

Supporting Information

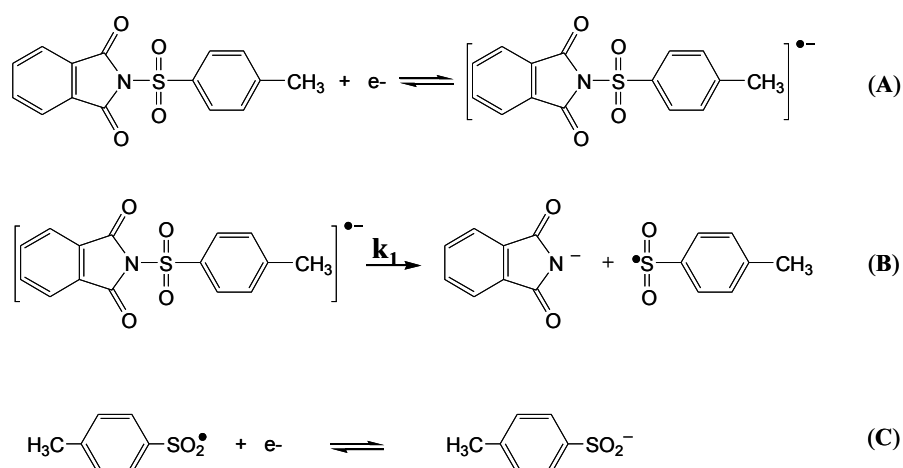
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I. Reduction mechanisms of compounds 1 and 2

I. 1. Reduction mechanism of compound 1

The cyclic voltammogram of the 4-methylphenyl sulfonyl phthalimide (**1**) at a scan rate of 200 mV/s shows a first reversible wave (Figure 1a in the manuscript) corresponding to the consumption of 1 electron per molecule, by comparison with the monoelectronic oxidative wave of ferrocene used as a reference. This indicates that the initial reduction of compound **1** leads to the corresponding radical anion, $\mathbf{1}^{\bullet-}$, (reaction **A** in Scheme 1). The reversibility is gradually lost when the scan rate is decreased and the number of electrons consumed per molecules increases accordingly. Figure S1 shows the reduction cyclic voltammogram of compound **1** at a scan rate of 75 mV/s. This means that at this time scale the radical anion is mainly consumed by a chemical reaction and is only partially oxidized when inverting the scan. Electrolysis of compound **1** at a potential corresponding to the first peak consumes 2 electron per molecule and leads to the formation of the phthalimide anion and the phenyl sulfinate anion indicating that the chemical reaction consuming the radical anion, $\mathbf{1}^{\bullet-}$, (at low scan rates) is the dissociation of the N-S chemical bond (reaction **B** in Scheme 1), leading to the phthalimidyl anion and the phenyl sulfonyl radical (see discussion in the manuscript). The phenyl sulfonyl radical is immediately reduced at the electrode (reaction **C** in Scheme 1) since it is easier to reduce than the parent phenyl sulfonyl phthalimide (**1**).



Scheme 1. Reduction mechanism of compound **1**.

