Atomic-Resolution Transmission Electron Microscopic Analysis of Individual C_{60} Dimerization Events: Kinetics and Mechanisms

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Observation of the motions and reactions of molecules, being quantum mechanical entities, has long been an impossible dream. Through advances in transmission electron microscopy (TEM) and methods to anchor molecules on a carbon nanotube (CNT), we can visually study the structural changes of molecules in situ using single-molecule atomic-resolution real-time TEM imaging (SMART-TEM).[1,2] To go one step further to study reaction kinetics, we need statistical information over time and temperature - information that is so far inaccessible by many of the single-molecule analytical methods, including TEM imaging. Here, a long-standing interest in this context is to know if the behavior of individual molecules conforms to the basic assumption of the Rice - Ramsperger - Kassel - Marcus (RRKM) theory that isolated molecules behave as if all their accessible states were occupied in random order.

To address this question, we chose to study [2 + 2] electrocyclic conversion of a van der Waals (vdW) complex of C_{60} **1** in a CNT to an adduct **2** (step 1, Figure 1b and c)[3] - a well-known reaction without mechanistic information.[4] Through counting reaction events one by one, we could identify four concurrent reactions. One observed at 393 - 493 K (step 1_H), where the CNT maintained its structural integrity, involves a singlet excited state [2 + 2] cycloaddition reaction with an activation energy of 33.5 $\pm$ 6.8 kJ/mol. Here the pristine CNT acts as a single sensitizer of the cycloaddition. Another pathway found at 103 - 203 K (step 1_L) to occur after CNT was heavily damaged by the electron beam (cf. Figure 2), is a temperature-insensitive reaction. This reaction takes place with an activation energy of only 1.9 $\pm$ 0.7 kJ/mol. Here an ionized form of the damaged CNT is considered to act as an oxidant to generate a reactive radical cation of C_{60}. The third is the further conversion of **2** to a fused dimer **3** (step 2), which is also temperature sensitive as studied at 393 - 493 K. The fourth is a purely thermal retro [2 + 2] reaction frequently occurring above 493 K. Overall we found that the rate profile of the [2 + 2] dimerization of the vdW complex **1** under the 1D constraints depends heavily on the reaction temperature, the quality of the CNT, and the competing thermal cycloreversion reaction, as controlled by the activation energy, the frequency of the reaction, and the concurrent reactions.

In this single molecule study, we needed only 25 - 70 molecules to analyze the frequency of the reaction events, and several hundred molecules in total to determine the activation energies. The systematic variable-temperature (VT) atomistic TEM study of chemical reactions represents, to our knowledge, a rare example of the kind, and suggests the potential of SMART-TEM imaging for chemical kinetics study on individual molecules and their assemblies in the field of chemistry, catalysis, materials, and biological science.

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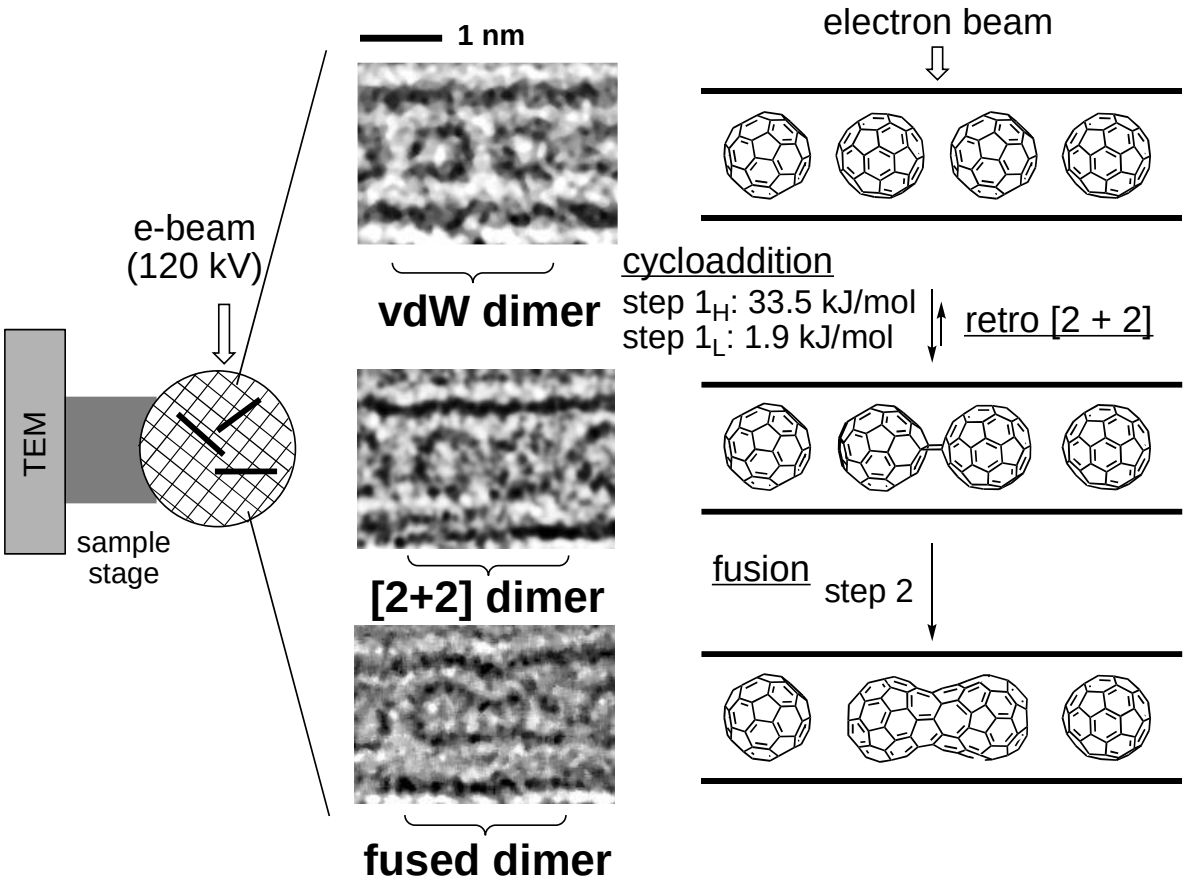

Figure. SMART-TEM imaging of the dimerization of C_{60}@CNT. (a) A schematic illustration of the experiments using C_{60}@CNTs on a temperature-controlled microgrid. (b) TEM images of intermediates in a 1.4-nm CNT. The scale bar is 1 nm. (c) Four types of reactions observed using TEM.