In Situ Identification of Intermediates of Benzyl Chloride Reduction at a Silver Electrode by SERS Coupled with DFT Calculations

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Abstract: Aiming to deeply understand the electrocatalytic mechanism of silver on reduction of benzyl chloride, we carried out an in situ electrochemical surface-enhanced Raman spectroscopic study to characterize various surface species in different electrode potential regions. A further analysis with DFT calculation reveals that the benzyl radical and its anionic derivate bonded on a silver electrode are the key intermediates, implying that the pathway could drastically differ from the outer sphere concerted electron reduction at inert electrodes.

Characterization of reaction mechanisms and intermediates of complex chemical reactions is a central topic in organic chemistry, catalysis, electrochemistry, polymer chemistry, toxicology, biology, etc.[1] In this context, the electrochemical reductive cleavage of carbon−halogen bonds at inert electrodes has played an important role in electroorganic synthesis, environmental applications, and electron transfer mechanisms.[2] Recent works evidenced that silver (Ag) cathodes possess surprisingly high electrocatalytic activity toward these reactions.[3−6] However, voltammetric data alone, lacking *in situ* characterization of transient surface intermediates, could not help unravel the exact origin of this strong catalysis by Ag.

On the other hand, surface-enhanced Raman spectroscopy (SERS) is a powerful *in situ* technique for probing the existence of transient surface species,[7] especially when coupled with density functional theory (DFT). So far, the combined SERS-DFT studies on electrochemical systems are very limited[8] and the majority focused on electrosorption behavior in aqueous solution. Herein, we report the first SERS-DFT study on electrochemical reduction of benzyl chloride ($PhCH_2Cl$) at a Ag electrode in acetonitrile (CH_3CN). The result reveals that the electrocatalytic reaction proceeds from a weakly adsorbed $PhCH_2Cl$ to benzyl intermediates bound strongly to the Ag surface.

Figure 1a shows cyclic voltammograms (CVs) of 5 mM $PhCH_2Cl$ at a Ag electrode, exhibiting a single irreversible reduction peak with a peak potential of $E_p = -1.82$ V vs SCE at 0.5 V/s ($\alpha \approx 0.3$).[4−6] As already reported, the voltammetric behavior was then quite similar to that observed at inert glassy carbon electrodes[2a] except for the remarkable positive shift by ca. 0.5 V of the CV peak.

To observe the presence of key surface intermediates possibly generated during the Ag-electrocatalyzed process[3b] and characterize

them at the molecular level, SERS spectra were recorded at different potentials spanning the voltammetric wave range from −0.6 to −2.2 V vs SCE (Figure 1b). At potentials positive to −1.2 V, the spectral features resembled that of free $PhCH_2Cl$ though a few significant changes indicated a weak interaction between benzyl chloride and the silver surface (see Supporting Information). When the cathode was held at ca. −1.2 V, the SERS spectrum changed dramatically. A strong and broad peak appeared at *ca.* 800 cm^{-1} and reached its maximum intensity at −1.4 V. This indicates that new species formed at (or near) the surface as soon as the electrochemical reduction occurred at a significant rate. A second drastic spectral change happened when the potential was set beyond −1.6 V. A peak grew gradually at *ca.* 1000 cm^{-1} and reached its maximum at −1.8 V, i.e., when the voltammetric peak was displayed. This new peak then is most likely due to the final reaction product(s) adsorbed at the surface, its decay indicating a progressive desorption at more negative potentials. This sequence of specific SERS features reflects the presence in each potential range of possibly important reaction intermediates or product(s).

Two distinct spectral features were observed at potentials around −1.4 V (Figure 1b). The first one was a broad peak centered at 350 cm^{-1} that could be assigned to Ag−C stretching bands, indicating that at least one reaction intermediate was strongly bound to the surface via a C−Ag bond. Since a halide anion is one necessary product of any two-electron reduction sequence at a silver electrode,[2−6] previous works hypothesized that their known interaction with silver surface cathodes may play a significant role in the overall catalytic effect.[3,4,9] However, the characteristic potential dependent Ag−Cl vibration band at approximately 230−240 cm^{-1} could not be observed in this work,[10] showing that under our conditions the chloride ion did not bind appreciably. This presumably reflects competition by other species (see below), probably reinforced by the strong electrostatic repulsion from negatively charged surfaces.[9]

A second remarkable feature consisted of an intense and unusually broad peak at ~800 cm^{-1}. To the best of our knowledge, no one has acquired surface-enhanced Raman data relevant to the $PhCH_2Cl$ reduction. Owing to the many possible reaction pathways and intermediates which could be envisioned, we relied on DFT to unambiguously identify the corresponding surface species.[11]

Figure 2 presents DFT simulated spectra (see Supporting Information for methods) for the free benzyl radical and benzyl anion whose formation could be hypothesized based on the final electrolysis products (see below)[5] and compares them to the spectra predicted for the same species bound to the Ag surface as well as to the experimental spectrum. The simulated spectra of the bound benzyl moieties displayed strong and characteristic bands between

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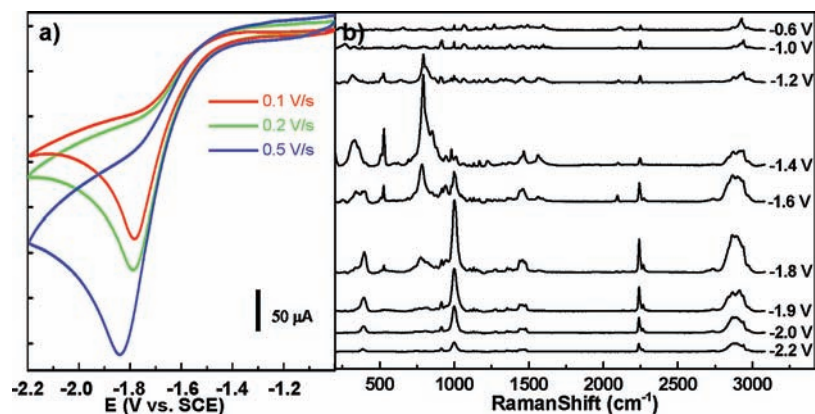‡ Università degli Studi di Milano.
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Figure 1. (a) CV of 5 mM PhCH$_2$Cl in 0.1 M TEAP + CH$_3$CN at a Ag electrode with different scan rates. (b) Potential dependent SERS spectra of PhCH$_2$Cl on a Ag electrode.

