Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Experimental and Theoretical Elucidation of Catalytic Pathways in TiO_2-initiated Prebiotic Polymerization

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Table of Contents

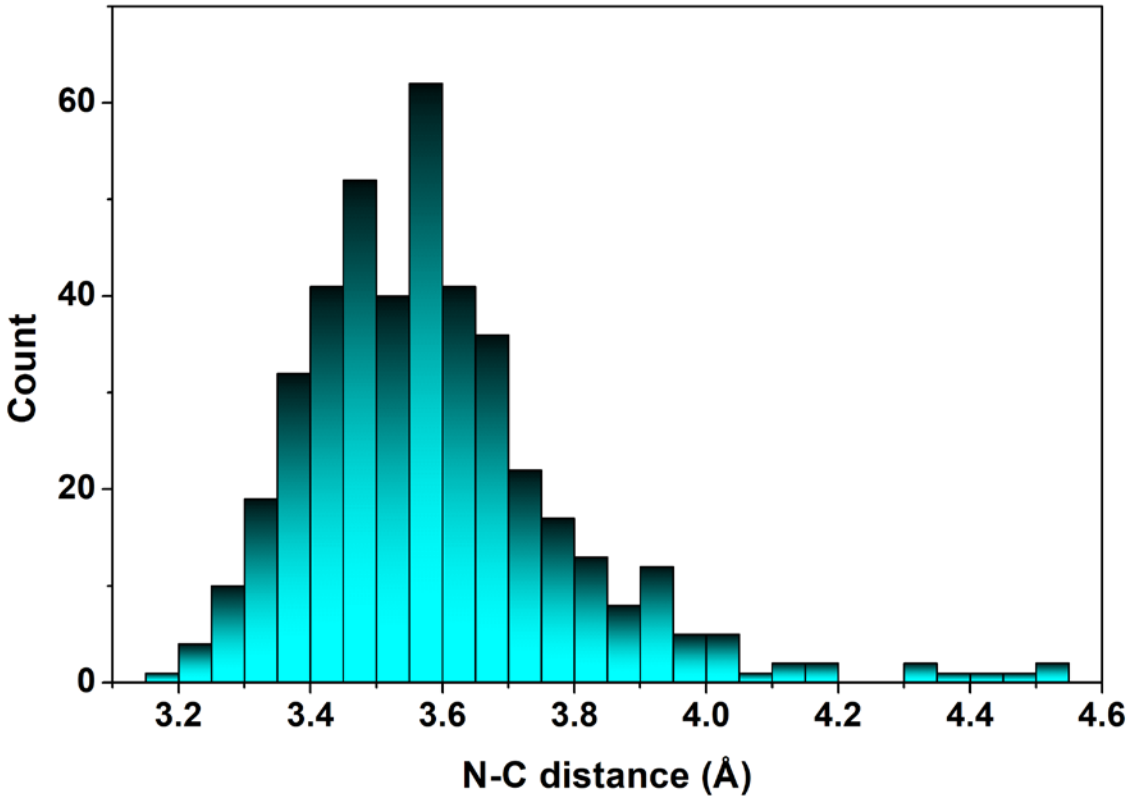

Figure S1. Distribution of the N-C distances (terminus groups) between the various Gly far from the TiO_2 slab (only closer distances were considered).

NEB simulations at the ReaxFF level.

The nudged elastic band (NEB) is used for identifying saddle points and minimum energy paths (MEPs) by optimizing a predefined number of intermediate images along the reaction path between selected reactants and products. A constrained optimization is carried out by adding spring forces along the band between images and by projecting out the component of the force from the potential perpendicular to the band. In this way each image finds the lowest energy preserving equal spacing to its neighbors.

Reactants and *products* were extracted from the RMD simulations by selecting a few configurations just before and after the peptide bond formation process. Both dipeptide and tripeptide formations were considered separately. Before starting the NEB calculations the number of soft degrees of freedom of the system, which were not relevant to the mechanism, were reduced to obtain a smooth and continuous MEP. These soft degrees of freedom were essentially those involving water, Gly molecules and hydroxyls far from the adsorbates. These molecules changed frequently their

arrangements but were not directly involved in the peptide bond formation. For identifying the most significant MEP a series of NEB calculations were carried out as a function of the number of surrounding species to define the most appropriate setup. It turned out that all the surrounding species did not affect substantially the mechanism which was mainly due to the relative immobilization of the molecules on the surface.

The NEB profile for the formation of the dipeptide is shown in **Figure S2**.

