

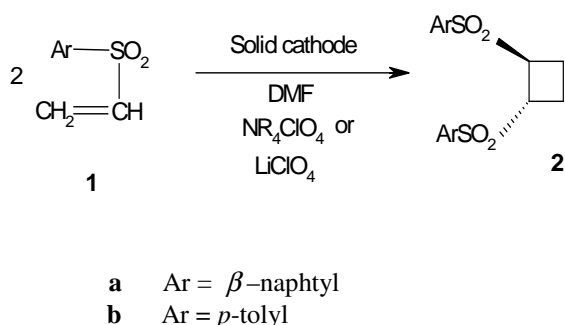
On the Mechanism of Formation of Cyclobutanes by Cathodic Cyclodimerization of Vinylarylsulfones: Spectroelectrochemical Study and MO-Modeling

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The cyclodimerization of vinylarylsulfones **1**:



can occur in high yield under electron transfer catalysis. The reaction appears to be stereo and regioselective. Very small amounts of electricity ($0.1 \text{ F} \times \text{mole}^{-1}$) are sufficient to permit the achievement of the reaction (1-3). This reaction is important because it easily produces building blocks of interest in cyclobutane and sulfone chemistry. It does not have its equivalent in organic chemistry: this reaction could not be reproduced by means of conventional reducing reagents (by electron transfer) frequently used in organic chemistry (such as dissolved metals in THF).

Cyclic voltammetry of **1a** in DMF/0.2M TBAPF₆ (Fig. 1) points out at small sweep rates two redox couples, assigned respectively to the monoelectronic reduction of the monomer (**1a/1a^{-•}**) and dimer (**2a/2a^{-•}**), the dimer couple being less shaped with increasing sweep rate. After preelectrolysis of **1a** for 1 min., only the dimer redox couple is apparent, whereas at high scan rates (200 Vs^{-1}) only the monomer couple is observed. In acetonitrile the drastic decrease of the **1a/1a^{-•}** peak is observed on subsequent scans. The relevant electrochemical data presented in Table 1 attest the reversibility of both redox couples and point out that the second redox couple observed on the cyclic voltammogram of the monomer **1a** corresponds to the first reduction wave of the dimer **2a**, *i.e.* the dimerization occurs at the potential of the monomer redox couple and implies the anion-radical **1a^{-•}**.

Electrochemical criteria suggest an ECE reaction sequence, where the chemical step is a dimerization anion radical - substrate. Therefore, the proposed mechanism lies on a catalytic cycle based on the fact that E_2^0 is smaller than E_1^0 and cleavage rates of sulfone anion radicals are slower than electron exchange rates.

Spectroelectrochemistry of the solutions of **1a** and **1b**, in acetonitrile using *in-situ* techniques outlines the

progressive transformation of the monomer into the dimer spectra.

Homogeneous ET from the dimer anion-radical to the substrate, analysed according to Marcus model, is favoured in polar solvents and seems to be more rapid than other follow-up reactions of the dimer anion radical. Semiempirical solvent dependent optimizations in acetonitrile (AM1 hamiltonian and SM5.4A Charge Model) reflect the localization of the first two vacant orbitals on the aromatic moiety (*i.e.* m.o.1) and the sulfone group (*i.e.* m.o.2). AM1 modeling of the reaction routes implying the anion radical-substrate dimerization leading to the anion radical of the dimer support the proposed reaction mechanism.

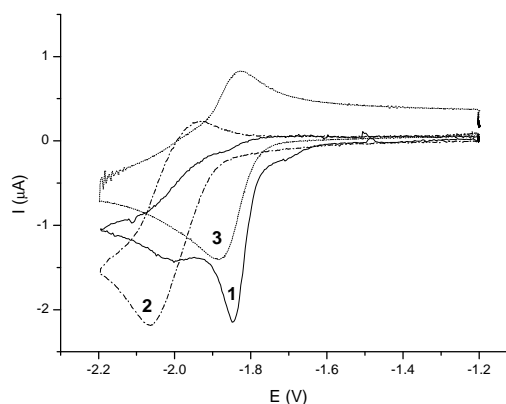


Fig. 1 Cyclic voltammetry of **1a** in DMF/0.2M TBAPF₆ ($c = 1.6 \times 10^{-3} \text{ M}$): 1 – $v = 50 \text{ mVs}^{-1}$; 2 – after preelectrolysis for 1 min.; 3 – $v = 200 \text{ Vs}^{-1}$.

Table 1. Relevant electrochemical data for compounds **1a** and **2a**.

V (V/s)	I-st wave 1a		II-nd wave 1a		I-st wave 2a	
	$-E_{pc}$ (V)	$-E_{pa}$ (V)	$-E_{pc}$ (V)	$-E_{pa}$ (V)	$-E_{pc}$ (V)	$-E_{pa}$ (V)
0.05	1.846	---	1.997	1.895	1.899	---
0.20	1.860	---	1.994	1.937	1.891	---
20	1.907	1.837	---	---	1.931	1.840
1000	1.880	1.813	---	---	1.976	1.827
$E_1^0 = -1.856 \text{ V}$			$E_2^0 = -1.952 \text{ V}$		$E^0 = -1.950 \text{ V}$	

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