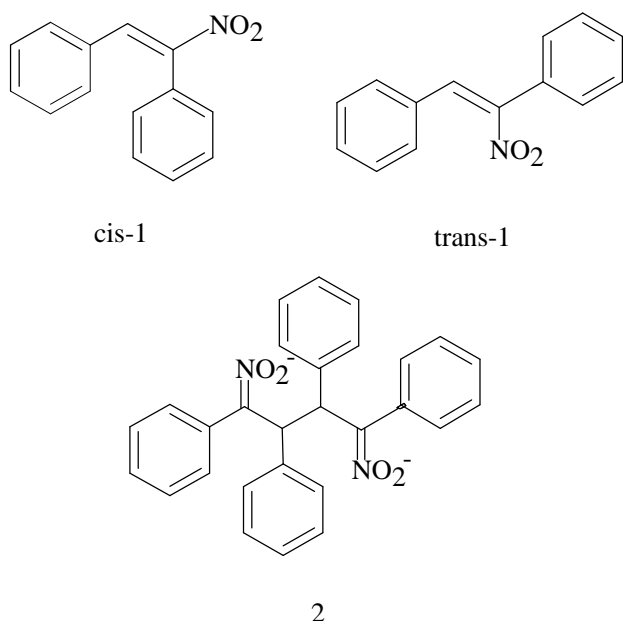


## Voltammetric Studies of the Reduction of *cis*- and *trans*- $\alpha$ -nitrostilbene

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$\alpha$ -Nitrostilbene (**1**) is an activated olefin that is expected to undergo cathodic reductive coupling reactions. Indeed, chemical reduction of **1** with dipotassium cyclooctatetraene in tetrahydrofuran leads to the dipotassium salt of a dimeric dianion **2**, isolated as the hydrodimer, 1,2,3,4-tetraphenyl-1,4-dinitrobutane. We have carried out voltammetric studies of the reduction of *cis*- and *trans*-**1** in acetonitrile to determine the mechanism of the electrochemical reduction.



The *cis* isomer was selected for initial investigation. Its reduction at glassy carbon and platinum electrodes exhibits some electron-transfer irreversibility but the reaction at mercury is much more reversible. A one-electron reduction is found at about  $-1.5$  V vs. ferrocenium/ferrocene. At low scan rates the anodic peak expected on the return scan for oxidation of the radical anion is absent but it grows in as the scan rate is increased. Data for five concentrations between 0.5 and 5 mM and eight scan rates between 1 and 200 V/s were successfully simulated by an  $EC_{\text{dim}}$  reaction featuring reversible reduction of *cis*-**1** to the radical anion followed by irreversible dimerization to **2**. The dimerization rate constant was  $6 \pm 1 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ . The fact that excellent fits of simulations to experimental

voltammograms were obtained for a ten-fold range of concentrations provides strong support for the second-order nature of the chemical reaction following electron transfer.

Controlled potential electrolysis confirms that the overall reaction is a one-electron process and voltammetric studies of the electrolyzed solution reveal an anodic peak near  $-0.5$  V, assigned to the oxidation of **2**, a peak that is also seen on the return scan of voltammograms of *cis*-**1** at low scan rates.

Cyclic voltammograms of *trans*-**1** are quite similar to those of the *cis* isomer. In fact, simulation of the voltammograms gives a standard potential for the neutral/radical anion couple that is almost identical to that seen for *cis*-**1** and a somewhat larger dimerization rate constant,  $1.4 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ . The ultimate reduction product is again **2**.

However, there is a subtle difference between the behaviors of *cis*- and *trans*-**1**. When comparing simulations with the experimental voltammograms of the *trans* isomer, it was noted that the simulation predicted that the current should begin to rise near the foot of the reduction peak sooner than was seen experimentally. However, the experimental current, once initiated, rose rapidly and near the cathodic peak began to coincide exactly with the simulation for the remainder of the voltammogram.

The exact cause of these subtle differences has not been determined. At this writing, our postulated mechanism is the following:

1. Reduction of *trans*-**1** to the *trans* radical anion.
2. Isomerization of *trans* to *cis* radical anion.
3. Dimerization of the *cis* radical anion with possible dimerization of *trans* radical anion competing with the isomerization.

This mechanism will qualitatively account for the differences in peak shape if the standard potential for the neutral/radical anion couple of *trans*-**1** is 50-100 mV negative of that of the *cis* isomer. The unexpected isomerization of *trans* to *cis* radical anion is supported by molecular orbital calculations that indicate that the *cis* form is 3 kcal/mol more stable than the *trans* radical anion.