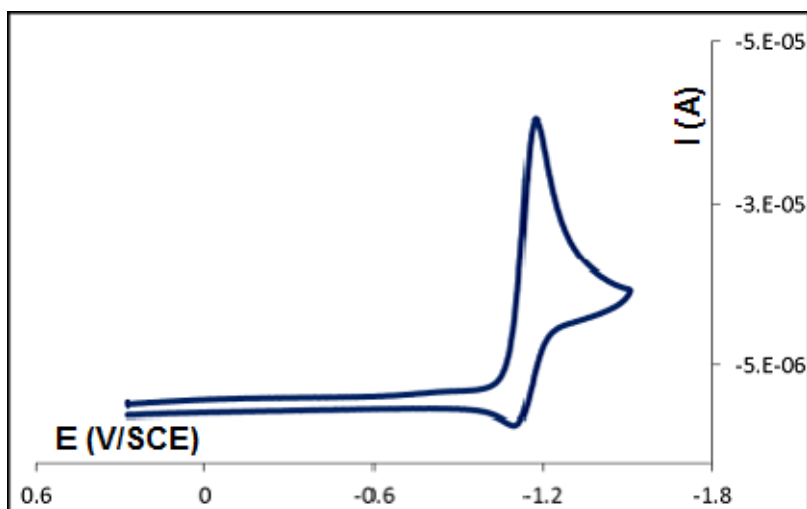
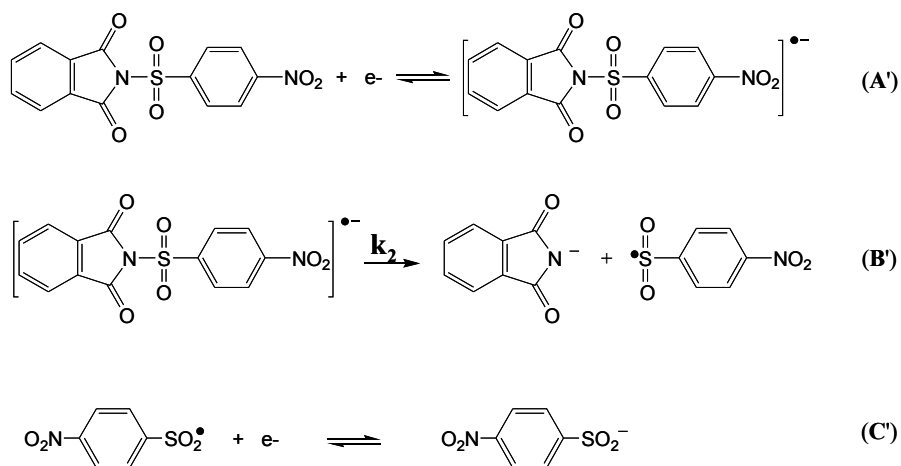


Figure S1. Cyclic voltammetry of 4-methylphenyl sulfonyl phthalimide (1.68 mM), in acetonitrile in the presence of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6 0.1 M) at a glassy carbon electrode, at a scan rate of 75 mV/s. Only the first peak is shown.

I. 2. Reduction mechanism of compound 2

The cyclic voltammogram of compound **2** shows an irreversible peak (at 200 mV/s, corresponding to the consumption of 2 electrons), which becomes reversible (and corresponds to the consumption of 1 electron per molecule) once the scan rate is increased to 80 V/s (Figure 1d, clipped CV showing only first peak in the manuscript and Figure S2 below). This indicates that a radical anion ($2^{\cdot-}$) is indeed generated when compound **2** is reduced (reaction **A'** in Scheme 2) similar to compound **1**. The difference is that $2^{\cdot-}$ is consumed by a faster chemical than $1^{\cdot-}$. As the scan rate is increased the radical anion $2^{\cdot-}$ is oxidized back to **2** before its consumption takes place by this chemical and this is why reversibility is seen when the scan rate is increased. We are specifying that this is a chemical step because by increasing the scan rate the number of electrons per molecule decreases to one. If the second step was a second electron transfer a two electron wave would be seen even if the scan rate is increased. Our electrolysis results show that the electrolysis of compound **2**, by reduction at the first peak potential, leads to the production of two anions (4-nitrophenylsulfonate and the phthalimide anion). This indicates that the chemical step following the formation of compound **2** is the dissociation of the N-S bond leading to the phthalimidyl anion and the 4-nitrophenylsulfonyl radical (as per reaction **B'** in Scheme 2). This

step is followed by the reduction of the 4-nitrophenyl radical (reaction C' in Scheme 2) since this radical (as most radicals generated this way) is easier to reduce than the parent compound (**2**) and is immediately reduced at the electrode as soon as it is generated. When the scan rate is increased the decomposition is not observed (within this new time scale) and therefore the reduction peak shows reversibility and the number of electrons per molecule decreases as observed in our case.



Scheme 2. Reduction mechanism of compound **2**.

