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The cathodic behaviour of poly(alkyl) and (aryl) sulfones revisited. Mechanistic and theoretical approaches

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A series of aromatic sulfones activated by 2, 3 or 4 sulfonyl groups were reduced electrochemically in aprotic media. The electrochemical behaviour is strongly directed by the nature and the number of the substituents bound to the aromatic ring. From the analyses of cyclic voltammetry experiments, the kinetics and thermodynamic parameters were evaluated for each system and a theoretical study at the B3LYP/6-31G* level was performed simultaneously to understand the reactivity of the radical anions stemmed from these aromatic sulfones.

Introduction

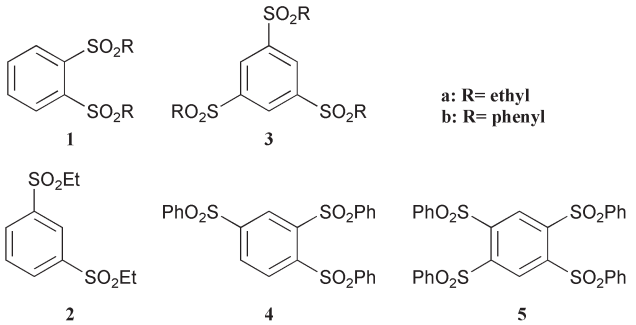
Over the past two decades, the reduction of alkyl- or aryl- sulfonylbenzenes has been the subject of numerous investigations because of interest in their use in organic synthesis[1] and the manifold of observed mechanisms (selective sulfur–carbon bond cleavage, coupling reaction, self alkylation,. . .).[1–8] After the cleavage step, whose nature depends on experimental conditions and selectivity, the produced radical may be involved in a series of reactions like H-atom transfer, $S_{RN}1$,. . .. Despite this large literature, the factors governing the selectivity of the S–C bond cleavage or more generally the changes in the nature of the chemical steps are still not well understood.[9,10] As a matter of fact, under electrochemical reduction, alkyl- or aryl-sulfonylbenzenes lead first to radical anions that are often unstable. The radical anion of the unsubstituted aryl alkyl-monosulfone undergoes a fast selective cleavage (cleavage kinetics rate constant around 10^5 s^{-1}) of the sulfur–carbon bond to yield aryl sulfinate ions and hydrocarbons (β-cleavage).[10,11] The reductive process for the aromatic polysulfones (**1–5**) is more complex and the electrogenerated radical anions decay along very different chemical pathways. Reduction of the *o*-bis(alkylsulfonyl)benzene **1a** leads to the the R-alkylated mono sulfone.[1,10,12] The proposed mechanism involves a regioselective β-cleavage reaction (formation of the aromatic sulfinate and the alkyl radical $R^•$) which is followed by a coupling reaction between $R^•$ and the substrate radical anion, then by an elimination.[5,10] When R is a phenyl (**1b**) group, the regioselectivity of the bond cleavage reaction changes and the reduction simply leads to the formation of the diphenylsulfone (selective cleavage of SO_2R^-). Surprisingly, completely different reactivities appear for the other polysulfones. When tri-sulfones **3** are reduced, coupling products are isolated, such as the tetra- or penta-(alkylsulfonyl) biaryls, depending on the nature of the alkyl groups.[6] 1,2,4,5-Tetrakis(phenylsulfonyl)benzene **5**[2] and pentakis(phenylsulfonyl)benzene[13] could be reversibly reduced into highly stabilized anion radical and dianion whereas hexakis(phenylsulfonyl)benzenes showed a specific behavior of a particularly stable radical anion owing to conformational changes associated with a single electron-transfer.[7]

In the present paper, we especially focused on the first steps of the global mechanisms to attempt a rationalization of the variations in the chemical pathways for different aromatic polysulfones (see Scheme 1 for the investigated compounds). The cathodic reductions of several aromatic poly-sulfones bearing two, three or four ethyl- and phenyl-sulfonyl groups have been systematically investigated in aprotic solvent (acetonitrile). Decays of the electrogenerated radical anions were analyzed as a function of the number and the nature of the sulfonyl substituents. Density functional calculations at the B3LYP/6-31G* level were performed and discussed in connection with the dissociative electron transfer model[14] in agreement with the electrochemical data: redox behaviour and reactivities of electrogenerated radical anion.