850 and 900 cm^{-1} which were absent for the free species. Furthermore, a superposition of the simulated spectra of the bound benzyl moieties, as illustrated in Figure 2f, shows that the overlap of the bands affords a broad peak which is quite similar to the experimental one (Figure 2c). Additionally, other bands such as the ones at ca. 530 and 1200 cm^{-1} were also successfully predicted for the bonded benzyl species (see Supporting Information for detailed assignment of all bands). This indicates that both neutral and anionic benzyl-silver adducts were formed, the anionic species being the dominant one over the main voltammetric wave potential range.
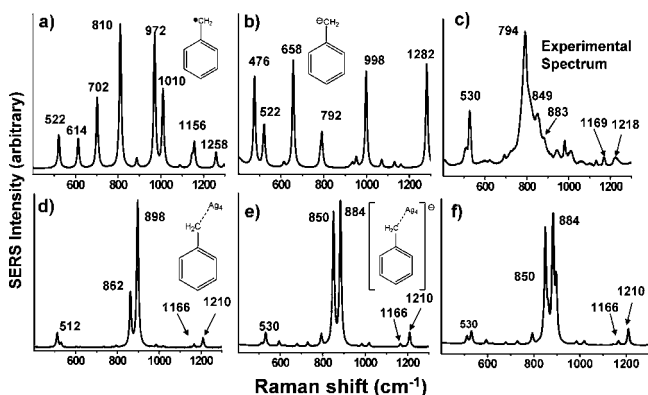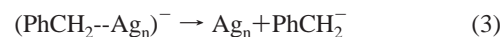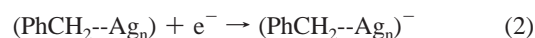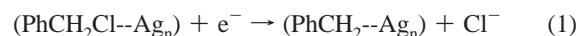

Figure 2. DFT calculated Raman spectra of the possible solvated reaction intermediates: (a) free benzyl radical, (b) free benzyl anion, (d) benzyl radical-Ag$_4$ adduct, (e) benzyl anion-Ag$_4$ adduct. These are compared with the experimental SERS spectrum at −1.4 V vs SCE (c) and a 1:5 superposition of the predicted spectra in d and e (f).

The same strategy was used to analyze the spectrum at −1.9 V. According to reported electrolyses,[5] reduction of benzyl chloride at a silver electrode yields toluene and 3-phenylpropanenitrile as the major products. Comparison of DFT-simulated and experimental spectra established that 3-phenylpropanenitrile was formed in a silver-bound state (see Supporting Information for details). Toluene presence could not be characterized by SERS, though formation of toluene is a necessary step on the route to 3-phenylpropanenitrile.[5] This indicates that toluene was not prone to interact sufficiently with the negative silver surface to provide a significant SERS signature.

The above integrated SERS and DFT study provides important mechanistic information, revealing that the catalytic property of silver cathodes stems from the fact that they involve reduction of benzyl chloride weakly adsorbed on the silver surface so as to yield

directly or ultimately a bound benzyl radical and then the bound benzyl anion. Desorption of the benzyl anion should then lead to the final products. Such a pathway drastically differs from the outer sphere concerted electron reduction at inert electrodes[2] and, hence, modifies the thermodynamics and kinetics of the first reduction stage. Such important mechanistic changes must then be responsible for the important anodic shift of the voltammetric wave at silver electrodes. A thorough kinetic and thermodynamic investigation of the mechanistic features outlined here requires quantitative predictions of adsorption energies of all surface species and their cross-comparison with electrochemical data. This work is currently in progress using DFT.[12]

$$(PhCH_2Cl\text{--}Ag_n) + e^- \rightarrow (PhCH_2\text{--}Ag_n) + Cl^- \quad (1)$$

$$(PhCH_2\text{--}Ag_n) + e^- \rightarrow (PhCH_2\text{--}Ag_n)^- \quad (2)$$

$$(PhCH_2\text{--}Ag_n)^- \rightarrow Ag_n + PhCH_2^- \quad (3)$$

$$PhCH_2^- \rightarrow products \quad (4)$$

In summary, combining SERS and DFT has afforded crucial *in situ* molecular entities, revealing the presence of unexpected key surface intermediates underlying the strong electrocatalytic properties of silver electrodes. Although metals with intrinsically high SERS activity are limited to gold, silver, and copper, mechanisms involving various inactive or weakly active metals such as iron, cobalt, nickel, platinum, palladium, etc. may also be investigated using core−shell nanoparticles. This strategy allows the outer metallic layer to "borrow" SERS activity from the SERS active core so as to yield enhancement factors up to 10^4 or 10^5 at the surface of the shell.[13] Hence, SERS may be used to gather *in situ* mechanistic information in many areas where strong interaction between reactants and catalytic metal surfaces are important, such as organic chemistry, catalysis, polymer chemistry, toxicology, astrochemistry, etc.

Supporting Information Available: Experimental procedures, detailed molecular configuration and assignment of the peaks in the spectra, discussion of the products, complete ref 11. This material is available free of charge via the Internet at http://pubs.acs.org.

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