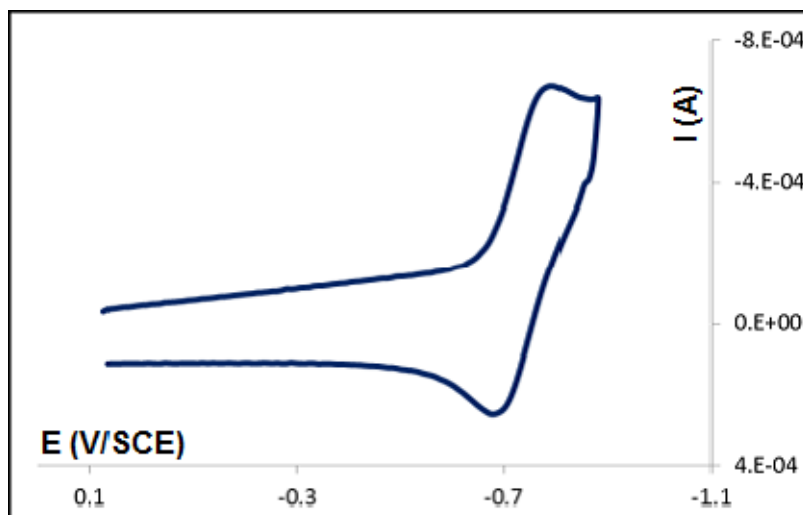


Figure S2. Cyclic voltammetry of 4-nitrophenyl sulfonyl phthalimide (1.23 mM), in acetonitrile in the presence of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6 0.1 M) at a glassy carbon electrode, at a scan rate of 80 V/s. Only the first peak is shown.

II. Application of the extensions of the dissociative electron transfer theory to the case of decomposition of radical anions

When applying the extensions of the dissociative electron transfer theory to the case of dissociation radical anions the activation free energy is similar for both the homolytic and the heterolytic mechanisms. Below are the detailed expressions showing the involved parameters for each radical anion. The intrinsic barrier on the other hand is different from one mechanism to the other. The main difference resides in the involvement of the standard potential of the leaving group (the anion product of the radical anion cleavage) in one case and in that of the other moiety (the radical product of the radical anion cleavage) in the other case. The detailed expressions for the cleavage of both radical anions are provided below.

II. 1. Activation free energy:

The thermodynamics of the dissociation of the radical anions of both compounds can be described by the same general expression (eq. 1). The main parameters include the standard reduction potential of the sulfonyl phthalimide, $E_{\text{ArX}/\text{ArX}^{\cdot-}}^0$, (ArX is a representation of the investigated compounds, where Ar refers to the 4-substituted phenyl sulfonyl group and X to the phthalimidyl group), the bond dissociation energy of the cleaved bond $D_{\text{Ar-X}}$ (N-SO₂ in both cases), the standard potential of the leaving group, $E_{\text{X}^{\cdot}/\text{X}^-}^0$, and the entropy of the homolytic dissociation reaction, $\Delta S_{\text{ArX}/\text{Ar}^{\cdot}+\text{X}^{\cdot}}$:

$$\Delta G^0 = E_{\text{ArX}/\text{ArX}^{\cdot-}}^0 + D_{\text{Ar-X}} - E_{\text{X}^{\cdot}/\text{X}^-}^0 - T\Delta S_{\text{ArX}/\text{Ar}^{\cdot}+\text{X}^{\cdot}} \quad (1)$$

The detailed activation free energy expressions for the decomposition of the two radical anions (**1**^{·-} and **2**^{·-}) are shown below. The thermodynamics of the two reactions are discussed since the main parameters are available.

a) Activation free energy for the decomposition of **1**^{·-}

$$\Delta G_{\text{MePhSO}_2\text{Phth}^- / \text{MePhSO}_2 + \text{Phth}^-}^0 = E_{\text{MePhSO}_2\text{Phth} / \text{MePhSO}_2\text{Phth}^-}^0 + D_{\text{MePhSO}_2-\text{Phth}} - E_{\text{Phth}^- / \text{Phth}}^0 - T\Delta S_{\text{MePhSO}_2\text{Phth} / \text{MePhSO}_2 + \text{Phth}}$$

b) Activation free energy for the decomposition of 2⁻

$$\Delta G_{\text{NO}_2\text{PhSO}_2\text{Phth}^- / \text{NO}_2\text{PhSO}_2 + \text{Phth}^-}^0 = E_{\text{NO}_2\text{PhSO}_2\text{Phth} / \text{NO}_2\text{PhSO}_2\text{Phth}^-}^0 + D_{\text{NO}_2\text{PhSO}_2-\text{Phth}} - E_{\text{Phth}^- / \text{Phth}}^0 - T\Delta S_{\text{NO}_2\text{PhSO}_2\text{Phth} / \text{NO}_2\text{PhSO}_2 + \text{Phth}}$$

