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Mechanism of Surface Alkylation of a Gold Aerogel with Tetra-*n*-butylstannane-*d*₃₆:

Identification of Byproducts

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Abstract. The surface of gold aerogel behaves similarly as a gold layer on a flat substrate and is alkylated with *n*-butyl-*d*₉ groups upon treatment with a solution of tetra-*n*-butylstannane-*d*₃₆ under ambient conditions. Due to its large specific surface area, reaction byproducts accumulate in the mother liquor in amounts sufficient for GC-MS analysis. They are hexabutyldistannane-*d*₅₄, octane-*d*₁₈, butene-*d*₈, and (probably) butane-*d*₁₀, compatible with an initial homolytic dissociation of a C-Si bond on the gold surface, followed by known radical processes.

Introduction

The attachment of organic molecules to gold surface has been of considerable interest for a long time.^{1,2,3} The recent discovery that under ambient conditions solutions of alkylstannanes coat a flat surface of gold, mostly Au(111), with alkyl-containing monolayers,⁴ is significant for at least two reasons: (i) the resulting layers are distinct from those commonly produced by treatment with alkanethiols in their permeability and thermal and chemical stability,⁵ and (ii) direct carbon-to-gold attachment has much higher electrical conductivity than attachment through a sulfur atom.⁶ While methyl groups are not transferred from the tin atom to the Au surface, and ethyl groups only very slowly, propyl and longer alkyl groups are transferred efficiently.⁵ Similar solution alkylation processes do not proceed under ambient conditions with alkylsilanes,⁴ but they do take place with organomercurials RHgX .^{7,8}

The mechanism of gold surface alkylation with alkylstannane solutions under ambient conditions is not known, nor is the detailed nature of the attachment. The initial assumption was that a $\text{R}_3\text{Sn-CH}_2\text{R}'$ bond is cleaved, the R_3Sn moiety is attached to a surface Au atom or atoms, and the $\text{R}'\text{CH}_2$ - alkyl group is either lost to solution⁴ or attached to the Au surface as well,⁶ but more recent experiments with deuteriated alkylstannanes showed that under the ambient conditions used, this cannot be entirely correct. Although tin is codeposited with the alkyls, it does not appear as a trialkylstannyl group, but as tin oxide.⁵ In the one case in which the alkylation reaction order with respect to stannane concentration in bulk solution was determined,⁵ it was found to be 0.5, and it was suggested that two butyls may be transferred simultaneously in a way reminiscent of reductive elimination, and that the resulting stannylene R_2Sn or $\text{Sn}(0)$ atom is then oxidized by atmospheric oxygen, leading ultimately to the formation of tin oxides. This would be analogous to the Au surface alkylation by RHgX , which co-deposits elemental mercury.^{7,8} An investigation of the mechanism of benzylation with benzyltrimethylstannane under ultrahigh vacuum conditions led to the conclusion that $\text{C}_6\text{H}_5\text{CH}_2$ and $(\text{CH}_3)_3\text{Sn}$ groups are attached to the surface,⁹ in contrast to the findings in solution,

but the mechanisms could well be different in the two environments.

Although additional kinetic studies are clearly desirable, they alone are not likely to elucidate the mechanism of gold surface alkylation with stannanes. A determination of the nature of reaction byproducts would appear very useful. However, the amounts formed on a flat surface of an easily obtainable size are likely to be insufficient for a positive identification. Although we are aware of the risk that the reaction mechanisms on different facets of gold surface need not be the same, we believe that at least some initial guidance could be obtained from work on gold that has a large surface area. We were unable to find anhydrous conditions for the formation of small (2-3 nm diameter) gold nanoparticles protected by ligands well enough to prevent coagulation but not so well that alkylation with a stannane is inhibited (it appears that hydroxylic solvents interfere with the alkylation process).

The recent development of procedures for the preparation of noble metal aerogels,¹⁰ including gold aerogels,¹¹ offers an easier route. We have now investigated the reaction of tetra-*n*-butylstannane-*d*₃₆ (**1**) with a gold aerogel of a 50 m²/g surface area and report the results presently. The use of a perdeuteriated reagent allows an easy identification of reaction products in the presence of impurities derived from the ambient atmosphere and the solvent.

Results

When produced as reported, Au aerogel contains significant amounts of impurities, primarily chlorides, borates, and dopamine.¹¹ We found that immersion of a flat gold surface into an aqueous solution of any one of these contaminants does not interfere with subsequent reaction with (**1**), as judged by the appearance of a C-D stretching vibration peak in PM IRRAS.

When 10 mg of Au aerogel¹¹ are treated with 2 mL of a 44 mM solution of **1** in *n*-hexane for 24 hours and the solid is then twice stirred for an hour with 2 mL of fresh hexane and dried, its IR

spectrum (Figure 1) shows a distinct broad peak at 2213 - 2217 cm^{-1} in the C-D stretching region that was devoid of any peaks before the reaction with **1**. The peak is not removed by subsequent extraction with 300 mL of hexane in a Soxhlet apparatus for 3 days. The frequency of its maximum, 2215 cm^{-1} , is similar to the values 2219 - 2220 cm^{-1} reported⁵ for deuteriated *n*-butyl groups on flat gold surface treated with a solution of **1**. The TEM images of the aerogel before and after the treatment with **1** appear identical (Figure 2) and suggest that treatment with **1** did not change the surface area.