Experimental

Chemicals

All substrates were prepared according to previously published procedures.[15] Acetonitrile (ACN) from SDS contained less than 50 ppm of water and was used without further



Scheme 1 General formula of poly-sulfones investigated in this work.

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purification. Tetra-n-butylammonium tetrafluoroborate was from Fluka and used as received (puriss, electrochemical grade)

Electrochemical experiments

Electrochemical instrumentation consisted of a Tacussel GSTP4 programmer and of a home-built potentiostat equipped with a positive-feedback compensation device.[16] The voltammograms were recorded with a 310 Nicolet oscilloscope. Electrochemical investigations were carried out in a one compartment, three-electrode cell, using a Pt wire as counter electrode and a SCE electrode as reference. Ferrocene was added to the electrolyte solution at the end of each series of experiments and the ferrocene/ferrocenium couple (E° = 0.405 V *vs.* SCE) served as an internal probe. The working electrode was a glassy carbon disk (1.5 mm or 3 mm diameter). The electrode was carefully polished before each voltammetry experiment with 1 µm diamond paste and ultrasonically rinsed in absolute ethanol. Electrolyte solutions were thoroughly purged and kept under a dry argon flow during each run. Experiments were performed at room-temperature ($20 \pm 2\,^\circ$C). Numerical simulations of the voltammograms were performed with the BAS DigiSim simulator 3.03, using the default numerical options with the assumption of planar diffusion and a Butler-Volmer law for the electron transfer. The charge-transfer coefficient, α, was taken as 0.5 and the diffusion coefficients were taken equal for all species ($D = 10^{-5}$ cm^2 s^{-1}).

Theoretical modeling

The calculations were performed using the Gaussian 98W package.[17] Gas phase geometries and electronic energies were calculated by full optimization without imposed symmetry of the conformations using the B3LYP[18] density functional with the 6-31G* basis set,[19,20] starting from preliminary optimizations performed with semi-empirical methods. Geometries were checked by frequency calculations except for the two largest polysulfone radical anions. Because of the difficulty in running frequency calculations with these molecules, the quality of the obtained minima were checked by restarting the optimizations from other conformations. We checked that the spin contamination remains low ($s^2 < 0.765$) for all the open-shell B3LYP calculations (radical anion). Total energies were obtained after calculation of the frequencies. These values were corrected by a scaling factor (0.9804) applied to the zero-point energies and thermal energy corrections.[21]

Results

Disulfones

The radical anion decay kinetics were derived from scrutiny analyses of the voltammetric current responses of the first reduction wave. In acetonitrile (ACN) and at low sweep rate (0.1 V s^{-1}), disulfones **1** display a partially reversible wave. The reversibility increases with the scan rate and becomes total for scan rates higher than 0.2 V s^{-1} for **1a** and 2 V s^{-1} for **1b** (for a 2×10^{-3} mol L^{-1} concentration). The formal potentials E° for the sulfone/sulfone radical anion couples were immediately derived as the half-sum between the forward and the backward scan from these reversible voltammograms (see also Table 1). For both compounds, we observed that the reversibility did not change when the sulfone concentration was increased by at least a factor of 10 for any investigated scan rates, showing that the corresponding radical anions decay according to a first-order kinetics.[22] This observation corresponds to a kinetic situation where the C–S bond cleavage is the rate-determining step and agrees with the previously published results.[6] For **1a**, the overall reaction is a self-alkylation process but the voltammetric behaviour indicates that the first chemical step following the formation of the radical anion is the S–C bond cleavage. To measure the kinetics parameters for both the heterogeneous electron transfer rate and its associated chemical steps, the experimental voltammograms were compared with theoretical curves calculated using the DigiSim software.[23] We obtained for k_s (standard electron-transfer rate constants uncorrected from the double layer effect) values of 0.08–0.1 cm s^{-1} and 0.3 cm s^{-1} for **1a** and **1b**, respectively, that correspond to moderately slow redox couples.