The main difference resides in the standard oxidation potential of the starting material where that of the p-methylphenyl sulfonyl phthalimide is 350 mV more negative than that of the 4-nitrophenyl sulfonyl phthalimide ($E_{\text{MePhSO}_2\text{Phth} / \text{MePhSO}_2\text{Phth}^-}^0 = -1.18$ V/SCE and $E_{\text{NO}_2\text{PhSO}_2\text{Phth} / \text{NO}_2\text{PhSO}_2\text{Phth}^-}^0 = -0.83$ V/SCE). The N-S bond dissociation energies for both compounds have very similar values ($D_{\text{MePhSO}_2-\text{Phth}} = 58.73$ kcal/mol and $D_{\text{NO}_2\text{PhSO}_2-\text{Phth}} = 59.28$ kcal/mol). The entropy terms are also very similar given that the two decomposition reactions involve similar reactants and products.

II. 2. Intrinsic barrier:

a) Intrinsic barrier for the decomposition of 1⁻: homolytic cleavage

$$\Delta G_{0,\text{hom}}^\ddagger = \frac{1}{4} \left(D_{\text{MePhSO}_2-\text{Phth}} + E_{\text{MePhSO}_2\text{Phth} / \text{MePhSO}_2\text{Phth}^-}^0 - E_{\text{Phth}^- / \text{Phth}}^0 + T\Delta \bar{S}_{\text{MePhSO}_2\text{Phth}^- / \text{MePhSO}_2 + \text{Phth}^-} \right) + \frac{\lambda_0}{4}$$

$$\Delta \bar{S}_{\text{MePhSO}_2\text{Phth}^- / \text{MePhSO}_2 + \text{Phth}^-} = \bar{S}_{\text{MePhSO}_2\text{Phth}} - \bar{S}_{\text{MePhSO}_2\text{Phth}^-} + \bar{S}_{(\text{Phth}^-)^-} - \bar{S}_{\text{MePhSO}_2^-}$$

b) Intrinsic barrier for the decomposition of 1⁻: homolytic cleavage

$$\Delta G_{0,\text{het}}^\ddagger = \frac{1}{4} \left(D_{\text{NO}_2\text{PhSO}_2-\text{Phth}} + E_{\text{NO}_2\text{PhSO}_2\text{Phth} / \text{NO}_2\text{PhSO}_2\text{Phth}^-}^0 - E_{\text{NO}_2\text{PhSO}_2^- / \text{NO}_2\text{PhSO}_2^-}^0 + T\Delta \bar{S}_{\text{NO}_2\text{PhSO}_2\text{Phth}^- / \text{NO}_2\text{PhSO}_2 + \text{Phth}^-} \right) + \frac{\lambda_0}{4}$$

$$\Delta \bar{S}_{\text{NO}_2\text{PhSO}_2\text{Phth}^- / \text{NO}_2\text{PhSO}_2 + \text{Phth}^-} = \bar{S}_{\text{NO}_2\text{PhSO}_2\text{Phth}} - \bar{S}_{\text{NO}_2\text{PhSO}_2\text{Phth}^-} + \bar{S}_{(\text{NO}_2\text{PhSO}_2)^-} - \bar{S}_{\text{NO}_2\text{PhSO}_2\text{Phth}}$$

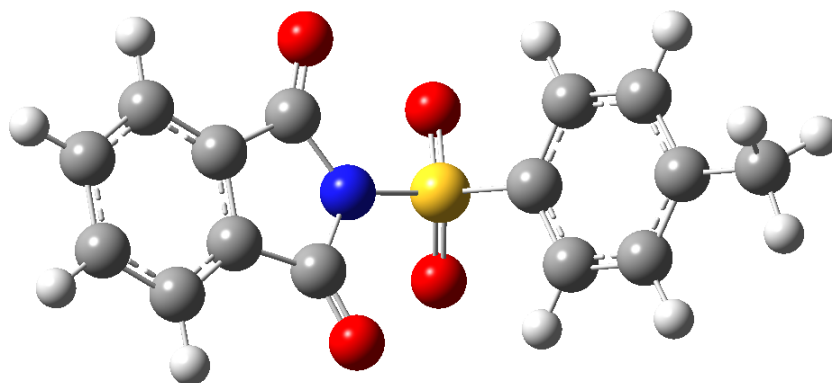
III. Computational calculations (method, structures, energies, LUMOs and coordinates)

All of the calculations were performed using the Gaussian 03 package.¹ B3LYP method with the 6-31G+(d,p) basis set starting from preliminary optimizations performed with semi-empirical methods. LUMO orbitals as well as radical structure minima were calculated after a full optimization without imposed symmetry of the conformations. Minimum energy structures were fully optimized and the obtained conformations were checked by running frequency calculations. No imaginary vibrational frequencies were seen.

