Epoxide-Opening Ether Cyclizations: The Role of Water and Electric-Field-Induced Anion-π Catalysis.

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Established in 2015[1], anion-π catalysis is defined as the stabilization of anionic transition states (TS) on electron poor aromatic surfaces. Epoxide opening polyether cascade cyclizations on π-acidic surfaces appeared as counterpart of steroid cyclization and are interesting because of their unique autocatalytic behavior and Baldwin selectivity. Here they are used as benchmark reactions to clarify the mechanism of anion-π autocatalysis[2] and to elaborate on electric-field-induced anion-π catalysis[3]. To elucidate the mechanism of anion-π autocatalysis, substrates **1**-**3** with increasing peripheral crowding were synthesized and studied. Based on the results, a revised **TS-2** with two water molecules included between substrate and product on the catalytic π-acidic surface was proposed (**Figure 1A**). The vision to accelerate and direct the charge displacements during molecular transformations with external electric fields is attractive because of the promise of general catalysis, emergent properties, and programmable devices. Here, we explored the cyclisation of a pyrene-tagged epoxide **7** on highly polarizable multi-walled carbon nanotubes (MWCNT) **8** using an electrochemical microfluidic reactor. Reaction rate was linearly voltage-dependent at positive voltages and negligible at negative voltages (**Figure 1B**).
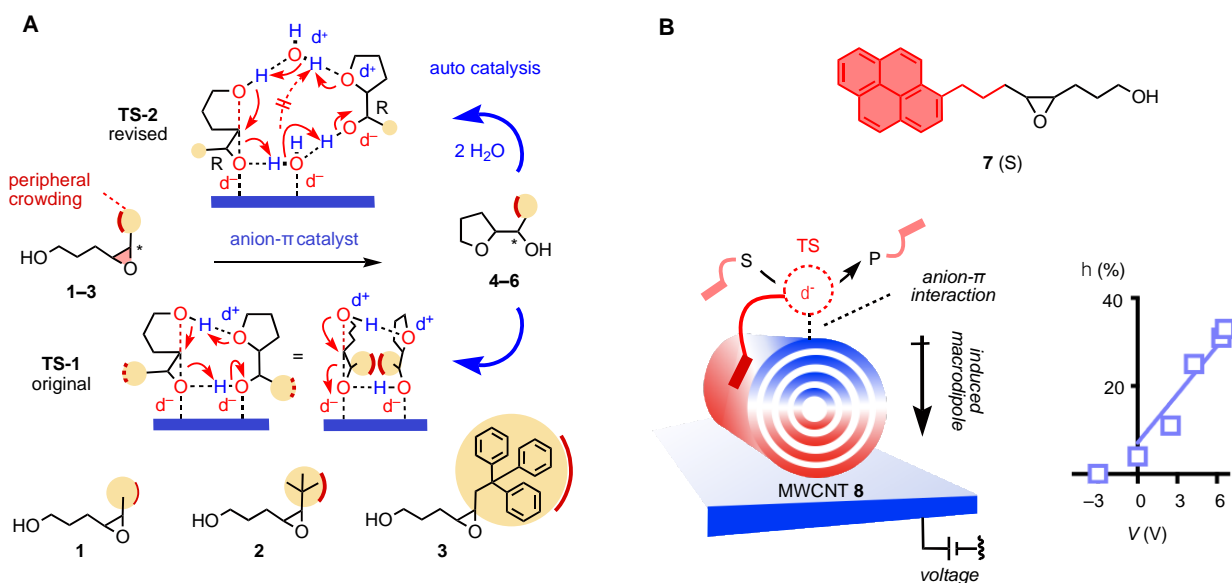

Figure 1. A Original (**TS-1**) and revised (**TS-2**) mechanism of autocatalysis of epoxide-opening ether cyclizations on anion-π catalysts. **B** Voltage dependent cyclization of epoxide **7** in electromicrofluidic reactors on polarized MWCNTs **8**.

References:

[1]   Y. Zhao, S. Benz, N. Sakai, S. Matile, *Chem. Sci.* **2015**, *6*, 6219–6223.
[2]   M. Á. Gutiérrez López, M.-L. Tan, A. Frontera, S. Matile, *JACS Au*, **2023**, *3*, 1039-1051
[3]   M. Á. Gutiérrez López, R. Ali, M.-L. Tan, N. Sakai, T. Wirth, S. Matile, *Sci. Adv.* **2023**, *9*, eadj5502