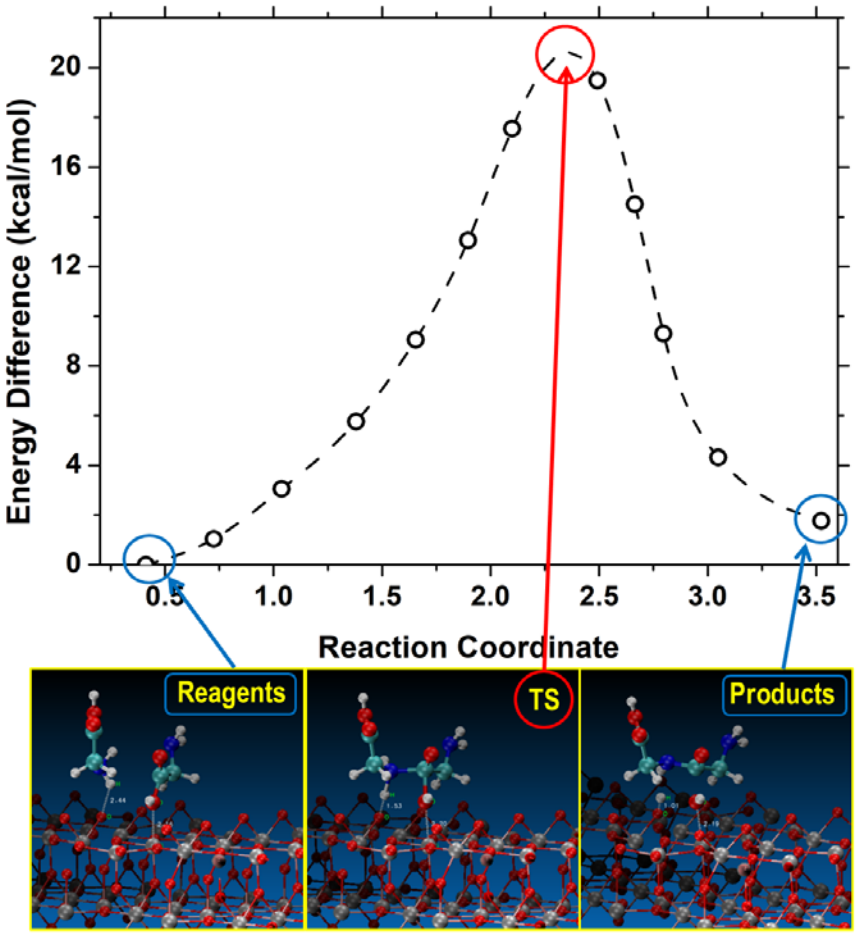

Figure S2. Dipeptide formation. NEB profile, at the classical ReaxFF level, obtained from the data extracted from the RMD simulations. All the configurations included the whole slab and two Gly. Twelve images were selected.

The NEB profile for the formation of the tripeptide is shown in **Figure S3**.

