representatives of the BH and CH series of compounds assembled on gold surfaces brings several interesting revelations. The thiol derivatives of both can be easily assembled onto gold

surfaces either from a solution or gas phase to form a densely packed monolayer. Despite the fact that alkanes can take up various conformations, they are reported to preferably form a straight-line arrangement when anchored via thiol groups to a gold flat surface [4]. However, disorders can be found in the form of various ball-like structures generated spontaneously by some of the alkyl chains. The straight-line assembly of alkanethiols, sometimes compared to a crystalline phase, is most likely favored due to attractive van der Waals forces between individual chains. Disorders similar to those in the monolayers of alkanethiolates are not likely to occur with the thiolated boron hydride clusters because of their steric demands. This feature typical of clusters allows us to precisely orient various functional groups at a gold surface, and construct more sophisticated assemblies without any predictable imperfections on very large areas of the surface. Figure 1 shows molecules of 1,12-(HS)₂-1,12-C₂B₁₀H₁₀ and octanethiol (C₈H₁₇SH) on a (111) gold flat surface.

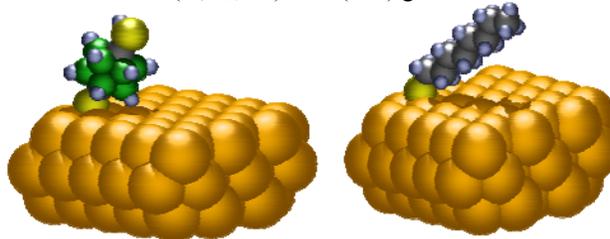


Figure 1. Space filling models of 1,12-(HS)₂-1,12-C₂B₁₀H₁₀ and octanethiol (C₈H₁₇SH) on a gold (111) surface.

2 RESULTS AND DISCUSSION

On the basis of investigations on thiolated hydrocarbons that have been described in the last three decades [5], and information that we have collected on thiolated BH clusters [6], we would like to report on a comparison of several aspects associated with these two classes of compounds. After brief consideration of the relevant differences between BH and CH chemistries, we would like to focus on the aspects of bonding and the character of the thiol groups attached to either hydrocarbons or boron hydrides, thermal stabilities and desorption experiments from gold nanoparticle surfaces, oxidation and radiation stabilities, and electrochemistry.

2.1 The aspects of bonding

It is recognized that alkanethiols bind to a gold flat surface as alkanethiolate units [7]. The value of binding energy for the S2p electrons is ~ 162.0 - 162.2 eV. To better understand this aspect, however, it is worthwhile to take a deeper look into the character of a thiol group and, in particular, its acidity. The acidity of a thiol group, respectively the value of pK_a , attached to an alkyl chain is ~ 10 - 11 . The value of pK_a of a single thiol group attached to aromatic hydrocarbons is ~ 7 - 8 . This decrease in basicity seen for thiolated aromatic compounds is due to the stabilization of the conjugate base by the electronically delocalized aromatic system. This means, that thiolated hydrocarbons are generally considered as relatively weak acids, and, within this group of compounds, the stronger acids are the aromatic thiols. Quite differently, if we look at the carborane skeleton, the value of pK_a depends on the vertex to which a thiol group is attached, if it is either to a boron or carbon vertex. Figure 2 shows two dithiol derivatives of $1,2-C_2B_{10}H_{12}$. The thiol groups are attached to the carbon atoms, indicated with grey arrows, in $1,2-(HS)_2-1,2-C_2B_{10}H_{10}$, and to boron atoms, marked with green arrows, in $9,12-(HS)_2-1,2-C_2B_{10}H_{10}$.

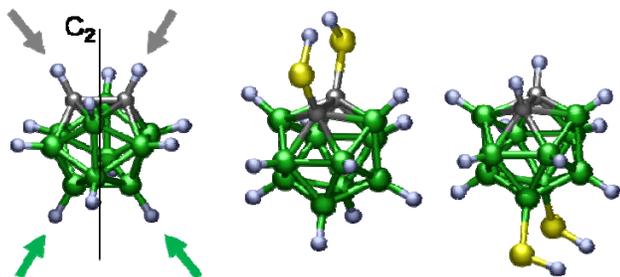


Figure 2. A cluster molecule of $1,2-C_2B_{10}H_{12}$ and its two dithiol derivatives: (from left) $1,2-(HS)_2-1,2-C_2B_{10}H_{10}$ and $9,12-(HS)_2-1,2-C_2B_{10}H_{10}$.

