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Tracking and Removing Br during the Bottom-Up Synthesis of a Graphene Nanoribbon CHRISTOPHER BRONNER, University of California, Berkeley, JONAS BJÖRK, Linköping University, PETRA TEGEDER, Ruprecht-Karls-Universität Heidelberg — Thermally induced, two-step bottom-up synthesis from halogen-substituted molecular precursors adsorbed at metal surfaces is an intriguing concept for obtaining graphene nanoribbons with well-defined edge structure and widths on the nanometer scale. The reaction pathways of the dissociated Br atoms have so far not been in the focus of research although they may very well interfere with the on-surface synthesis. Using temperature-programmed desorption we show that Br leaves the surface as HBr in an associative desorption process during the second reaction step, the cyclodehydrogenation. Density functional theory is employed to compare this process to the competing desorption of molecular hydrogen and furthermore shows that prior to desorption, Br is submerged under the three-dimensional intermediate reaction product, polyanthrylene. Upon exposure of this intermediate co-adsorbate to an atmosphere of molecular hydrogen, Br is removed from the surface but the cyclodehydrogenation step is still feasible which demonstrates that Br does not influence the on-surface synthesis. Generally, the ability to remove Br by providing molecular hydrogen opens an effective way to exclude unfavorable influences of the halogen (e.g. side-products, steric effects) in on-surface coupling reactions.

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