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EPR Study of a Place-Exchange Reaction on Au Nanoparticles: Two Branches of a Disulfide Molecule Do Not Adsorb Adjacent to Each Other

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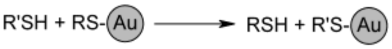
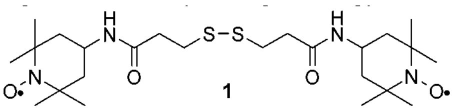
Here, we report a mechanistic study of a place-exchange reaction of a stable radical-functionalized disulfide on Au nanoparticles (NPs). EPR evidence suggests that the two branches of the disulfide molecule do not adsorb adjacent to each other on the Au surface. The reaction shows zeroth-order with respect to the disulfide concentration, indicative of a dissociative exchange mechanism.

Place-exchange reaction of thiols on the surface of NPs is a versatile method for preparation of functionalized supramolecular assemblies.[1] Detailed studies by R. W. Murray's group[2] revealed that this reaction is first-order with respect to the concentrations of both reagents (e.g., NPs and thiol). This led to the suggestion of an "S_N2"-type associative mechanism.[3]



We noticed that disulfides are also active in place-exchange reactions with some NPs protected by short-chain thiols. To investigate the mechanism of such exchange, we prepared a stable diradical disulfide 1[4] and monitored its interactions with *n*-butanethiol-protected NPs[5] by EPR spectroscopy.[1]



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The EPR spectra of nitroxide *monoradicals* show three lines due to the hyperfine splitting from the nitrogen nuclei. The EPR spectrum of a toluene solution of *diradical* **1**, however, shows five lines (Figure 1a), as the exchange interaction between the two unpaired electrons effectively couples each radical center to two nitrogen nuclei.[6]

Addition of diradical **1** to *n*-butanethiol-protected NPs leads to the gradual disappearance of the second and fourth lines and decreasing peak height of the fifth (high-field) line in the EPR spectra (Figure 1b).[7] The selective broadening of this high-field line (which results in decreased peak height) is caused by the slower tumbling of the radical adsorbed on the surface of NPs.[8]

The spectrum at the end of the reaction (Figure 1b) contains just three lines which apparently correspond to a *monoradical*. Double integration of the spectra in Figure 1b showed constant total intensity. This rules out decomposition of the radical in the course of reaction. The disappearance of the second and fourth lines in the EPR spectra suggests therefore that the two radical centers in disulfide **1** get *separated* during reaction.

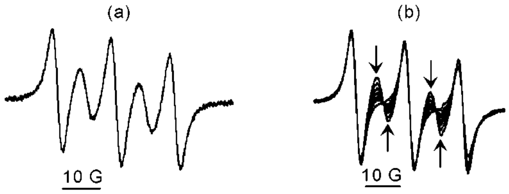

Figure 1. EPR spectra of (a) 0.1 mM solution of diradical **1** in toluene, (b) toluene solution of 0.2 mM diradical **1** and 0.2 mM *n*-butanethiol-protected Au nanoparticles taken at 0, 4, 8, 14, 21, 29, and 60 min after mixing. Peaks shown with the arrows decrease over time.

This result is completely unexpected. Adsorption of the intact molecule **1** on the surface should bring the radical centers closer to each other and should therefore lead to *increase* in the intensity of the second and fourth lines in the EPR spectrum. The *disappearance* of these peaks suggests that the S−S bond is broken during adsorption on the NPs[9] and the two branches of the disulfide molecule do not adsorb adjacent to each other on the Au surface.

To test if this phenomenon is specific to place-exchange reactions on thiol-protected NPs, we monitored the exchange of diradical **1** with NPs protected by other weakly bound ligands, viz., *n*-dodecylamine[10] and *n*-dodecylsulfide.[11] EPR spectra showed complete disappearance of the second and fourth lines immediately after mixing. This suggests that the separation of radicals during adsorption does not depend on the protecting ligand. We believe therefore that our data highlight generic features of the disulfide reactions at the Au surface.

The failure of the two branches of diradical **1** to adsorb close to each other on the surface of *n*-butanethiol-protected NPs can be explained by two possible mechanisms: (a) high mobility of the adsorbed branches on the surface, leading to fast diffusion of the two adsorbed radicals away from each other or (b) adsorption of only one branch during reaction, with another branch forming a mixed disulfide with the butanethiolate (leaving group). This mixed disulfide can participate in further place-exchange with NPs, so that both mechanisms result in adsorption of all radical on the Au surface at the end of the reaction.

To probe the validity of the mechanism b, we have isolated NPs from the reaction mixture at ca. 90% conversion by precipitation with methanol, and recorded the EPR spectra of both isolated NPs (Figure 2b) and methanol extract (Figure 2a). The high-field line in Figure 2b is substantially smaller than the other lines, consistent with the adsorption of the radical on the Au surface (vide supra*)*. Methanol extract, on the other hand, shows three lines of equal intensity, suggesting the presence of a monoradical in solution (presumably a mixed disulfide). The total signal intensity of the radical in methanol extract accounted for ca. 30% of the sample before separation, in an excellent agreement with the theoretical value assuming mechanism b is correct (see Supporting Information for