Let us take this icosahedral carborane skeleton as a suitable system for the evaluation of BH vertices, and therefore, the respective B-SH groups. The molecule of $1,2-C_2B_{10}H_{12}$ cluster is a relatively strong dipole with the value of 4.3 D. The selective thiolation of this carborane derivative on either the 1 and 2 carbon vertices, or the 9 and 12 boron positions has been described in the literature [8]. Both B-SH and C-SH dithiol derivatives of the $1,2-C_2B_{10}H_{12}$ have also been used for the purposes of a gold surface modification [6]. Table 1 lists the values of pK_a , and the binding energies of S2p electrons. The sulphur atoms in $9,12-(HS)_2-1,2-C_2B_{10}H_{10}$, that are attached to a gold film, bear a higher negative charge in comparison to both $1,2-(HS)_2-1,2-C_2B_{10}H_{10}$, and alkanethiols attached to a gold surface. This can potentially have an impact on the stability of this particular derivative.

Table 1. The pK_a values and the binding energies of S2p electrons (eV) for the selected representatives of thiolated hydrocarbons and boron hydrides.

| | pK_1, pK_2 | S2p (BE) |
|-----------------------------------|------------------|----------------|
| $1,2-(HS)_2-1,2-C_2B_{10}H_{10}$ | 4.47, 8.87 | $162.2^{[6]}$ |
| $9,12-(HS)_2-1,2-C_2B_{10}H_{10}$ | 5.5, 10.45 | $161.7^{[6]}$ |
| $1-(HS)-1,2-C_2B_{10}H_{11}$ | $3.30^{[8]}$ | - |
| $9-(HS)-1,2-C_2B_{10}H_{11}$ | $3.30^{[8]}$ | - |
| 1-octanethiol ($C_8H_{17}SH$) | ~ 10 - 11 | $162.2^{[9]}$ |
| 1-butanethiol (C_4H_9SH) | ~ 10 - 11 | $162.0^{[10]}$ |
| Benzenethiol (C_6H_5SH) | ~ 7 - 8 | 161.9 |

2.2 Thermal stability

Using the technique of electron ionization in a heated inlet of a mass spectrometer, we were able to make some qualitative assessments about the desorption of both the carboranethiolate and alkanethiolate species from the surface of gold nanoparticles. The samples suitable for these experiments were prepared using the two-phase method [11]. The average size of the nanoparticles is ~ 2 - 5 nm. The solid products, as prepared, had black waxy appearances. However, the carboranethiol-stabilized particles were dissolvable in acetone, and can be purified by chromatography on a silica-gel column, using acetone as the eluting agent. To understand the material before and after the chromatography purification, we carried out desorption experiments for both of these samples, and a typical desorption curve with mass spectra at two points is shown in Figure 3. The desorbing species were identified as $C_2B_{10}H_{10}$ clusters and, as shown in the second mass spectrum, tetraoctylammonium with its characteristic fragmentation.

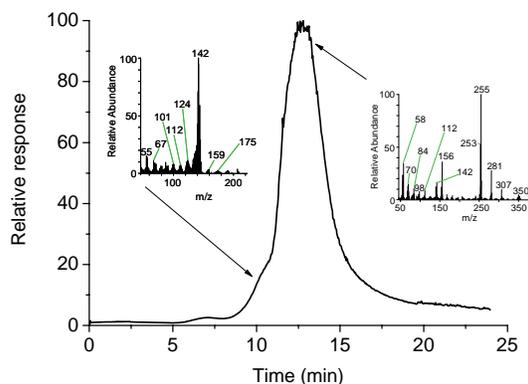


Figure 3. Total ion current profile of the desorbing molecules from the surface of gold nanoparticles before chromatography purification, obtained with a temperature program starting at 35 °C (0 min) followed by 20 °C/min increase to 280 °C (12.25 min), where it was held to the end of analysis.

