Nanoparticles

Radical Mechanism of a Place-Exchange Reaction of Au Nanoparticles**

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The exchange reaction shown in Equation (1) is a convenient method to prepare functionalized metal nanoparticles, and its

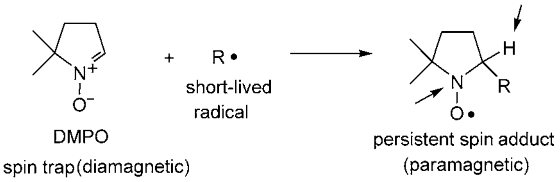
$$\text{Au}\,S{-}R + HS{-}R' \longrightarrow \text{Au}\,S{-}R' + HS{-}R \qquad (1)$$

mechanism has been studied by several research groups.[1–3] Murray and co-workers carried out detailed kinetic studies on the exchange of thiol-protecting groups on Au particles with other thiols.[4,5] The exchange was shown to be an associative (bimolecular) process, with both the incoming ligand and Au nanoparticles participating in the rate-determining step. As well as by evidence from kinetic studies, this mechanism is supported by the sensitivity of the place-exchange reaction to the electronic effects of the incoming ligand. The fact that the reaction is facilitated under oxidizing conditions, for example, in an electrochemical cell or in the presence of oxygen, is particularly intriguing.[6] To explain the apparent catalytic effect of oxidizing reagents, it was tentatively proposed that Au^I thiolates could act as reaction intermediates.

Recently, we applied a spin-labeling method to study an exchange reaction with disulfides.[7] We found with EPR spectroscopy that Au nanoparticles protected with weakly bound ligands (for example, phosphines or amines) undergo a rapid place-exchange reaction with disulfides. The S–S bond in the disulfide is broken during the reaction, and the two branches of the disulfide molecule do not adsorb adjacent to each other on the Au surface.[7,8]

We noticed, however, that although spin-labeled disulfides are very stable under exchange-reaction conditions, the EPR signal of the parent (spin-labeled) thiol decays rapidly during the reaction. The apparent destruction of the spin label (a nitroxide group) is most likely brought about by a redox reaction that involves either Au ions or organic free radicals. To detect the possible formation of free radicals during the exchange reaction of triphenylphosphane-protected Au nanoparticles with alkanethiols, we performed a series of EPR spin-trapping experiments.

The spin-trapping technique used in this study relies on the fast addition (trapping) of short-lived radicals to the diamagnetic spin trap DMPO (5,5-dimethyl-4,5-dihydro-3*H*-pyrrole-*N*-oxide). The product of such an addition is a persistent free radical, with a lifetime that is long enough that it can be detected by direct EPR measurements (Scheme 1).[9]



Scheme 1. Spin trapping of short-lived radicals by DMPO.

An important feature of the DMPO spin adducts is the sensitivity of the hyperfine coupling constants of the unpaired electron in the adduct with the hydrogen and nitrogen atoms (shown by arrows in Scheme 1) to the chemical composition of the short-lived radical. The EPR spectra of the spin adducts, therefore, provide useful information about the structure of the original radical.

In a typical spin-trapping experiment, a solution of *n*-butanethiol (2.5×10^{-3} M) in toluene/CH_2Cl_2 (4:1, *v*/*v*) was added to a mixture of triphenylphosphane-protected Au nanoparticles ($1.25–10\times10^{-4}$ M) and DMPO ($1.25–5\times10^{-2}$ M) in the same solvent mixture. The formation of spin adducts in the reaction mixture was monitored by EPR spectroscopic analysis.

A strong EPR signal was observed immediately after mixing (Figure 1a). Analysis of the hyperfine splitting allowed us to assign its structure to the spin adduct of DMPO and butanethiol radical $C_4H_9S^•$ (Table 1). The spectrum was also identical to that of an authentic spin adduct

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Figure 1. EPR spectra of DMPO–SC_4H_9 spin adducts a) trapped during the exchange reaction of triphenylphosphane-protected Au nanoparticles with butanethiol and b) prepared by the oxidation of butanethiol with PbO_2 in the presence of DMPO.