Table 1 Electrochemical data for aromatic poly-sulfones

Compounds	E°/V *vs.* SCE	k_s/cm s^{-1}	Chemical rate constant[a]
1a	−1.688	0.08	0.1 s^{-1}
1b	−1.591	0.3	1–2 s^{-1}
2	−1.844	0.15	5×10^5 L mol^{-1}.s^{-1}
3a	−1.55	0.07–0.08	8×10^3 L mol^{-1}.s^{-1}
3b	−1.351	0.2	1×10^2 L mol^{-1}.s^{-1}
4	−1.038	0.3	No reaction[a]
5	−0.607	0.2	No reaction[a]

[a] First order rate constant for cleavage bond reactions. Second order rate constants for dimerization.

From comparison with calculated curves, the voltammogram reversibility *versus* the scan rate allow determination of the kinetics parameters of the chemical step triggered by electron transfer. Thus, the kinetics rate constants for the C–S bond cleavage were found to be $k_1 = 0.1$ s^{-1} for **1a** and $k_1 = 1$–2 s^{-1} for **1b**. Both k_1 values are rather modest, but it is noticeable that the cleavage rate is more than 10 times higher for **1b** when the leaving group is a phenyl sulfinate. A very different behaviour from that described for **1a** is observed for the di-sulfone **2** (Fig. 1). Irreversible monoelectronic[24] voltammograms are recorded in the scan-rate range 0.1–20 V s^{-1}. A partial reversibility becomes visible when the scan rate is greater than 50 V s^{-1} indicating a considerable decrease of the radical

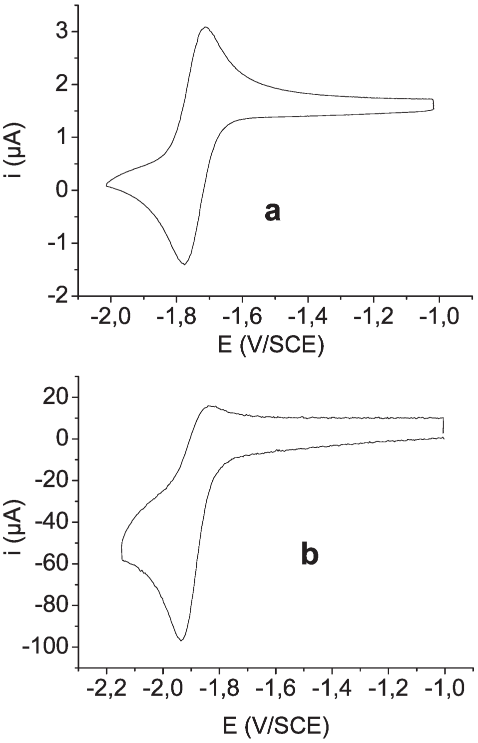


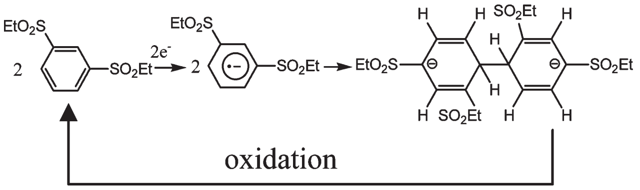
Fig. 1 Cyclic voltammetry of $\approx 10^{-3}$ mol L^{-1} **1a** (a) and **2** (b) in ACN-0.1 mol L^{-1} Bu$_4$NBF$_4$ on a glassy carbon disk electrode at 0.5 (a) and 50 V s^{-1} (b).

anion life-time from comparison with those from the *ortho* disulfones.[25] It is also noticeable that the $E°_{2/2^{\bullet-}}$ value (−1.844 V) is 200 mV more negative than those of **1a** or **1b**, showing that **2** is more difficult to reduce than **1** in agreement with a better stabilization of the radical anion by two conjugated sulfone groups. To characterize the nature of the follow-up reaction to the electron-transfer step for **2**, we investigated the peak-potential variations in the irreversible voltammograms as a function of scan rate and initial sulfone concentration (Fig. 2).[26] The peak potential (E_p) was found to vary linearly as a function of log(v) with a slope $\partial E_p/\partial \log(v) = -19.5$ mV decade^{-1} and the linear bulk concentration[27] dependence of the peak potential was measured $\partial E_p/\partial \log(c) = 19.52$ mV decade^{-1}. These slopes show a second-order character for the follow-up reaction and suggest a DIM1 mechanism *i.e.* a fast electron transfer followed by a coupling reaction between two electrogenerated radical anions (see Scheme 2), leading to the formation of coupling products.[26] However, the resulting coupling product is observed to be very easily oxidized at low anodic potential (−0.70 V *vs.* SCE). This behaviour has been already described in previous studies concerning tri-sulfones **3** for which the transient formation of a dianion was demonstrated.[6a] By analogy, the chemically reversible process can be written as in Scheme 2.

