

## Summary of Parameters and Conditions Used in Simulations

### **Spatio-Temporal Detachment of Homogeneous Electron Transfer in Controlling Selectivity in Mediated Organic Electrosynthesis**

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## General Information

- 1D simulations were carried out using DigiElch v.8 and COMSOL Multiphysics v.6.0 whereas 2D simulations were performed with COMSOL Multiphysics v.6.0. The simulations modelled 2 boundary conditions for 1 D. An inert wall that acted to constrain the model to a finite geometry and an electrode. For 2D models an inflow and outflow were added as extra boundary conditions.
- Heterogeneous electrochemical reactions were modelled with Butler-Volmer kinetics after an application of a potential step to  $-2.8$  V unless otherwise stated. Simulations modelled the current response and concentration profiles for this potentiostatic control.
- Charge transfer coefficients were left at their default value of 0.5 and were not investigated in this work.
- Rate constants for homogeneous reaction steps were taken from the literature where appropriate or approximated from similar steps.
- Diffusion coefficients were determined by recording voltammograms over a range of sweep rates and analysing the sweep rate dependence of the background corrected reduction peaks at  $\sim -2.2$  V vs SCE for **1** and  $\sim -2.5$  V vs SCE for **M**. The following values were obtained and used in simulations.  $D_1 = 3.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  and  $D_M = 2.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ .
- The diffusion coefficients of **1**<sup>-</sup>, **2**, **3**, **6**, **15** were assumed to be equal to that on **1**.
- The diffusion coefficient of **M**<sup>-</sup> assumed to be equal to that of **M**.

## Rate constants

Step	Reaction	Parameters
1 <sup>[a]</sup>	$\mathbf{1} + e^- \rightarrow \mathbf{1}^{\cdot-}$	$E^0 = -2.2 \text{ V vs SCE, BV kinetics, } \alpha = 0.5, k_s = 5 \times 10^{-3} \text{ cm s}^{-1}$
2 <sup>[1]</sup>	$\mathbf{1}^{\cdot-} \rightarrow \mathbf{4}$	$k = 10^{10} \text{ s}^{-1}$
3 <sup>[2, b]</sup>	$\mathbf{4} + e^- \rightarrow \mathbf{3}$	$E^0 = 0.0 \text{ V vs SCE, BV kinetics, } \alpha = 0.5, k_s = 3 \times 10^{-2} \text{ cm s}^{-1}$
4 <sup>[a]</sup>	$\mathbf{M} + e^- \rightarrow \mathbf{M}^{\cdot-}$	$E^0 = -2.5 \text{ V vs SCE, BV kinetics, } \alpha = 0.5, k_s = 3 \times 10^{-2} \text{ cm s}^{-1}$
5 <sup>[3]</sup>	$\mathbf{1} + \mathbf{M}^{\cdot-} \rightarrow \mathbf{1}^{\cdot-} + \mathbf{M}$	$k = 4.0 \times 10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
6 <sup>[4]</sup>	$\mathbf{4} \rightarrow \mathbf{6}$	$k = 8 \times 10^9 \text{ s}^{-1}$
7 <sup>[5, c]</sup>	$\mathbf{6} + \mathbf{M}^{\cdot-} \rightarrow \mathbf{2} + \mathbf{M}$	$k = 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
8 <sup>[6]</sup>	$\mathbf{6} + \mathbf{6} \rightarrow \mathbf{15}$	$k = 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
9 <sup>[3, c]</sup>	$\mathbf{6} + e^- \rightarrow \mathbf{2}$	$E^0 = -1.36 \text{ V vs SCE, BV kinetics, } \alpha = 0.5, k_s = 2 \times 10^{-12} \text{ cm s}^{-1}$
10 <sup>[7]</sup>	$\mathbf{4} + \mathbf{M}^{\cdot-} \rightarrow \mathbf{3} + \mathbf{M}$	$k = 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
11 <sup>[7]</sup>	$\mathbf{1}^{\cdot-} + \mathbf{4} \rightarrow \mathbf{1} + \mathbf{3}$	$k = 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

<sup>[a]</sup> The standard potential and rate constant for heterogeneous electron transfer were obtained from simulated voltammograms fitted to the experimental voltammetry. <sup>[b]</sup> Aryl radical **4** was considered to convert directly to product **3** upon reduction at electrode and via mediated reduction. <sup>[c]</sup> Alkyl radical **6** was considered to convert directly to product **2** upon reduction at electrode and via mediated reduction.

## References

- [1] For excellent reviews of reductive electrochemistry of aryl halides, see: (a) J.-M. Savéant in *Advances in Physical Organic Chemistry*, Vol. 26 (Ed.: D. Bethel), Academic Press, New York, 1990, pp. 1–130; (b) J. Grimshaw in *Electrochemical Reactions and Mechanisms in Organic Chemistry*, Elsevier Science, Amsterdam, 2000, pp. 89–157 (c) Faster Dissociation: Measured Rates and Computed Effects on Barriers in Aryl Halide Radical Anions Norihiko Takeda, Pavel V. Poliakov, Andrew R. Cook, and John R. Miller, *J. Am. Chem. Soc.*, 2004, **126**, 4301-4309
- [2] Claude P. Andrieux and Jean Pinson, *J. Am. Chem. Soc.*, 2003, **125**, 14801-14806
- [3] Claude P. Andrieux, C. Blocman, J.-M. Dumas-Bouchiat and Jean-Michel Saveant, *J. Am. Chem. Soc.*, 1979, **101**, 3431-3441
- [4] a) A. Annunziata, C. Galli, M. Marinelli and T. Pau, *Eur. J. Org. Chem.*, 2001, **7**, 1323-1329. b) A. N. Abeywickrema and A. L. J. Beckwith, *J. Chem. Soc., Chem. Commun.*, 1986, 464-465
- [5] D. Occhialini, J. S. Krisensen, K. Daasbjerg and H. Lund, *Acta Chemica Scandinavica*, 1992, **46**, 474-481.
- [6] The rate constant ( $k_8 = 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ ) for homocoupling of alkyl radical **6** to give the dimer **15** (step (8)) is approximated to a literature value for dimerisation of 2-phenylethyl. *Journal of Physical and Chemical Reference Data* 25, 709 (1996); [https:// doi.org/10.1063/1.555978](https://doi.org/10.1063/1.555978)
- [7] Reactions are thought to be diffusion limited. Chami, Z., Gareil M., Pinson J., Saveant J.-M. and Thiebault A., *J. Org. Chem.*, 1991, **56**, 586-595