113a Enantioselective Surface Chemistry of Chiral Alkyl Bromides on Naturally Chiral Copper Surfaces

David M. Rampulla and Andrew J. Gellman

Enantioselective reactions are integral to most biological chemistry and large-scale pharmaceutical production. Enantioselective reactions require chiral media such as solvents, surfaces, or catalysts of a single handedness. Enantioselective heterogeneous catalysis is a promising method for the preparation of chiral compounds but requires catalytic surfaces with inherently chiral structure. The stepped and kinked high index Miller surfaces of metals are naturally chiral and have been shown to interact enantiospecifically with chiral adsorbates. Enantioselective desorption of small chiral molecules from such surfaces has been demonstrated and studied, but enantioselective reactivity on naturally chiral metal surfaces has only been explored in a cursory manner.

The enantioselective surface chemistry of two similar, yet structurally different chiral alkyl halides (R-2-bromobutane and S-1-bromo-2-methylbutane) was studied on two different chiral copper surfaces (Cu(643)$^{R\&S}$ and Cu(531)$^{R\&S}$). A molecularly adsorbed alkyl halide can desorb intact or decompose by debromination to form an alkyl group bonded to the surface. The alkyl group can decompose further by β-hydride elimination to form an olefin or hydrogenate to form an alkane. Temperature Programmed Desorption (TPD) was used to quantify the yields of the various reaction products. At low coverages of R-2-bromobutane on both Cu(643) and Cu(531) the surface chemistry is not enantioselective. Also, at low coverages of S-1-bromo-2-methylbutane on Cu(643) the surface chemistry is not enantioselective. At monolayer coverage, however, the product yields indicate that the reactions of both alkyl halides are sensitive to the handedness of the two chiral surfaces.

Initially, the impact on enantioselectivity was measured, when the structure of the chiral surface was changed. R-2-bromobutane was studied on Cu(643) and Cu(531). The yields of R-2-bromobutane (from molecular desorption) and R-2-butyl group (from debromination) are sensitive to the chirality of the surface, upon which R-2-bromobutane is adsorbed. The selectivity between desorption and debromination differs significantly from Cu(643) to Cu(531). The yields of butene (from β-hydride elimination) and butane (from hydrogenation) are sensitive to the chirality of the surface, upon which the chiral R-2-butyl group is adsorbed. Although enantioselectivity is detected, the selectivity between β-hydride elimination and hydrogenation does not differ significantly from Cu(643) to Cu(531).

Secondly, the impact on enantioselectivity was measured, when the chiral center of the molecule was moved relative to its reactive center. R-2-bromobutane and S-1-bromo-2-methylbutane were studied on Cu(643). The reaction yields of R-2-bromobutane and S-1-bromo-2-methylbutane also show that reactions, in which the reaction centers coincide with the chiral centers, exhibit greater enantiospecific behavior than reactions, in which the reaction centers are adjacent to the chiral centers.