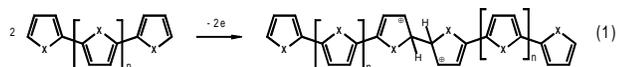


σ -"Dimers" - Key Intermediates and Products during Generation and Redox Switching of Conjugated Oligomers and Polymers

J. Heinze, H. John, M. Pagels, B. Geschke
 Institute of Physical Chemistry
 University of Freiburg, Albertstr. 21,
 79104 Freiburg, Germany

Although the physics and chemistry of conducting polymers have been studied for almost twenty years, a large number of phenomena are not well understood. This may be due to the fact that theories and models borrowed from solid-state inorganic systems and macromolecular chemistry are often used to interpret the experimental data. One consequence of this practice is the application of the bipolaron model to conducting polymers. Another is that the mechanism of their electropolymerization has been described in terms of a classical chain propagation process in which monomers are attached step by step to a growing chain.

Electrochemical measurements of chain-like conjugated oligomers and polymers show that σ -bonded "dimers" are formed during polymerization and charging of such systems (Eqn. 1). [1, 2]



As a typical example the dimerization of 3,3'-dimethoxy-2,2'-bithiophene (**1**) is presented.[3] Cyclic voltammetric measurements at different scan rates (Fig. 1) and temperatures show that after the formation of the radical cation of **1** dimerization occurs leading to a stable σ -intermediate. Simulations and the application of working curves prove that at room temperature a coupling rate constant of $6.5 \cdot 10^5 \text{ M}^{-1}\text{s}^{-1}$ is valid, while the first order rate constant of the proton elimination does not exceed a very low value of 10 s^{-1} . Consequently, the rate determining step is the elimination of protons from the σ -coupling product. (Scheme 1)

The stability of the σ -dimers increases with chain length due to the fact that the basicity of such σ -complexes rises. Therefore, the elimination of protons becomes slow and even stops for oligomers with chain lengths higher than sixteen units. All experimental findings strongly support the view that, in contrast to the established chain mechanism, the reaction pathway involves a sequence of successive "dimerization" steps, leading to the formation of oligomers in solution (Eqn. 1). The final reaction steps are typical solid-state reactions in which oligomers with chain lengths between 6 and 12 units after their deposition on the electrode form the polymeric material by successive coupling steps. At the end of the polymerization a charged system has been formed which contains σ -bonded sites $[\text{C}(\text{sp}^3) - \text{C}(\text{sp}^3)]$ between different chains. During discharging of the polymer these σ -bonds decay, but they are regenerated upon the next charging cycle. This surprising result calls

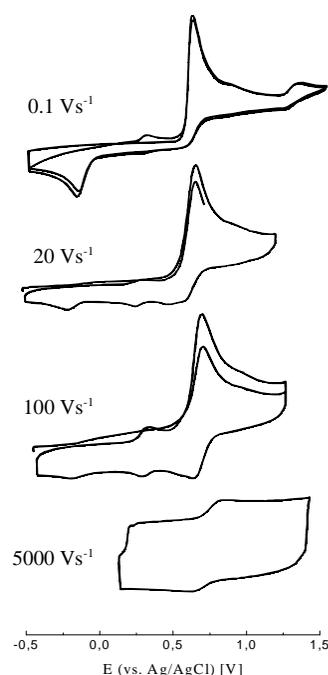
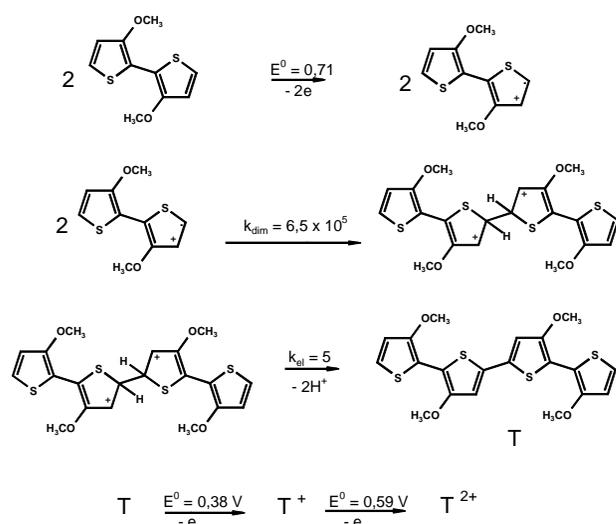


Fig. 1. Cyclic voltammograms of 3,3'-dimethoxy-2,2'-bithiophene at different scan rates in CH_2Cl_2 / 0.1 M TBAPF₆, $c = 1 \cdot 10^{-3} \text{ mol l}^{-1}$, top voltammogram $c = 3 \cdot 10^{-3} \text{ mol l}^{-1}$, $T = 298 \text{ K}$.



Scheme 1. Reaction path of the oxidation of **1**

for a reinterpretation of the charge storage mechanism of conjugated oligomers and polymers and opens the way for a new understanding of the hysteresis, and the bipolaron model.

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- [2] J. Heinze, P. Tschuncky, A. Smie, *J. Solid State Electrochem.* 2 (1998) 102.
- [3] J. Heinze, H. John, M. Dietrich, P. Tschuncky, *Synth. Met.*, in press.