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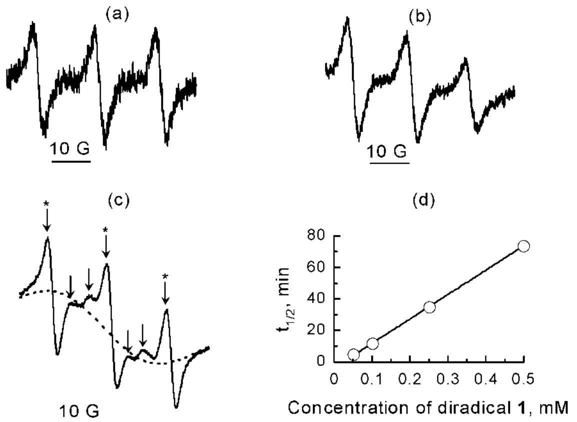


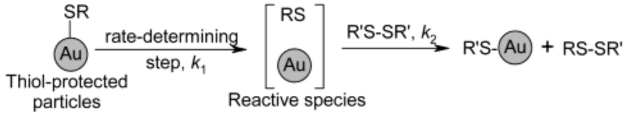
Figure 2. EPR spectra of (a) MeOH extract of the solution of 0.1 mM diradical **1** and 0.1 mM *n*-butanethiol-protected Au nanoparticles 200 min after mixing, (b) MeOH-insoluble residue (Au nanoparticles), (c) solution of 1 mM diradical **1** and 0.05 mM *n*-dodecylamine-protected Au nanoparticles (see text for more details). All spectra were recorded in toluene. (d) Plot of half-reaction time of the place-exchange reaction vs initial concentration of diradical **1** (concentration of Au particles 2 mM).

more details). To prove that formation of a monoradical is not due to a disproportionation reaction between diradical **1** and *n*-butane disulfide, we added a large excess of *n*-butane disulfide to a reaction mixture containing diradical **1** and *n*-butanethiol-protected NPs. EPR showed no change in the spectrum after 1 h, indicating that disproportionation does not take place under these conditions. The monoradical in the methanol extract must therefore be a byproduct of the place-exchange reaction. We believe these observations strongly support mechanism b, as mechanism a cannot explain the formation of a monoradical in solution (desorption of the monoradical during the place-exchange reaction is highly unlikely as adsorbed *n*-butanethiol is in large excess to the adsorbed radical).[7]

Although reaction of NPs with the equivalent amount of diradical **1** produces low coverage of *isolated* monoradicals on the Au surface, reaction with excess diradical **1** leads to a higher density of monoradicals on the surface, thus making it possible to observe their interactions with each other. Figure 2c shows the EPR spectrum of a reaction mixture containing 1 mM diradical **1** and ca. 0.05 mM dodecylamine-protected NPs. The spectrum reveals the presence of some adsorbed radicals strongly interacting with the surrounding adsorbed radicals (which account for a very broad peak schematically shown with a dotted line), some isolated *pairs* of monoradicals weakly interacting with each other, which produce a complicated pattern (shown with arrows in Figure 2c), and possibly some isolated radicals (overlapping peaks shown with asterisks). The spectral pattern of diradicals is determined by the J/a_N ratio (J is the exchange integral and a_N is the coupling constant). J strongly depends on the distance between the radical centers. The complicated pattern in Figure 2c (shown with arrows) corresponds to $J \approx 2a_N$ and was, for instance, observed for a rigid diradical with the 10 Å distance between radical centers.[12] The sensitivity of the spectral pattern to the distance between the radicals illustrates the potential of EPR spectroscopy in determining the structure of supramolecular assemblies.

Further details about the mechanism of exchange reaction can be obtained from kinetic measurements. We studied the rate of the place exchange of 0.2 mM *n*-butanethiol protected NPs with different concentrations of diradical **1**. The rate profiles were obtained by monitoring the disappearance of the second line of the EPR quintet signal. Interestingly, plot of half-reaction time versus concentration showed a straight line, indicating a zeroth-order reaction with respect to the concentration of diradical **1**.

Scheme 1. Proposed Mechanism of the Place-Exchange Reaction



The zeroth order of the exchange reaction suggests that the rate-determining step is dissociation of the leaving group (butanethiolate) from the surface of the NPs. The possibility of such dissociative, "S_N1"-type process has been discussed in the literature but never observed experimentally.[3] This mechanism is consistent with the observed reactivities of various ligands: both *n*-dodecylamine and *n*-dodecylsulfide protected particles (weak ligands) react very fast, *n*-butanethiol protected particles (stronger ligand) react more slowly, while *n*-octadecanethiol protected particles (strong ligand) do not undergo place exchange with disulfide **1** at all.

Scheme 1 shows the most likely mechanism of the place-exchange reaction consistent with all our observations. To explain the formation of mixed disulfides during the reaction (Figure 2a), we must assume that the rate-determining step includes desorption of a single thiolate group (as opposed to disulfide). It is not clear at this stage what is the composition of this reactive species; it could be a physisorbed thiolate anion.

In conclusion, we have found that weakly bound ligands (e.g., short-chain thiolates, amines, sulfides) can be partially replaced from the surface of Au nanoparticles by disulfides. The exchange reaction shows zeroth-order with respect to the adsorbing disulfide. Interestingly, the two branches of the disulfide molecule do not adsorb close to each other on the surface of Au particle.

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Supporting Information Available: Kinetic model of the proposed mechanism (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Nanoparticle: diradical molar ratio was ca. 1:1 which corresponds to at least 100: 1 *n*-butanethiol: diradical ratio, as each Au nanoparticle has >100 alkanethiol groups adsorbed on the surface (see ref 3). Reactions were carried out at room temperature. EPR spectra were recorded on a Bruker ESP300 instrument. Typical acquisition parameters: mod. frequency 100 kHz, mod. amplitude 0.05 mT, power 5 mW.
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