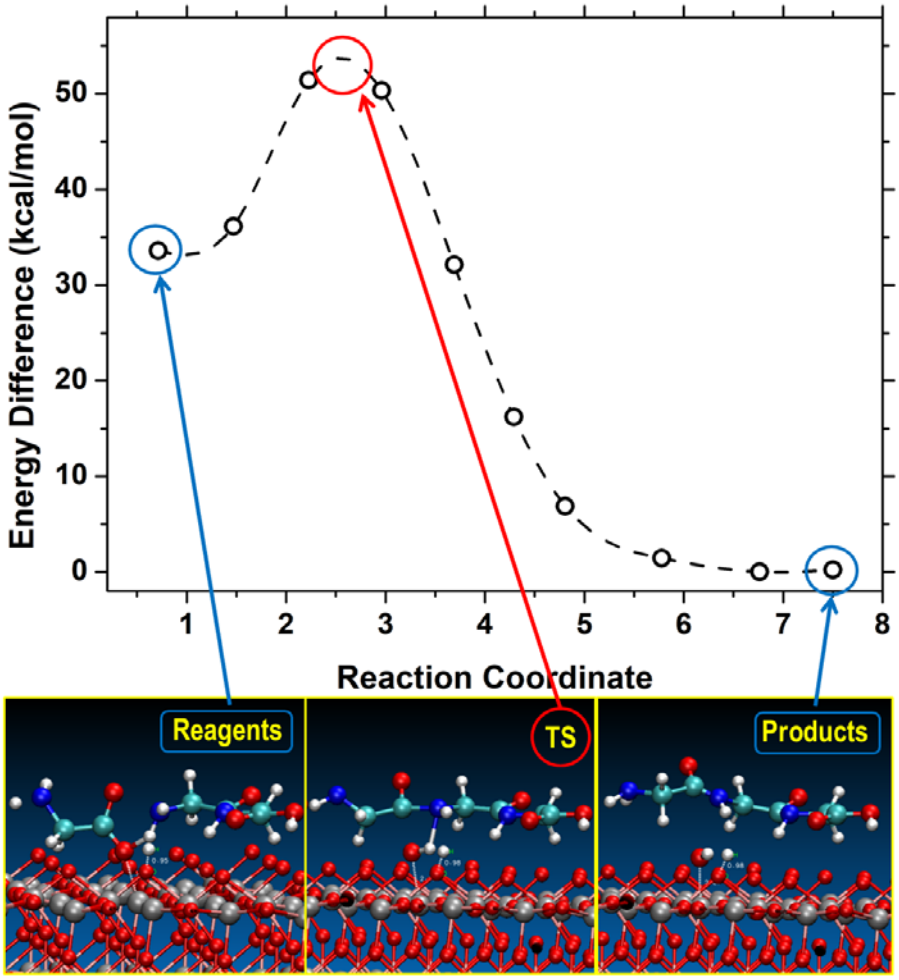

Figure S3. Tripeptide formation (dipeptide + Gly). NEB profile, at the classical ReaxFF level, obtained from the data extracted from the RMD simulations. All the configurations included the whole slab and the dipeptide and another Gly. Ten images were selected.

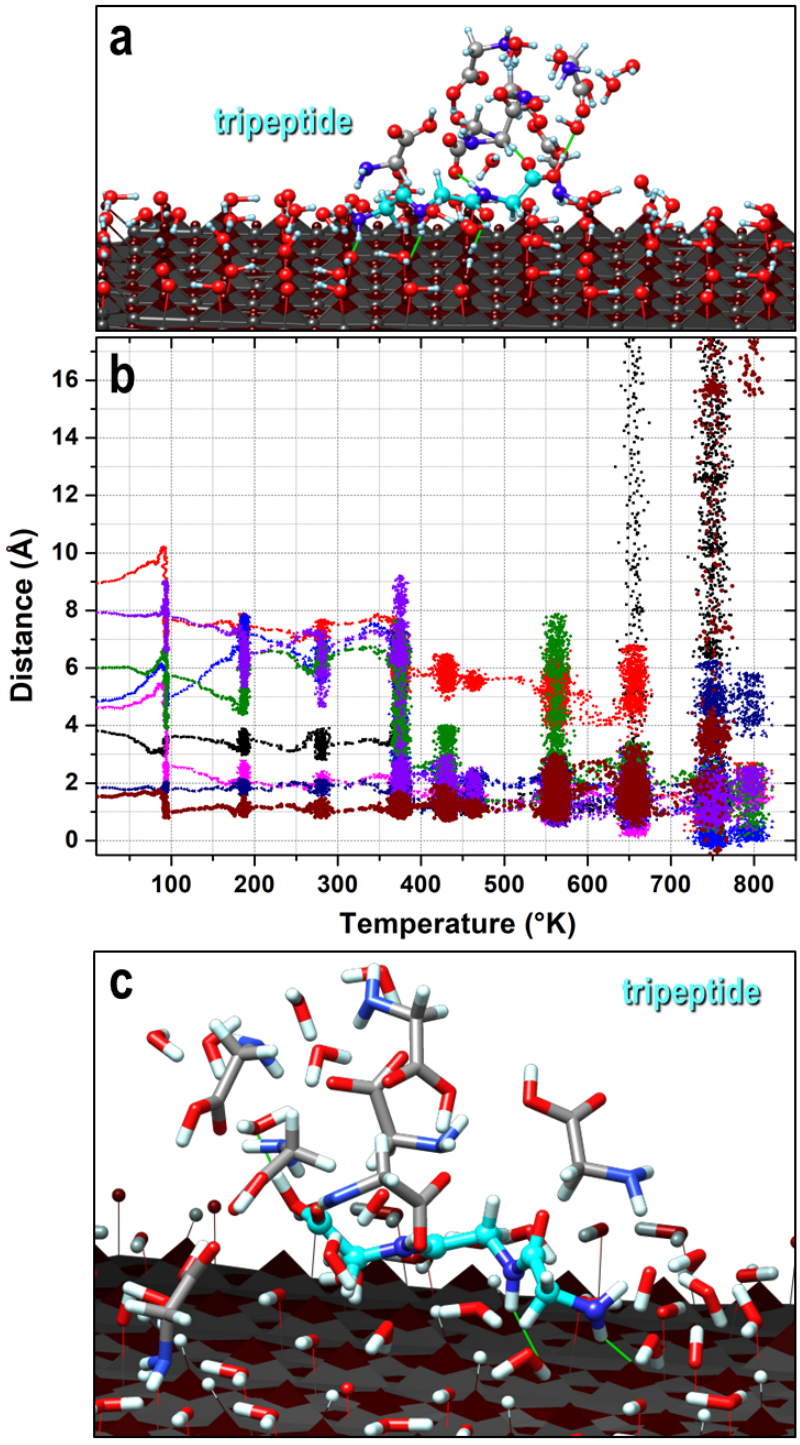

Figure S4. (a) Initial configuration of the increasing temperature RMD simulation (desorption process). **(b)** Distance of the center of mass of each Gly from the top layer of the substrate as a function of the simulation temperature. The tripeptide distance is dark red. **(c)** Details of the tripeptide arrangement on the surface (hydrogen bond connections are green lines).