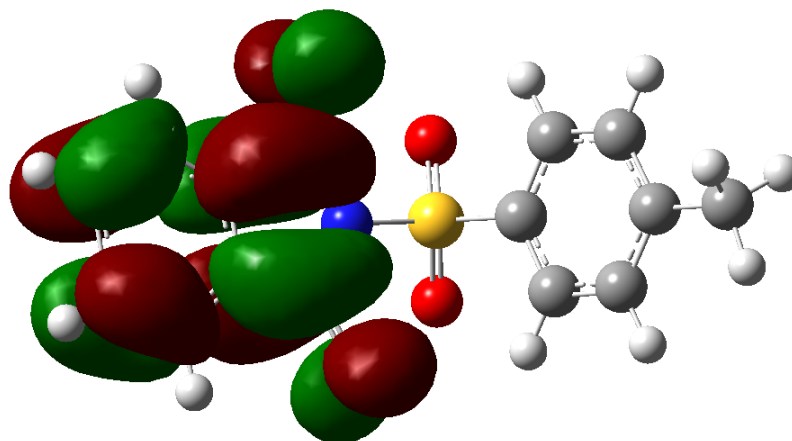
1. Gaussian 03, Revision B.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr. J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C. and Pople, J. A. Gaussian, Inc., Pittsburgh PA, 2003.

III. 1. 4-Methylphenyl sulfonyl phthalimide (1)

Optimized structure:



Deduced LUMO:

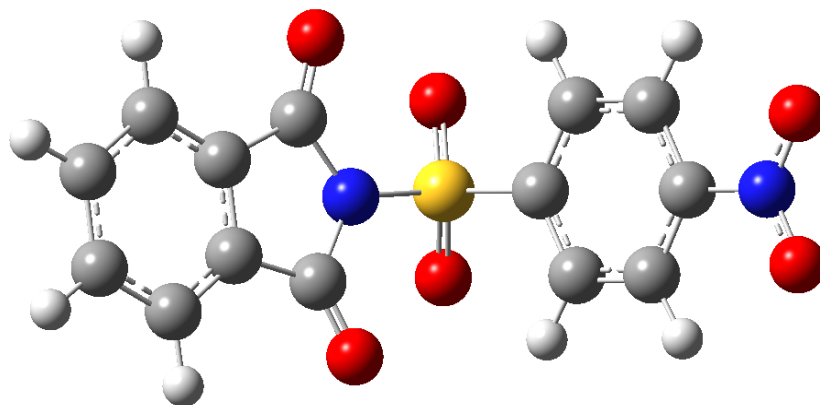


Total Energy: -1332.06396141 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.900929	-1.507056	0.557564
2	6	0	0.183997	-0.472214	1.166411
3	6	0	0.696397	0.822854	1.255177
4	6	0	1.957589	1.079472	0.715361
5	6	0	2.705404	0.066804	0.096715
6	6	0	2.157458	-1.225829	0.026846
7	1	0	0.481679	-2.506597	0.514366
8	1	0	0.117877	1.605193	1.733604
9	1	0	2.366736	2.083660	0.781788
10	1	0	2.725125	-2.024583	-0.443324
11	16	0	-1.422173	-0.826447	1.860691
12	8	0	-1.559258	-2.261343	2.063618
13	8	0	-1.727504	0.135352	2.910785
14	6	0	-2.904120	0.910030	0.220813
15	6	0	-3.107759	-1.369903	-0.375782
16	6	0	-3.911913	0.784927	-0.867553
17	6	0	-4.031581	-0.558525	-1.219311
18	6	0	-4.646582	1.774755	-1.509825
19	6	0	-4.891525	-0.972879	-2.229557
20	6	0	-5.523869	1.367641	-2.523071
21	1	0	-4.541612	2.817914	-1.230320
22	6	0	-5.644268	0.015003	-2.877509
23	1	0	-4.972497	-2.021097	-2.497851
24	1	0	-6.120530	2.109400	-3.045265
25	7	0	-2.511796	-0.430035	0.534219
26	8	0	-2.463283	1.919503	0.721957
27	8	0	-2.876676	-2.552428	-0.453210
28	1	0	-6.332071	-0.268341	-3.668441
29	6	0	4.072595	0.348220	-0.478994
30	1	0	4.839061	-0.262337	0.011915
31	1	0	4.106568	0.111532	-1.548559
32	1	0	4.350154	1.398451	-0.357111