After chromatography samples did not exhibit the waxy character as before, and the mass spectra did not show any

fragments characteristic of teraocetylammmonium. It is worthy to note that only $C_2B_{10}H_{10}$ clusters were observed to escape from the surface, and, from this view, gold nanoparticles were stabilized purely by carboranethiol derivatives. Further details of the desorption experiments of the chromatography purified carboranethiol-stabilized nanoparticles were described recently [6]. Indeed, all attempts to purify the alkanethiol-stabilized gold nanoparticles were not successful, and therefore, the fragments characteristic of tetraoctylammmonium ions are observed in all desorption curves apart from the desorption products originating from the molecules of alkanethiolate units. These latter species escape from the surface as dialkydisulfide molecules, and leave the surface of gold nanoparticles bare. As a consequence of the desorption process, the aggregation of 'naked' nanoparticles is observed, and the desorption product is not dissolvable in any solvent. At this point, it is worthy to note another difference between the hydrocarbon- and boron hydride-based thiol derivatives. The carboranethiolate units escape from the surface as carboryne $C_2B_{10}H_{10}$ clusters, and leave the atoms of sulphur atoms on the surface. This means that the carborane-S-Au bond is cleaved at between the sulphur and carborane cluster. In comparison to alkanethiolates on gold, the escaping 'carboryne' clusters can be stabilized by their *quasi*-aromatic character. Also the formation of a disulphide molecule during the desorption is less probable because of steric demands of the vicinal dithiolcarborane. These sulphur atoms can henceforth stabilize the surface of gold nanoparticles, and the desorption product is still nicely dissolvable to a colloidal solution. Methanethiol stabilized gold particles were prepared for the purposes of a comparison. Figure 4 shows that the methanethiolate species escape from the surface as dimethyldisulphide molecules. Therefore, these molecules do not leave sulphur atoms on the surface as carboranethiol derivatives. Also the desorbing temperature is lower by approximately 35 °C than with carboranethiol derivatized gold nanoparticles.

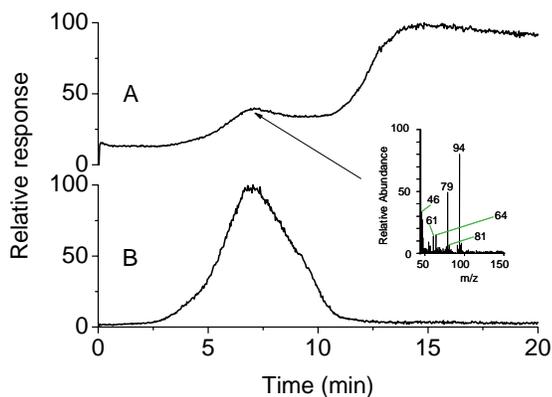


Figure 4. (A) Total ion current profile of the desorbing molecules from the nanoparticle surface stabilized by methanethiol. The mass spectrum indicates species that

escape from the surface at 185 °C. (B) Extracted profile for the ion-radical $m/z = 94$.

2.3 Oxidation and radiation stability

The carboranethiol derivatives are white solids, which can be purified by sublimation, and which are soluble in various organic solvents including for example hexane, chloroform, acetone, or ethanol. To dissolve these derivatives in water, however, it is necessary to prepare the respective thiolate salts with for example sodium (Na^+) counter ion. The sodium carboranethiolate salts can oxidize to disulphide molecules in an aqueous solution because water usually contains traces of dissolved oxygen. Figure 5A shows the XP spectrum of S2p electrons in a solid disodium salt of 1,12-(S^-)₂-1,12- $C_2B_{10}H_{10}$. The spectrum shows two components. The major one corresponds to thiolate sulphur atoms with a binding energy of 161.2 eV, and the minor component has a binding energy of 163.0 eV, which can be attributed to sulphur atoms typical of a disulphide molecule. The product of this partial oxidation is shown in the inset of Fig. 5. This oxidation occurs also on a gold surface at ambient conditions, and Figure 5B shows that the disulfide component becomes major.