Table 1: EPR hyperfine coupling constants (G) of the DMPO spin adducts in toluene/CH_2Cl_2 (4:1, v/v).

	a_N [G]	$a_{H(1)}$ [G]	$a_{H(2)}$ [G]
DMPO–SC_4H_9	13.69[a] (13.73)[b]	11.69[a] (11.71)[b]	–
DMPO–OOC_4H_9	12.85[a] (12.72)[c]	9.31[a] (9.36)[c]	1.53[a] (1.44)[c]
DMPO–H	14.88[a] (14.83)[b]	19.32[a] (19.27)[b]	19.32[a] (19.27)[b]

[a] Observed during exchange reaction. [b] Observed on oxidation with PbO_2. [c] Previously reported values (toluene).[9]

DMPO–SC_4H_9 prepared by the oxidation of butanethiol with lead dioxide (Figure 1, Table 1). The exact amount of the spin adduct formed varied, but double integration of the EPR spectra revealed that the amount of the spin adduct accounted for 3–12 % of the amount of butanethiol used in the reaction. Importantly, no EPR signal was observed if the reaction was carried out in the absence of oxygen (for example, in an argon atmosphere).

As well as by the trapping of free radicals, the spin adducts can sometimes form by two alternative reactions,[10,11] namely, the Forrester–Hepburn mechanism (nucleophilic addition followed by oxidation) and the Eberson mechanism (inverse spin-trapping; Equations (2) and (3), respectively).

$$\mathrm{DMPO} + \mathrm{Nu}^- \rightarrow \mathrm{DMPO{-}Nu}^- \xrightarrow{\mathrm{ox}} \mathrm{DMPO{-}Nu}^{\cdot} \qquad (2)$$

$$\mathrm{DMPO} \xrightarrow{\mathrm{ox}} \mathrm{DMPO}^{+\cdot} \xrightarrow{\mathrm{Nu}^-} \mathrm{DMPO{-}Nu}^{\cdot} \qquad (3)$$

To test if the spin adducts are formed by the reaction given in Equation (2), we studied the nucleophilic addition of butanethiol to the DMPO spin trap under exchange-reaction conditions. NMR spectroscopic experiments showed the absence of a Michael addition on the reaction timescale. The Eberson mechanism can also be ruled out, as we observed no EPR signal with a control reaction mixture of the DMPO spin trap with Au nanoparticles in the presence of oxygen. This lack of a signal implies that the spin trap can not be oxidized under the reaction conditions.

We conclude, therefore, that the observed spin adducts are formed by trapping of the parent short-lived radicals formed during the exchange reaction. As the relative amount of the observed spin adduct was quite high (up to 12 % of the added alkanethiol, see above), the radical pathway must play a key role in the mechanism of the exchange reaction.

A likely route to $RS^{\cdot}$ radicals is the Au-nanoparticle-catalyzed oxidation of RSH with molecular oxygen. This mechanism is consistent with the fact that no radicals are formed when the exchange reaction is carried out in an inert atmosphere, and with reports that exchange reactions are significantly slower in the absence of air (confirmed by our own control experiments with alkanethiols and triphenylphosphane-protected Au nanoparticles). The oxidation of thiols is further supported by the formation of alkane disulfides (as observed by NMR spectroscopic analysis) when the exchange reaction is carried out in the absence of the spin trap.

To test the feasibility of such a mechanism, we set out to explore whether Au nanoparticles can catalyze the air oxidation of organic compounds. Indeed, the addition of *tert*-butyl hydroperoxide or sodium borohydride to a mixture of phosphine-protected Au nanoparticles and DMPO in air led to intense EPR spectra of the corresponding spin adducts of DMPO with $t\mathrm{BuOO}^{\cdot}$ and $\mathrm{H}^{\cdot}$ radicals (Figure 2). The structure of the $\mathrm{H}^{\cdot}$ adduct was confirmed by comparison with an authentic radical generated by the oxidation of $NaBH_4$ with PbO_2 (Figure 2, Table 1). The peroxide adduct was identified by comparison with previously reported data (Table 1).[9] No radicals were detected in the absence of Au nanoparticles or air. These experiments confirmed the oxidizing power of the mixture of Au nanoparticles and air.