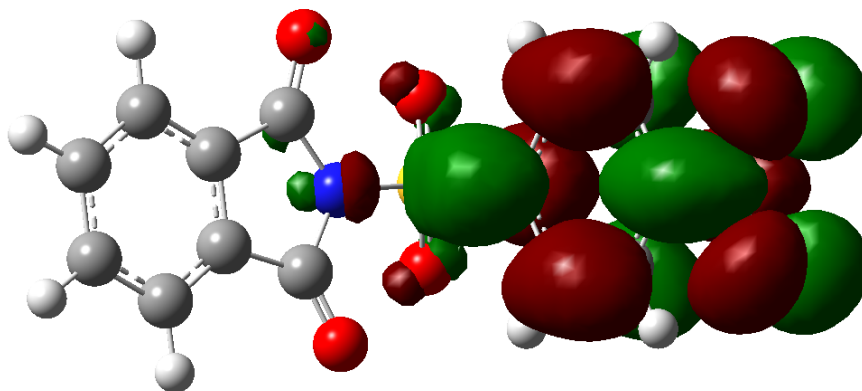
III. 2. 4-Nitrophenyl sulfonyl phthalimide (2).

Optimized structure:



Deducted

LUMO:



Total Energy: -1497.24608895 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.743019	-1.125339	0.155526
2	6	0	0.919913	-0.789535	1.496798
3	6	0	1.312450	0.512860	1.815926

4	6	0	1.527138	1.492312	0.843043
5	6	0	1.349361	1.155382	-0.497905
6	6	0	0.961870	-0.146650	-0.813818
7	1	0	0.438439	-2.120917	-0.141963
8	1	0	0.760519	-1.518569	2.283344
9	1	0	1.819782	2.495083	1.134483
10	1	0	1.500791	1.880607	-1.287563
11	7	0	0.773388	-0.504558	-2.237766
12	8	0	0.972725	0.373150	-3.076530
13	8	0	0.430490	-1.657907	-2.494178
14	16	0	1.539234	0.950045	3.544728
15	8	0	1.485403	2.396991	3.679854
16	8	0	0.737749	0.059690	4.370011
17	6	0	3.621093	-0.847821	4.110028
18	6	0	4.336616	1.383929	3.740822
19	6	0	5.078650	-0.752578	4.387910
20	6	0	5.499212	0.559436	4.169929
21	6	0	5.968546	-1.747740	4.775735
22	6	0	6.827913	0.934695	4.330337
23	6	0	7.308106	-1.378019	4.950917
24	1	0	5.631678	-2.766421	4.936856
25	6	0	7.731092	-0.057877	4.731678
26	1	0	7.144379	1.957112	4.152351
27	1	0	8.033524	-2.124520	5.259397
28	1	0	8.777033	0.195929	4.873963
29	8	0	2.920093	-1.832326	4.080122
30	8	0	4.326476	2.531689	3.368989
31	7	0	3.203248	0.495604	3.817307

III. 3. 4-Methylphenyl sulfonyl radical.

Total Energy: -819.54523656 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.000571	-0.292767	-0.037386
2	6	0	-0.048895	-0.353555	1.353926
3	6	0	1.119372	-0.095817	2.075527
4	6	0	2.328792	0.183381	1.438518
5	6	0	2.351931	0.239048	0.044135
6	6	0	1.195833	-0.000088	-0.714112
7	1	0	-0.908719	-0.471634	-0.607113
8	1	0	-0.976255	-0.569172	1.873389
9	1	0	3.222456	0.378395	2.021311
10	1	0	3.284381	0.476274	-0.460699
11	16	0	1.086108	-0.232052	3.882938
12	8	0	2.225202	0.569566	4.416558