According to this coupling scheme, numerical simulations give the standard electron-transfer rate constant $k_s = 0.15$ cm s^{-1} and a second order dimerization rate constant $k_{dim} = 5 \times 10^5$ L mol^{-1} s^{-1}.

Trisulfones

We were then interested in the reduction of symmetrical trisulfones **3a** and **3b**. Both of these compounds displayed reversible (or quasi-reversible) voltammograms in the scan-rate range 0.1–50 V s^{-1}. In contrast to what was observed for di-sulfones **1**, the reversibility of the voltammogram decreases when the concentration of sulfone **3** is increased, indicating that the rate-determining step is a bimolecular process involving the corresponding anion radical $\mathbf{3}^{\bullet-}$. Because of the long lifetime of $\mathbf{3}^{\bullet-}$ that is close to the longest available experimental time in cyclic voltammetry,[28] it was difficult to obtain a clear-cut answer about the nature of the bimolecular kinetic step as we did for **2**. However in previous investigations, dihydro-dimer compounds were isolated from the cathodic reduction of **3a** and **3b** and it is likely that the decay of $\mathbf{3a}^{\bullet-}$ and $\mathbf{3b}^{\bullet-}$ follow the same radical–radical coupling mechanism as obtained for **2**.[6a] Both compounds behave similarly regarding the variation of the voltammogram's reversibility with concentration, but for the same scan rate and concentrations, **3a** displays a lower reversibility corresponding to a higher reactivity for $\mathbf{3a}^{\bullet-}$ than that for $\mathbf{3b}^{\bullet-}$. Assuming the DIM1 mechanism, the calculated coupling rate constant k_{dim} is 10 times higher for **3a** ($k_{dim} = 8 \times 10^3$ L mol^{-1} s^{-1}) than that for **3b** ($k_{dim} = 1 \times 10^2$ L mol^{-1} s^{-1}) that can be explained because of different steric bulk effects. Concerning the heterogeneous charge-transfer rate constants, the k_s value is slightly higher for **3b**, $k_s = 0.2$ cm s^{-1} than **3a** (0.07–0.08 cm s^{-1}).



Scheme 2 DIM1 mechanism.

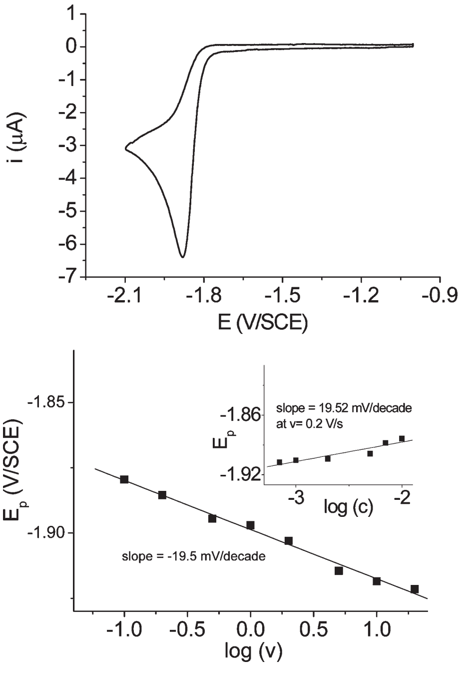


Fig. 2 Cyclic voltammetry of 1.6×10^{-3} mol L^{-1} **2** in ACN + 0.1 mol L^{-1} Bu_4NBF_4 at a glassy carbon disk electrode. sweep rate = 0.1 V s^{-1} (up). Variation of the reduction peak potential E_p with the logarithm of the scan rates, v in V s^{-1}. Insert: Variations of the reduction peak potential E_p with the logarithm of the concentration of **2**, at 0.2 V s^{-1} (down).

