

FACTORS THAT INFLUENCE THE REDUCTION OF ORGANIC HALIDES AT SILVER CATHODES

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Reduction of ω -halo-1-phenyl-1-alkynes at silver cathodes has demonstrated that (a) preference for intramolecular cyclization depends on the identity of the halogen and on the chain length of the alkyne and (b) that dimer formation depends on the dryness of the solvent–electrolyte, namely, dimethylformamide (DMF) containing 0.050 M tetramethylammonium perchlorate (TMAP).¹ This work, in combination with research by Rondinini and associates² and by Isse and co-workers^{3–5} with silver electrodes, has inspired us to investigate how (i) position (primary, secondary, and tertiary) and identity of the halogen, (ii) cleaning procedure for the silver, and (iii) dryness of the solvent–electrolyte influence adsorption and reduction of various organic halides at silver.

Cyclic Voltammetry

Comparison of cyclic voltammograms for the reduction of 1-halodecanes and cyclohexyl halides in undried DMF–0.050 M TMAP at a scan rate of 100 mV s⁻¹ reveal two cathodic peaks for both iodides, one clear cathodic peak for both bromides, and a shoulder or hump immediately prior to electrolyte breakdown for both chlorides. Interestingly, despite the appearance of two cathodic peaks for reduction of both 1-iododecane (**1**) and cyclohexyl iodide (**2**), the two cyclic voltammograms are dramatically different (Figure 1).

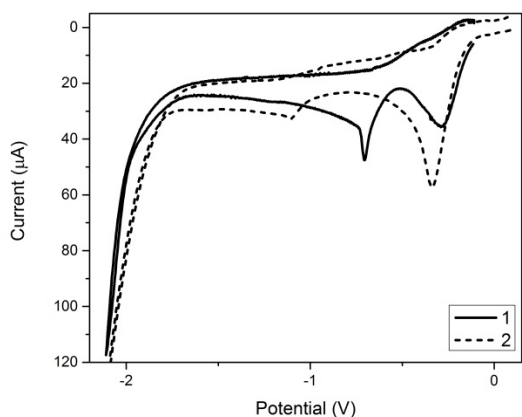


Figure 1. Voltammograms recorded at 100 mV s⁻¹ for reduction of 2.0 mM 1-iododecane (**1**) and cyclohexyl iodide (**2**) at silver in DMF containing 0.050 M TMAP. Potentials are with respect to a saturated cadmium amalgam reference electrode whose potential is -0.76 V vs. SCE.¹

For **1**, the second cathodic peak is approximately the same height, but much sharper, than the first peak. A typical peak width ($E_{p/2} - E_p$) for an irreversible process is 47.7/ α mV; the width of the second cathodic peak of **1** was measured to be 40 mV, thus

indicating adsorption–desorption phenomena. On the other hand, a cyclic voltammogram for **2** at 100 mV s⁻¹ shows a second cathodic wave that is relatively small and not narrow. Peak widths for the brominated and chlorinated analogues of **1** and **2** do not suggest adsorption.

Controlled-Potential Electrolysis

Several cleaning procedures for silver cathodes were investigated to determine if the method used to clean a silver mesh cathode affects the product distribution for a controlled-potential (bulk) electrolysis: (a) rinsed with distilled water and oven dried; (b) rinsed with distilled water, sonicated in sodium bicarbonate, rinsed again, and oven dried; and (c) procedure (b) then rubbed with emery paper, rinsed with DMF, and oven dried. Product yields were identical within experimental error ($\pm 10\%$) for each cleaning method; however, the time for completion of electrolyses was significantly longer for procedure c.

Efficacy of these cleaning methods was further investigated by means of scanning electron microscopy (SEM). A newly fabricated silver mesh electrode imaged before electrolysis of **1**, and then compared to the same electrode imaged after reduction of **1** and subjected to cleaning procedure b, showed no evidence of unremoved adsorbates.

Bulk electrolyses at silver electrodes (cleaned by means of procedure b) of 1-iodo-, 1-bromo-, and 1-chlorodecane and of cyclohexyl iodide, bromide, and chloride in undried DMF–0.050 M TMAP reveal that dimer formation depends on the position and identity of the halogen. Reductions of **1** were performed at two different potentials to probe each cathodic peak by means of bulk electrolysis; these experiments revealed that the potential also plays a role in the yield of dimer. Coulometric n values for reduction of **1** at the two different potentials suggest a one-electron pathway; however, electrolyses performed in the presence of 100-fold excess of deuterium oxide resulted in 10% and 46% incorporation of deuterium ions at the first and second reduction potential, respectively.

References

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