

Electrochemical and computational study of the initiation step in the photoinduced electron transfer reaction between sulphur and selenide nucleophiles toward 1-bromonaphthalene

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The initiation step of the photosubstitution reaction between 1-bromonaphthalene and a number of nucleophilic sulphur and selenium centred anions to afford 1-naphthylsulphide/selenide derivatives was investigated experimentally and by means of quantum chemical calculations. The frontier orbital energies of the anions were computed, and the values obtained agree with the lack of reactivity in the ground state. This model fails in accounting different reactivity of the anions toward the triplet state of 1-bromonaphthalene. Basicity and E_{ox} were also calculated for all the anions finding a better agreement with the experimental reactivity and other measured properties such as pKa and oxidation potentials. Copyright © 2016 John Wiley & Sons, Ltd.

Keywords: DFT calculation; photoinduced electron transfer; redox properties

INTRODUCTION

The important role of chalcogenide compounds in both environmental and biological systems has long been recognized.^[1] The synthetic applicability of chalcogenide compounds is also well established and has been studied extensively over the past 30 years.^[2]

We have reported both the selenide and sulphide incorporation into aromatic ring by selenobenzamide (SeCNH(Ph)), selenourea ($\text{SeCNH(NH}_2\text{)}$), selenocyanate (SeCN), thiourea ($\text{SCNH(NH}_2\text{)}$), tioacetate and tiobenzoate (SC(O)CH_3 , SC(O)Ph) anions to afford areneseleolate/thiolate ions (ArSe/S^-) under photostimulation in the presence of *tert*-butoxide ion as electron donor (entrainment conditions) in DMSO.^[3] By using this methodology in a “one-pot” procedure, aryl selenide/sulphide anions (ArSe/S^-) can be trapped by a subsequent aliphatic nucleophilic substitution giving aryl alkyl selenides from good to excellent yields (67–100%). Diarylselenide/sulphides are also found as side product. These compounds are rationalized as $S_{\text{RN}}1$ products coming from the addition reaction between aryl radicals and ArSe/S^- anions produced in the reaction course. This simple approach is compatible with electron donating and electron withdrawing substituents such as nitro and carbonyl groups, and it turns to be an interesting alternative from an organic synthetic point of view.

The chain reaction of the $S_{\text{RN}}1$ process requires an initiation step, which involves an electron transfer (ET) from the nucleophile or from a suitable electron source to the substrate. The most frequently used method in our reaction protocols is the photoinitiation (photoinduced electron transfer, PET); however, other initiation procedures such as chemical initiation by alkali metals in liquid ammonia, electrochemical initiation at a cathode and the use of Fe^{2+} , Sml_2 , and

Na(Hg) have been reported.^[4] The $S_{\text{RN}}1$ substitution of aromatic systems is presented in the Scheme 1.

In Scheme 1 it is possible to see that PET initiation step triggers the $S_{\text{RN}}1$ reaction, and it is a critical step for the whole photosubstitution process. When the nucleophile is not able to initiate the reaction an “entrainment” reagent is added to the reaction mixture; in most of the cases, an excess of a base like potassium *tert*-butoxide (*tert*-BuOK) is used. Even there is a general trend between the basicity of the nucleophile and its reduction power,^[5] in most of the cases a comprehensive study including proton affinity, reducing power and photochemical behaviour is not considered. In addition, for our particular interest, very little is known about the redox properties of chalcogenide compounds. A few papers have been devoted to electrochemical investigation of aryl sulphide and aryl selenide anions,^[6] but no reports have appeared so far on these reactive nucleophiles in PET reactions. In this paper, we report our results regarding the reactivity of a number of selenium and sulphur centred anions depicted in chart 1 in the photo-substitution reaction toward 1-bromonaphthalene as an aryl halide generic model. In addition, molecular properties such as reducing power measured by means of cyclic voltammetry, proton affinities, oxidation potentials and ΔG_{ET}^0 values obtained by DFT calculations will be presented.

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Biography

Lydia M. Bouchet received her PhD in chemistry from the National University of Cordoba, Argentina under the supervision of Prof Juan E. Argüello (2013). Dr Bouchet worked in the development of synthetic methodologies for organoselenium compounds, via oxidative and reductive electro transfer reactions. During the PhD, Dr Bouchet, also worked under the supervision of Dr Raquel Galián (2011 in University of Valencia) and Prof Marc Robert (2012 in University of Paris Diderot). Dr. Bouchet was a postdoctoral research fellow at National University of Cordoba (2014-2016, Prof Verónica Brunetti). In 2016, she joined the Research Group of Prof. Marcelo Calderón at the Freie Universität Berlin for her Postdoctoral work.

**Biography**

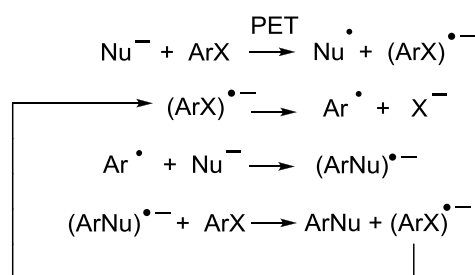
Adriana B. Pierini graduated as Licentiate (1975) and PhD in Organic Chemistry (1979) from the Faculty of Chemical Sciences, National University of Córdoba (FCQ, UNC), Argentina. Postdoctoral Fellow at the University of Texas at Austin (1979-1981, 1988) to work with Professor Michael J. S. Dewar. Full Professor (since 1996) and Principal Researcher (since 2005) of the National Research Council of Argentina (CONICET) at FCQ, UNC, Argentina. Faculty Vice Dean (1994-1996) and Head of the Organic Chemistry Department (2010-2012, 1996-1998) (FCQ, UNC). President of the Organic Chemistry Research Argentina Society (2011-2013). Recipient of the Rafael Labriola (1995) and Konex-Diploma Awards (2013). Co-author of five chapters in books and one article in Chem. Rev. Main area of interest: Molecular Modeling of Organic Reaction Mechanisms and Reactivity in Electron Transfer Processes.