We also performed cyclic voltammetry experiments of trisulfone **4**. Despite a lower apparent steric hindrance (two adjacent positions are free on the aromatic ring), reversible voltammograms are obtained in the whole scan-rate range 0.1–200 V s^{-1} for all used concentrations of **4** (1–10 mmol L^{-1} range) showing a longer life-time than those of $\mathbf{2}^{\bullet-}$ and $\mathbf{3}^{\bullet-}$. Similar observations were made for the cathodic reduction of the tetra-sulfone **5** that also exhibits reversible voltammograms in the scan-rate range 0.1–100 V s^{-1}, associated with a quasi-Nernstian electrochemical behaviour. Values of $k_s = 0.3$ cm s^{-1} and $k_s = 0.2$ cm s^{-1} for $\mathbf{4}/\mathbf{4}^{\bullet-}$ and $\mathbf{5}/\mathbf{5}^{\bullet-}$ couples, respectively, were extracted from the peak to peak potential difference.

Discussion

As a general trend, increasing the number of sulfonyl groups onto the aromatic core induces a better stabilization of the transient radical anion that can be partly ascribed to an increasing delocalization of the unpaired electron in the radical anion and steric hindrance. We also note that k_s values are higher for poly(arylsulfonyl)benzenes (**1b** and **3b**, for instance) than for the poly(alkylsulfonyl)benzenes (**1a** and **3a**) (Table 1) in agreement with a better delocalization of the charge in the radical anion that results in a lower solvent reorganization during the electron transfer. However, the stabilization of the radical anion is not an "absolute" requisite as demonstrated by the comparison between $\mathbf{3b}^{\bullet-}$ and $\mathbf{4}^{\bullet-}$ on one hand and between $\mathbf{1a}^{\bullet-}$, $\mathbf{1b}^{\bullet-}$ and $\mathbf{2}^{\bullet-}$ on the other hand. For the last two types of sulfone, we observed for the *o*-disulfone radical anion a bond cleavage contrary to the *meta* disulfone $\mathbf{2}^{\bullet-}$ for which coupling reactions are observed. In a situation where bond cleavage occurs, the other question concerns the factors governing the regio-selectivity (α- or β-bond cleavage). To explain these behaviours, we performed a series of theoretical calculations using the B3LYP density functional method.

We first try to explain and predict the $E°$ variations with the number and position of sulfonyl groups. Theoretical $E°$s were estimated from the difference between the electronic energies for the radical anion and the neutral sulfone in the gas phase.

Table 2 Comparison of electrochemical data with B3LYP calculations[a].

Compounds	U_{neutral} (a.u.)	$U_{\mathrm{radical\ anion}}$ (a.u.)	$\Delta E^\circ_{\mathrm{theo}}$/ eV	$\Delta E^\circ_{\mathrm{exp}}$/ eV
1a	−1486.647692	−1486.664777	−1.36	−1.081
1b	−1791.473968	−1791.500621	−1.10	−0.985
2	−1486.651817	−1486.665752	−1.45	−1.237
3a	−2113.848332	−2113.882980	−0.89	−0.943
3b	−2571.1023623	−2571.140571	−0.79	−0.744
4	−2571.090022	−2571.139942	−0.47	−0.431
5	−3350.693409	−3350.760573	0.0	0.0

[a] E° for compound **5** is taken as an internal reference.

As seen in Table 2 and Fig. 3, a good correlation is obtained between the calculated values and the experimental data. The slope value is lower than the unity (slope = 0.83) that falls in line with a lesser solvation of the radical anion when the size of the molecule increases.

