

**The Effects of Delocalization upon Electron Transfer
Rates of Gold Monolayer Protected Clusters**

Ben Hahn and David Clifffel

Department of Chemistry, Vanderbilt University
Station B 351822, Nashville, TN 37235

INTRODUCTION

Over the past decade, gold monolayer protected clusters (MPCs) have been gaining attention in the literature due to their unusual electrochemical properties(1) resulting from their nanoscale dimensions, stability to air, and the relatively simple method of preparation (2,3). MPCs are three dimensional self-assembling monolayers (SAMs) consisting of a ligand reduced onto a metal core. Radii of gold cores are typically reported within the range of 1.0-3.0 nm (2-4). Unlike their 2-dimensional self-assembled thiols on flat Au, MPCs can be easily characterized with traditional analytic techniques including TEM, TGA, UV-Vis spectrophotometry, and proton NMR spectrometry. Moreover, properties of MPCs can be varied as a function of the ligand type, core type, core size, ligand-to-metal synthetic ratio, temperature, etc (2-5). Suggested future applications of MPCs rest in fields such as molecular electronics, drug-delivery, and catalysis.

In light of the aforementioned possibilities, it is desirable to know how the structural effects of the ligand alter the electron transfer rate into the cluster. With respect to the classical rules of chemistry, some assumptions must be made. It must be presumed that electrons move faster through shorter distances than longer distances, that electrons move faster through delocalized systems than saturated systems, and that conjugated molecules are rigid while saturated molecules are flexible. The difference in distance between the length of a double bond and a single bond will be considered negligible. With these assumptions in mind, the purpose of this experiment will be to compare the electron transfer rates of two different gold MPCs, one with a rigid, aromatic thiophenol (PhS) monolayer and the other with a flexible, saturated cyclohexyl mercaptan (C6S) monolayer.

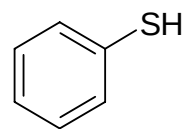
EXPERIMENTAL PROCEDURE

Thiophenol and cyclohexyl mercaptan MPC preparation was adapted from the method outlined in the Schiffrin synthesis (7). H-NMR, TGA, TEM and UV-Vis were used to characterize the clusters before the scanning electrochemical microscopy analysis with a 10 micron platinum electrode. The SECM approach curves give kinetic information about the electron transfer rates into MPCs as a function of monolayer composition.

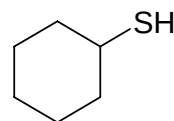
DISCUSSION

Analytical data received thus far indicates that the adapted synthetic route mentioned earlier yields small, relatively monodisperse MPCs. This is encouraging because smaller cores will have larger percent ligand coverage resulting in higher quantities of ligand adsorbed per gold core (3,4). Longer stir times would be ideal, but the literature(6), confirmed by personal observation, indicates that the arenethiolate thiophenol MPC shows questionable long-term stability in solution (6). The electron transfer rates of these MPCs have not yet been determined; further analytical tests and electrochemical

studies are pending.



Thiophenol



Cyclohexyl mercaptan

Scheme 1. Comparison of Electron Transfer Rates for Metal Nanoparticles with different monolayer coatings.

ACKNOWLEDGEMENTS

Much thanks to Rachel Peterson and Dr. Sven Eklund for their advice and assistance. Also, the experimenter appreciates the help of Aren Gerdon for assisting with TEM studies.

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