Deciphering the kinetic and thermodynamic pathways for the on-surface dual-reactivity of a dibromo-sulfoxide derivative

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On-surface synthesis is a recently developed field of research that aims at making use of well-defined solid surfaces as confinement templates to initiate chemical reactions.[1] We studied the dual reactivity of 4,6-dibromodibenzo[*b,d*]thiophene 5-oxide [2,3] on Au(111). Upon annealing, the deoxygenation of the sulfoxide moiety takes place, concomitant to debromination. Temperature-programmed X-ray photoemission spectroscopy (TP-XPS) measurements with constant heating rate were performed to investigate the reaction kinetics (see Figure). Dissymmetric debromination was proposed based on the two-step evolution of the bromine peak and on the structural models derived from low-temperature scanning probe microscopy imaging.

With the help of a kinetic model involving all kinds of intermediate species, we could propose a reaction pathway reproducing the experimental behavior. The interplay between both deoxygenation and debromination reactions is discussed. Also, we found that, when conducting isothermal measurements, the thermodynamic equilibrium is achieved for the first debromination reaction, in contrast to the kinetic control obtained during annealing at constant heating rate.

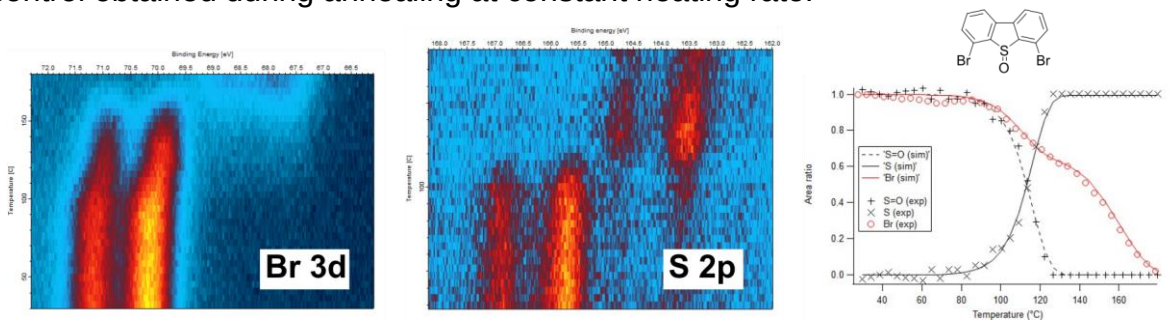

Figure: TP-XPS of Br 3d (left) and S 2p (middle). The evolution of the different peaks in function of the annealing temperature is reported (right), together with the results from the simulation of the kinetic model. Inset: Chemical structure of the dibromo-dibenzothiophene *S*-sulfoxide precursor.

REFERENCES

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