Concerning the reactivity of the radical anion, the first addressed point concerns the higher bond cleavage rate and the variation of the regioselectivity when R is an aliphatic or aromatic group (see **1a** and **1b** for example). In the framework of the dissociative ET model, the standard free energy of the dissociation energy of the C–S bond is related to the various characteristic standard potentials and to the dissociation energy of the C–S bond.[29]

$$\Delta G^0_{\mathrm{ArSR}^{\bullet-}\rightarrow\mathrm{Ar}^{\bullet}+\mathrm{SR}^-} = D_{\mathrm{Ar-SR}} - E^0_{\mathrm{SR}^{\bullet}/\mathrm{SR}^-} + E^0_{\mathrm{ArSR/ArSR}^{\bullet-}} + T\left(\bar{S}_{\mathrm{ArSR}} - \bar{S}_{\mathrm{Ar}^{\bullet}} - \bar{S}_{\mathrm{SR}^-}\right)$$

The two main factors governing the selectivity are the bond dissociation energy D and the oxidation potential of the leaving group. Concerning the bond dissociation energies, the D values can be estimated by means of B3LYP density functional calculations (see Table 3) for the disulfones **1a**, **1b** and trisulfones **3a**, **3b**. When R is an aliphatic group, the α-bond (Ar–SR) is 7–8 kcal mol^{-1} stronger than the β- (ArS–R) bond. When R is a phenyl group an opposite situation is observed, the α-bond becomes weaker than the β-bond by around 3 kcal mol^{-1}. The same effect also affects the kinetics barrier as the standard intrinsic energy, depends on D, a lower D value leads to a lower intrinsic barrier.[30] Concerning the oxidation potential of the fragment that will take the charge, there are no precise determinations of all the $E^\circ_{\mathrm{SR}^{\bullet}/\mathrm{SR}^-}$ values. However, two possibilities exist: the charge is taken either by the carbon atoms (production of the carbanion) or by the group bearing the $\mathrm{SO_2}^-$ (formation of a sulfinate $\mathrm{RSO_2}^-$). Since the sulfinate is always more difficult to oxidize than the carbanion, the charge will be taken by the $\mathrm{SO_2}$ moieties. Both effects are in agreement with the inversion in the regioselectivity observed when passing from the alkyl to the aromatic substituents.

Table 3 Comparison of electrochemical data with B3LYP calculations[a]

Compounds	$D_{\mathrm{Ar\text{-}SR}}$/kcal mol^{-1}	$D_{\mathrm{ArS\text{-}R}}$/kcal mol^{-1}
1a	62.4	54.7
1b	56.5	61.6
3a	62.5	55.0
3b	62.6	66.0

The next point is the evolution of the reactivity *i.e.* passage from a cleavage reaction to a coupling reaction. The most remarkable fact is the change of reactivity as illustrated by the change in the E_p *vs.* log(v) and E_p *vs.* log(c°) curves that corresponds to a dimerization reaction. As a possible explanation, it was suggested that coupling reactions are simply observed because of a decrease of the cleavage rate with the number of the sulfonyl groups or positions makes it possible for other slow reactions to occur. This explanation is not entirely suitable, as the radical anion lifetimes are shorter for **2** (when the coupling reaction occurs) than for **1** (when the cleavage reaction occurs). Radical–radical dimerizations are strongly dependent on the localization and density of the unpaired electron on the aromatic ring. It is therefore useful to examine the spin delocalization in the radical anion especially on the aromatic carbon bearing the sulfone groups and on the opposite position. Spin densities were calculated using the B3LYP method and are displayed on Fig. 4. The EPR spectrum for **1a**$^{\bullet-}$ has previously been obtained, a good agreement with the calculated spin density is observed.[8] When passing from the disulfone **1a**$^{\bullet-}$ to **2**$^{\bullet-}$, a large increase of the spin localization on the *para* (to sulfonyl groups) aromatic carbon (0.201 and 0.434) together with a large decrease on the ring carbon adjacent between both sulfone groups (0.289 and 0.128) is observed. This result explains the increase of the radical–radical coupling reactivity due to an orientation and localization of the unpaired electron by the two *meta* sulfone groups. The same results are expected and found for the radical anion of trisulfones **3a** and **3b**.