We conclude that deuteriated butyl groups are chemisorbed on the gold aerogel surface and were transferred there from the stannane, as in earlier experiments with flat gold surfaces.

In Figure 3, the GC trace of the recovered mother liquor is compared with that of the hexane solvent. In addition to peaks of **1** (retention time $t_r = 19.46$ min) and the *n*-hexane solvent ($t_r = 1.93$), which are off scale, and the occasionally present peak of $(n\text{-C}_4\text{D}_9)_3\text{SnCl}$ ($t_r = 16.13$), a known impurity in our sample of **1**, we observe small peaks due to ($t_r = 1.28$), pentanes ($t_r = 1.46, 1.51$), hexanes ($t_r = 1.74, 1.81$), and heptanes ($t_r = 2.38$) in both traces. The dominant isomers are the *n*-alkanes, identified by comparison of retention times and mass spectra with authentic samples. The mass spectra of these alkane impurities obtained in both runs are identical.

When hexane is replaced with hexane- d_{14} , the results are the same in both runs except that an additional GC peak appears at $t_r = 1.34$. From its high-resolution mass spectrum (HRMS), it contains no deuterium.

With certain batches of the aerogel, a peak at $t_r = 3.82$ appears and its MS spectrum shows a strong peak for C_7H_7^+ (with hexane- d_{14} , C_7D_7^+) suggesting that it is due to toluene (and toluene- d_8).

The intensity of this peak is not increased noticeably when *n*-heptane is used as the solvent or when it is added to the *n*-hexane solvent, and we have not examined it further.

Mass spectra of peaks that were absent in the GC of the pure solvent but appeared after contact with **1** are shown in Figure 4. HRMS and a comparison with GCMS of authentic samples permitted the identification of the new peak at $t_r = 4.18$ as *n*-octane- d_{18} (**2**) and the new peak at $t_r = 26.37$ as hexakis(*n*-butyl- d_9)distannane (**3**). The identification of C_4 products in these samples is difficult because of interferences with impurities and we have turned to chloroform as the solvent for this purpose. A treatment of the aerogel under identical conditions with a solution of **1** in $CHCl_3$ new peaks of **2** at $t_r = 4.18$, butene- d_8 (**4**) at $t_r = 1.37$, and at $t_r = 2.26$, all identified by HRMS, appear in the GC trace of the mother liquor, but the peak of **3** does not.

The MS of the peak at $t_r = 1.37$ strongly suggests the it contains a mixture of butene- d_8 and butane- d_{10} , which has been independently determined to have the same retention time.

Discussion

The byproducts **2** - **4** only form in the presence of both **1** and the aerogel, and not in the presence of the aerogel alone, suggesting that they form during the surface alkylation reaction and most likely are its primary byproducts, or have arisen from the further transformations of such byproducts. All three can be accounted for easily as resulting from a dissociation of a Sn-C bond of **1** upon contact with the gold surface to produce a radical pair, presumably at least initially physisorbed on the surface (indicated by the / sign):

This would be in keeping with the original mechanistic suggestions.^{4,6} Neither radical is likely to accumulate on the surface or in the solution above the surface, and their most likely modes of disappearance are bimolecular: the reversal of reaction (1) or dimerization (2) and disproportionation (3) of the surface-bound or free butyl radical **5**,

and dimerization (4) of the surface-bound or free stannyl radical **6**,

The processes (2) - (4) would be expected to compete with monomolecular reactions in which a physisorbed radical attaches covalently to the gold surface, possibly keeping its simple alkyl structure but possibly not,

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Reaction (5) is probably relatively facile and may be the main route to the observed alkylation of the gold surface. In contrast, against the original guesses, reaction (6) apparently occurs rarely or never, since trialkylstannyl groups are not found on the surface by spectroscopy. It is easy to imagine alternative fates for this species, such as reductive elimination of dibutylstannylene- d_{18} (**8**) with transfer of an alkyl to the surface (7), which offers an alternative main route to the observed surface alkylation

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The expected polymerization of the stannylene **8** would preclude its observation in the GCMS experiment. The stannylene **8** or the radical **6** would be a source of reactivity with oxygen, which needs to be invoked ultimately to explain the formation of tin oxides. The radical **6** would be likely to abstract a chlorine atom from chloroform and it is thus not surprising that the dimer **3** is not observed when the alkylation reaction is performed in this solvent.

The set of reactions (1) - (7) accounts for all of the definitely observed byproducts **2** - **4**, and also for the less secure formation of **7**. This reaction set is compatible with other observations that have been made. For instance, it is easy to believe that the smallest radicals, especially methyl,

would dimerize the fastest (reaction 2) and would be less likely to become covalently attached to the gold surface. As for the kinetic observations that have been made on di-*n*-butyldimethylstannane and showed an order of 0.5 with respect to bulk stannane concentration, we prefer not to speculate until byproduct analysis and kinetic analysis are available for the same set of stannanes.

Summary

Byproduct analysis of the alkylation of gold surfaces with tetra-*n*-butylstannane-*d*₃₆ is compatible with the proposal that the dissociation of a C-Sn bond upon contact with gold is the first step. However, it merely represents a beginning in what is likely to be a tortuous route toward a detailed mechanistic understanding of the process. Both byproduct and kinetic studies need to be extended to additional stannanes before a more convincing picture can emerge.

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