13	8	0	-0.318139	0.004705	4.326812
14	6	0	1.232840	0.036956	-2.222823
15	1	0	2.155160	0.494847	-2.589970
16	1	0	1.175142	-0.976044	-2.639441
17	1	0	0.386993	0.602473	-2.627327

III. 4. 4-Nitrophenyl sulfonyl radical.

Total Energy: -984.72647834 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.016126	0.410182	-0.042183
2	6	0	-0.013549	0.464177	1.350572
3	6	0	1.131130	0.095093	2.060067
4	6	0	2.312949	-0.297737	1.428467
5	6	0	2.341273	-0.351354	0.035673
6	6	0	1.193460	0.006181	-0.671215
7	1	0	-0.850280	0.672567	-0.636514
8	1	0	-0.913016	0.764144	1.876310
9	1	0	3.182020	-0.576897	2.013452
10	1	0	3.229164	-0.663657	-0.499913
11	7	0	1.225472	-0.047280	-2.149670
12	8	0	2.273988	-0.407174	-2.682748
13	8	0	0.201879	0.272500	-2.752217
14	16	0	1.112587	0.224741	3.879172
15	8	0	-0.309331	0.120316	4.309386
16	8	0	2.169498	-0.690528	4.392374

III. 5. Phthalimide radical

Total Energy: -512.42512908 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.026580	-0.000188	0.023976
2	6	0	0.026827	-0.000253	1.423488
3	6	0	1.213690	-0.000031	2.152211
4	6	0	2.409320	0.000237	1.427576
5	6	0	2.409078	0.000305	0.019048

6	6	0	1.213198	0.000107	-0.705163
7	6	0	-1.395897	-0.000443	-0.423504
8	6	0	-1.395520	-0.000541	1.871442
9	1	0	1.203615	-0.000071	3.237259
10	1	0	3.357928	0.000420	1.955950
11	1	0	3.357502	0.000538	-0.509654
12	1	0	1.202740	0.000168	-1.790209
13	8	0	-1.824400	0.000144	3.011543
14	8	0	-1.825138	0.000364	-1.563453
15	7	0	-2.250716	-0.000112	0.724119

IV. Synthesis

4-methyl and 4-nitrobenzene sulfonyl phthalimides were synthesized, as described in the literature with minor modification,² by refluxing equal molar amounts of potassium phthalimide and the corresponding substituted phenyl sulfonyl chloride with continuous stirring in 25 ml acetonitrile for 48 hours. The product was precipitated by addition of 50 mL of milli-Q water, then filtered and washed with water and left to dry. The methyl substituted sulfonamide was purified by recrystallization in p-xylenes, and nitro substituted one was recrystallized in acetonitrile to afford pure products

2. M. S. Heller, *J. Chem. Eng. Data*, **15**, 351 (1970).

N-(p-methylbenzenesulfonyl)phthalimide- 73.0%

mp 241-243 °C lit (239-240°C)¹; IR (KBr, cm⁻¹) 1793.9, 1753.2, 1701.3, 1385.7, 1258.8, 1193.6, 1180.2, 1144.1, 1089.9 and 1035.0; ¹H-NMR (CDCl₃) δ (ppm): 2.41 (3H, s), 7.34 (2H, d, J = 8.04Hz), 7.77-7.80 (2H, m), 7.87-7.90 (2H, m), 8.07 (2H, d, J = 8.4Hz); ¹³C-NMR (CDCl₃) δ (ppm): 21.77, 124.59, 128.45, 129.97, 130.93, 135.44, 135.49, 146.11, and 163.04.