However, if, in this last case, the radical–radical coupling process is the most favored process from the spin localization point of view, the simultaneous increase of the steric hindrances leads to a decrease of the dimerization rates. Another illustration of the localization effect comes from the trisulfone **4**, for which a reversible voltammogram is observed. This indicates that the radical anion has a low reactivity *versus* both the

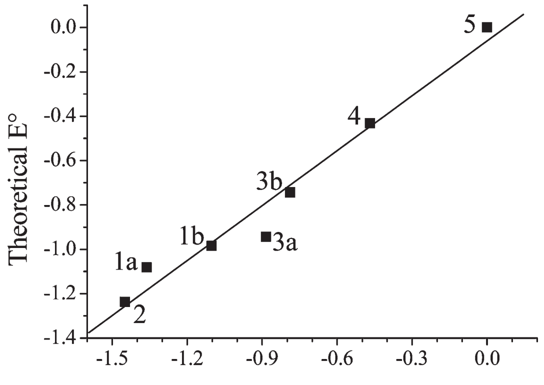


Fig. 3 Variations of experimental E° with DFT calculations predictions.

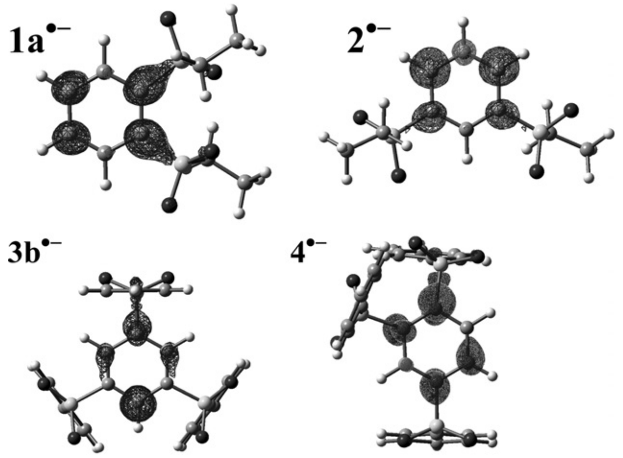


Fig. 4 Spin densities from B3LYP/6-31G* calculations predictions (iso spin density curves for 0.005 a.u).

bond cleavage and the dimerization, despite the same number of sulfone groups and an expected lower steric hindrance due to two adjacent free aromatic carbons.

Conclusion

The reactivity of electrogenerated radical anions of sulfone follows a manifold of mechanisms. The specificity can be explained by a subtle competition between bond cleavage influence, by the stability of the different fragments and their bond energy on the one hand and by the localisation of the unpaired electron on the other hand. All these parameters have to be considered to explain a change in the mechanism when introducing or modifying the position of the sulfone group. A detailed analysis of the electrochemical data with the help of DFT calculations allows a clean rationalization of all these observations.

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22 C. P. Andrieux and J.-M. Savéant, in *Investigations of rates Mechanism of reactions*, ed. C. F. Bernasconi, Wiley, New York, 1986, vol. 6, 4/E, Part 2 p. 305–390.

23 From reversible or quasi-reversible voltammograms, peak-potential separations between the cathodic and anodic processes give a measurement of the kinetics parameters for the heterogeneous electron transfer.

24 By comparison with the reversible one-electron oxidation wave of ferrocene.

25 Concentration of **2** is 1.6×10^{-3} mol L^{-1}.

26 C. P. Andrieux, L. Nadjo and J.-M. Savéant, *J. Electroanal. Chem.*, 1973, **42**, 223.

27 Concentrations were varied between 7×10^{-4} and 10^{-2} mol L^{-1}.

28 The reversibility for $\mathbf{3b}/\mathbf{3b}^{\bullet -}$ was almost total at 0.1 V s^{-1} for a 10^{-3} mol L^{-1} concentration of **3b**.

29 (*a*) C. P. Andrieux, A. Le Gorande and J.-M. Savéant, *J. Am. Chem. Soc.*, 1992, **112**, 6892; (*b*) J.-M. Savéant, *J. Phys. Chem.*, 1994, **98**, 3716; (*c*) C. P. Andrieux, C. Combellas, F. Kanoufi, J.-M. Savéant and A. Thiébault, *J. Am. Chem. Soc.*, 1997, **119**, 9540; (*d*) J.-M. Savéant, in *Advances in Physical Organic Chemistry*, ed. T. T. Tidwell, Academic Press, New York, 2000, vol. 35, p. 177–192 and references therein.

30 According to a development of the dissociative ET model to the decomposition of radical anion, the standard activation energy depends directly on the bond dissociation energy ($\Delta G^{\circ\ddagger}$ proportional to $D/4$) (ref. 14).