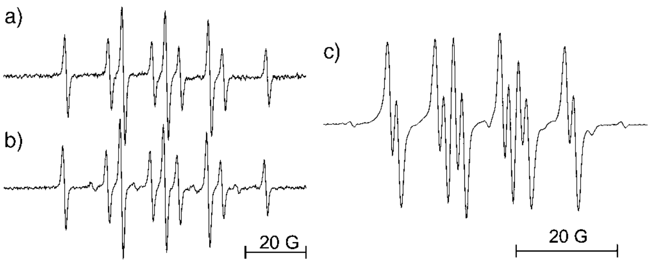
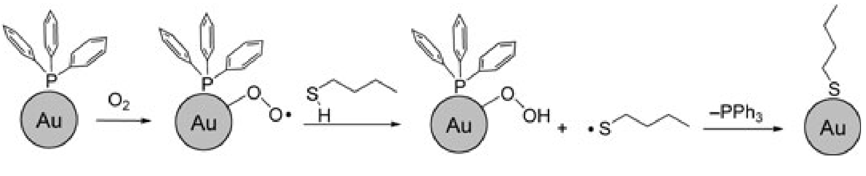


Figure 2. EPR spectra of the spin adducts DMPO–H produced by a) Au-nanoparticle-catalyzed oxidation of BH_4^- with air and b) oxidation of BH_4^- with PbO_2. c) EPR spectrum of DMPO–OO*t*Bu produced by nanoparticle-catalyzed oxidation of *t*BuOOH with air.

On the basis of our findings, we propose a mechanism for the exchange reaction (Scheme 2). The reaction starts with the adsorption of oxygen on the phosphine-protected nanoparticle surface to form an active catalyst. This superoxide-type species then abstracts a hydrogen atom from the incoming ligand (alkanethiol) to form a sulfur-centred radical, which is then successfully trapped with DMPO. We speculate that in the absence of the spin traps, the sulfur-centred



Scheme 2. Proposed mechanism of radical formation.

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radicals rapidly replace the outgoing ligands (triphenylphosphane) from the Au surface.

This mechanism is consistent with several features of previously reported exchange reactions.[12,13] Meisel and co-workers described the oxidation of 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (4-amino-tempo) to 4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl (4-oxo-tempo) with Au nanoparticles in the presence of oxygen.[14] The authors proposed that this reaction included Au nanoparticle mediated electron transfer from the NH_2 group to oxygen (to form a hydroperoxide radical), in a similar process to the mechanism given in Scheme 2. The electrocatalytic reduction of oxygen on Au nanoparticles was also reported by Murray and co-workers.[15]

Interestingly, we were unable to trap free radicals when the exchange reaction was carried out with thiol-protected Au nanoparticles. This failure to trap radicals could result from a number of factors, including the relatively slow kinetics of exchange reactions that involve thiol-protected nanoparticles, or the reduction of radicals by the outgoing ligand. There is, however, some indirect evidence for the involvement of free radicals in the reactions of thiol-protected Au nanoparticles, for example, the suppression of the exchange reaction in the absence of oxygen, the destruction of the nitroxide spin labels during the exchange of thiols with Au nanoparticles, and the oxidation of 4-amino-tempo (see above). It is, therefore, likely that at least some features of the proposed mechanism are quite general and not restricted to the phosphine-protected nanoparticles.

In conclusion, we have shown that the exchange reaction of phosphine-protected Au nanoparticles with alkanethiols in air proceeds by a free-radical pathway. Oxidation of the alkanethiols by molecular oxygen adsorbed on the nanoparticles is proposed as the key step in these reactions. The feasibility of such a reaction is demonstrated by the Au-nanoparticle-catalyzed oxidation of BH_4^- and *t*BuOOH with air.

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