N-(p-nitrobenzenesulfonyl)phthalimide) 76.7%

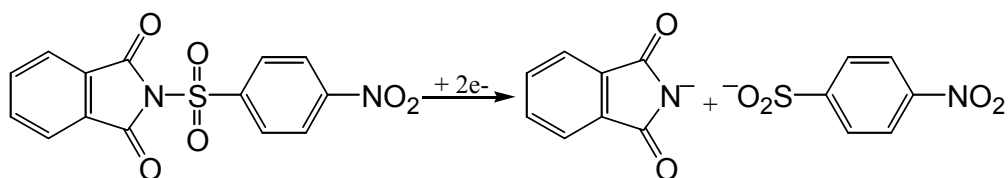
mp 280-282°C; IR (KBr, cm⁻¹); 1799.1, 1756.6, 1530.6, 1466.3, 1403.0, 1348.9, 1255.6, 1190.2, 1139.6, 1086.5 and 1021.9; ¹H-NMR (CDCl₃) δ (ppm): 7.80-7.83 (2H, m), 7.90-7.93 (2H, m), 8.38 (4H, br s); ¹³C-NMR (CDCl₃) δ (ppm): 124.59, 124.96, 129.93, 130.65, 135.98, 143.62, 151.23, 162.49.

V. Cyclic Voltammetry

Electrochemical measurements were conducted in three electrode glass cells, thermostatted at 25 °C, and under dry nitrogen. The working electrode is a 2 mm diameter glassy carbon electrode (Ekochemie). The electrode was carefully polished and ultrasonically rinsed with ethanol before each run. The reference electrode is a saturated calomel electrode (SCE). The counter electrode was a platinum wire. The electrochemical instrument used is an Autolab PGSTAT30. A feedback correction was applied to minimize the Ohmic drop between the working and reference electrodes.

VI. Electrolysis

The electrolysis was carried out in a 50 ml cell with a glassy carbon (Electrosynthesis) rectangular plate working electrode of 8 cm². The counter electrode was a platinum grid, separated from the cathodic compartment by means of a glass frit. The reference electrode was the same as for CV. The cell was thermostatted at 25 °C, and the solution was kept under a nitrogen stream during the whole electrolysis. The electrolysis of the 4-nitrophenyl sulfonyl phthalimide was performed in acetonitrile in the presence of tetramethyl ammonium hexafluotophosphate (0.1 M) at the first reduction peak potential (-0.8 V/SCE). The disappearance of the starting material and the formation of the products were followed by in situ cyclic voltammetry and by HPLC. The Reduction leads to the phthalimidy anion and the 4-nitrophenyl sulfinate anion (Scheme 3). Electrolysis of compound **1** (at -1.2 V/SCE) similarly provided the phthalimide and the phenyl sulfinate anions.



Scheme 3. Global electrochemical reduction reaction of **2**.

VII. Variation of the peak potential with the scan rate for compound 2

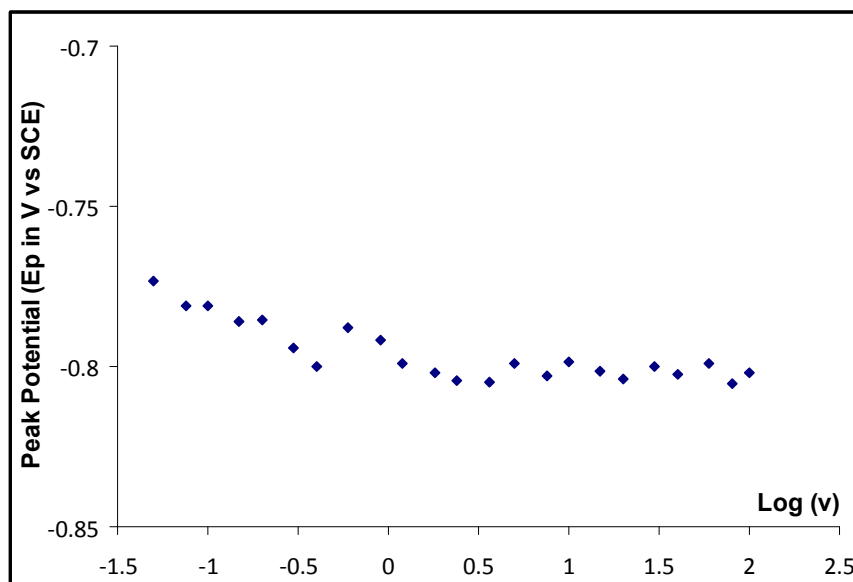


Figure S3. Variation of the reduction peak potential of 4-nitrophenyl sulfonyl phthalimide (1.23 mM in acetonitrile) as a function of log (v).