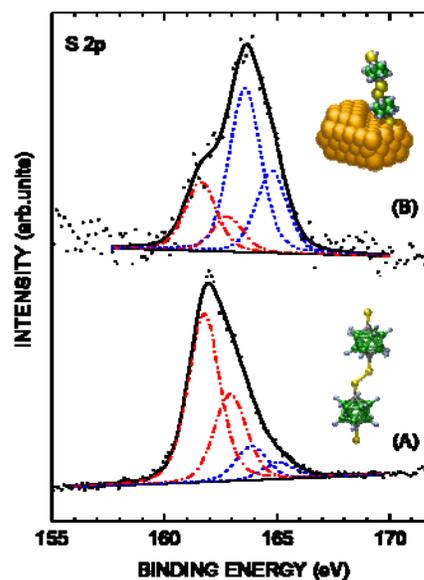


Figure 5. XP spectra of S2p electrons for a (A) solid disodium salt of 1,12-(S^-)₂-1,12- $C_2B_{10}H_{10}$ and (B) 1,12-(HS)₂-1,12- $C_2B_{10}H_{10}$ assembled on a gold surface. There are two components with binding energies of 161.2 eV, 163.0 eV (A), and 161.6 eV, 163.6 eV (B).

The carborane cluster species are extremely stable toward heating. They do not decompose at temperatures of up to 700 °C. This behavior has been discussed previously in the literature. Also, these species do not exhibit any decomposition upon their X-ray [6] or radioactive

irradiation [12]. Compounds based on boron hydrides have been studied and successfully applied for the retreatment of nuclear waste.

2.4 Electrochemistry and surface passivation

The electrochemical investigation provides us useful information about the interface between gold and the environment of an electrolyte, usually an aqueous solution. A redox system based on $[\text{Fe}(\text{CN})_6]^{3+}$ and $[\text{Fe}(\text{CN})_6]^{4+}$ complex ions has been used to investigate how effectively the alkanethiol or carboranethiol self-assembled monolayers block the access to the surface. Alkanethiol derivatives assembled on a gold surface have been reported to block the surface as a function of the alkyl chain length [4]. The longer the alkyl chain is, the more effective is the passivation of the surface. Thus, the oxidation and reduction $\text{Fe}^{2+}/\text{Fe}^{3+}$ can easily occur on a surface modified with methanethiol because a molecule of methanethiol has only one carbon atom. The molecules of octanethiol derivative block the surface more effectively. Carboranethiol derivatives can also block the surface of a gold surface. However, in this case, the passivation of a gold film depends on the orientation of the $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$ icosahedral cluster [6]. The precise orientation of the cluster changes also the value of work function from the gold surface. The same effect can be achieved only if perfluorinated, or partially fluorinated alkanes are used for the modification of a gold surface.

3 EXPERIMENTAL SECTION

The experimental data including the methods and instrumentation are in detail described in the literature [6]. Desorption experiments were monitored by MS analysis of the gaseous phase evolving from the samples. The time dependency of the desorption experiments, presented in Figures 3 and 4, was obtained by using the following experimental setup: 35 °C (0 min), linear increase of temperature by 20 °C/min up to 280 °C (12.25 min), 280 °C kept till the end of analysis.

4 CONCLUSION

In this report, we compared selected aspects of hydrocarbon- and boron hydride-based thiol derivatives assembled on gold surfaces. Both systems have some features in common, they easily anchor to gold surfaces, and to some extent, block it for further reactions that usually occur on the interface. However, several interesting and specific phenomena were observed with the carboranethiol derivatives. These molecules are more stable toward heating than their alkanethiol counterparts, and exhibit different behavior during heating. Also, they do not exhibit any decomposition upon X-ray irradiation. There was not any decomposition observed in the XP spectra even after heating to the temperatures of 400 °C. In comparison

with most of the organic compounds, they have rigid structures derived from an icosahedron. The precise thiolation of its vertices allows us to attach these molecules to gold flat film via either one or two vertices. Therefore, these rigid architectures can be used as potential building blocks for further molecular assemblies.

5 ACKNOWLEDGEMENT

We thank to Dr. Zbyněk Plzák for MS measurements. For financial support, we thank the Ministry of Education, Youth and Sports of the Czech Republic (grant no. LC06041) and the Grant Agency of the Academy of Sciences of the Czech Republic (grant nos. KAN400480701, 1ET400400413, and project nos. AVOZ40320502, AVOZ40400503).

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