Kinetic control in molecular self-assembly on an insulating surface

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When molecules are deposited on a crystal surface, it is often expected that they form the thermodynamically most stable = structure. However, recent investigations demonstrated that simple benzoic acid molecules deposited on the insulating calcite (10.4) = surface upon increase of temperature undergo a series of structural transitions from clusters to an ordered striped network, followed by an = ordered dense network, and finally a disordered structure. Here, we combine high-resolution dynamic atomic force microscopy (AFM) and = density-functional theory (DFT) to provide a comprehensive analysis of the fundamental principles driving a specific sequence of molecular = transitions on insulating calcite. In particular, we elucidate the transition rates of relevant atomistic processes, rationalizing the = formation/dissolution of all observed networks. A key finding to understand the observed structural transitions is the system initial = state immediately after the deposition, which consists mostly of dimers. Moreover, we argue that the observed = sequence of self-assembled structures is entirely controlled by the kinetics of the system, as the smallest energy barriers rather than the = thermodynamic stability dictate the specific structural path taken. Finally, we discover a =E2=80=9Cnetwork-assisted=E2=80=9D dimer = dissociation that catalyzes the growth of the dense network. This atomistic insight into the kinetics of on-surface transitions is = essential for a detailed understanding of the formation of the observed network sequence (see Figure). Our study, thus, emphasizes the = importance of a kinetic control as a promising strategy for achieving tailored molecular architectures on insulator surfaces