

Assignment - Solutions

- a) In order to determine the mechanism of the first electron transfer one should first determine the coefficient transfer (α). This can readily be obtained from the value of the peak width (70 mV) using equation 1.

$$\alpha = 47.5 / (E_p - E_{p/2})^{-1} \quad (1)$$

$$\alpha = 0.68 \quad \text{higher than 0.5!}$$

The electron transfer to the methyl-thianthrenium follows a stepwise mechanism.

- b) One can determine the slope of the E_p vs $\log(v)$ plot from the value of the coefficient transfer (α) using equation 2.

$$\alpha = -29.6 / (\partial E_p / \partial \log v)^{-1} \quad (2)$$

$$\partial E_p / \partial \log v = -43 \text{ mV}$$

- c) The number of electrons (n) per molecule consumed at the first reduction peak can be calculated by comparison with the monoelectronic oxidation wave of ferrocene assuming that the diffusion coefficients are similar.

$$(I_{p,\text{compound}} / C_{\text{compound}}) (I_{p,\text{ferrocene}} / C_{\text{ferrocene}})^{-1} = n_{\text{compound}} / n_{\text{ferrocene}}$$

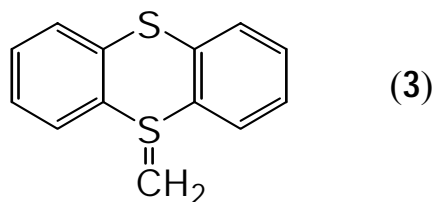
where I_p represents the peak current, C the concentration and n the electron number.

$n_{\text{ferrocene}} = 1$ since the ferrocene shows a monoelectronic oxidation wave.

$$n_{\text{compound}} = (60/2) (29/1)^{-1} = 1$$

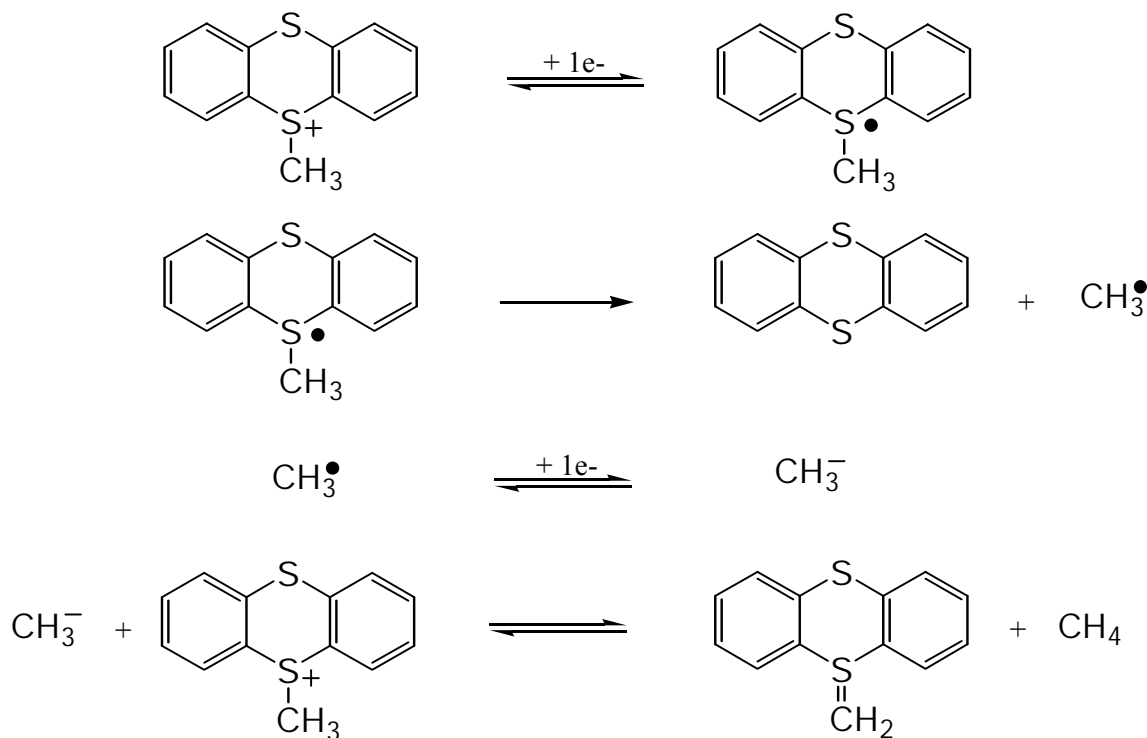
- d) Upon adding a proton donor the height of the 1st reduction peak doubles (from 1 to 2 e/mol). This indicates that an anionic intermediate (generated at the electrode by reduction of **1**) was deprotonating the initial thianthrenium salt and that this intermediate is quenched with the proton donor.

Knowing that the last reduction peak corresponds to the reduction of thianthrene (**2**) one should understand that the dissociative electron transfer to the methyl-thianthrenium salt results in the dissociation of the S-CH₃ bond leading to the formation of thianthrene (**2**) and a methyl radical. Alkyl radicals being (in general) easier to reduce than their parent sulfonium salts, the methyl radical will be immediately reduced to the corresponding anion which, being a strong base, will deprotonate another molecule of **1**, the protons at the α -position of the sulfonium centre being acidic enough. The yielded compound is compound **3**.

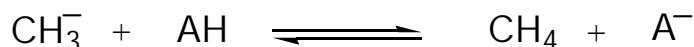


e) The global mechanism of the reaction can be written as follows:

In the absence of a proton donor:



In the presence of a proton donor the three first steps remain unchanged while the last reaction will no more take place. The carbanion will be quenched by the proton donor (AH) as follows:



f) In the presence of 1 mM phenol, half of the (2 mM) anionic intermediate will react with the phenol and the other half will react with the methyl thianthrenium 1. The reduction cyclic voltammogram of methyl-thianthrenium perchlorate (2mM) will show three reduction peaks. The first reduction peak will correspond to the consumption of more than 1 and less than 2 electrons per molecule (1.33 exactly or in other terms 4 electrons will be consumed per three molecule of 1). The second peak will decrease (less 3 formed) and the third peak will increase (more thianthrene (2) formed).