**Biography**

Verónica Brunetti graduated from the Faculty of Chemical Sciences of National University of Córdoba (UNC) in 1994. She studied passive salts film formation on silver mainly by electrochemical methods and received her PhD from UNC in 2000. She carried out post-doctoral work on the dynamics at the adsorbate-metal interface investigated with a scanning tunneling microscope operating under electrochemical control, supervised by Professors A.J. Arvia and R. Salvarezza at the National University of La Plata, Argentina, from 2000 to 2002. She then returned to the Physical Chemistry Department at UNC and became a Researcher at CONICET (National Council of Scientific and Technical Research) in 2004. At present, she is Independent Researcher of CONICET and Adjunct Professor at UNC. Her research interests include surface chemistry, electrochemistry, catalysis and sensors by using dendronized materials.

**Biography**

Juan E. Argüello graduated from the Faculty of Chemical Sciences of National University of Córdoba (UNC) in 1996. He studied the photoinduced initiation step in the aliphatic $S_{RN}1$ reaction under the supervision of Prof. Peñeñory and received his PhD from UNC in 2001. He carried out post-doctoral work on the electrochemical properties of cobalt complexes, supervised by Professor Savéant at the Paris 7 University in France from 2003 to 2004. After a second post-doctoral stay at Prof. Miranda's laboratory in Polytechnic University of Valencia (Spain), he returned to the Organic Chemistry Department at UNC as a Researcher at CONICET (National Council of Scientific and Technical Research) in 2006. At present, he is Independent Researcher of CONICET and Assistant Professor at UNC. His research interests include photocatalysis, electrochemistry and synthetic organic chemistry.



Scheme 1. $S_{RN}1$ mechanism for aromatic systems

EXPERIMENTAL**General procedures**

The general methods and procedure for the photoinduced reaction are the same as published before.³ ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, on a Bruker AC-400 (400 MHz) spectrometer, and all spectra are reported in δ (ppm) relative to Me_4Si , with CDCl_3 as solvent. Gas chromatographic analyses were performed on a Hewlett Packard 6890 A with a flame-ionization detector. GS/MS analyses were carried out on a Shimadzu GC-MS QP 5050 spectrometer.

Materials

Potassium *tert*-butoxide, selenourea, KSCN, KSeCN, thiourea, *N*-phenylthiourea, *N,N'*-diphenylthiourea, potassium thioacetate, thiobenzoic acid, tetrabutylammonium tetrafluoroborate (TBATFB), *n*-butyl lithium, methyl iodide (MeI) and 1-bromonaphthalene were all high purity commercial samples which were used without further purification. Selenobenzamide was prepared by the addition of "in-situ" generated H_2Se to benzonitrile.^[7]

DMSO was distilled under vacuum and stored over molecular sieves (4 Å). The anions were generated in situ by acid-base deprotonation using *tert*-BuOK in the photochemical experiments,

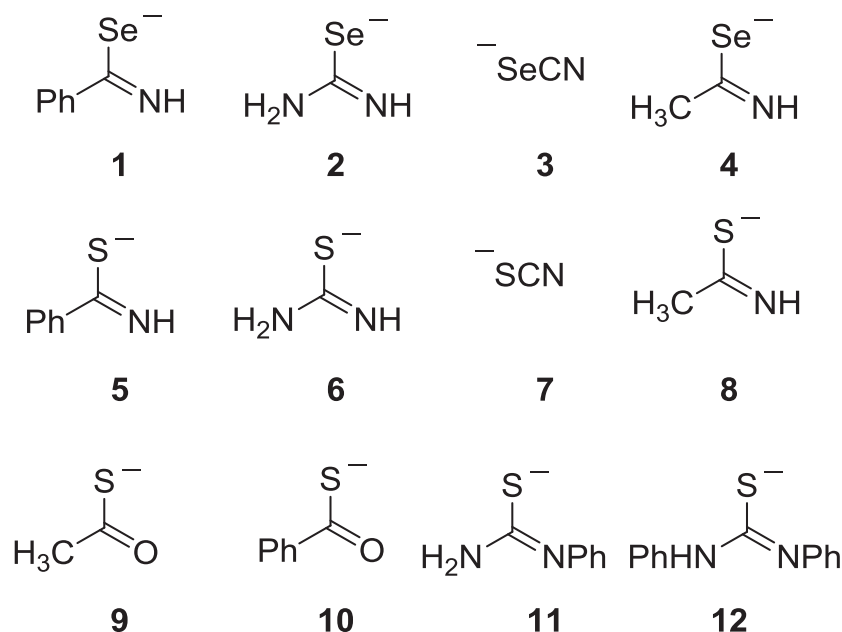


Chart 1. Selenium and sulphur centred anions under study

while in the cyclic voltammetry experiments, *n*-butyl lithium was used as a base.

All the products are known and exhibited physical properties identical to those reported in the literature. Also, they were isolated by radial chromatography from the reaction mixture and characterized by ^1H and ^{13}C NMR and mass spectrometry.

Photoinduced reactions of anion 5, 8, 11, 12 with 1-bromonaphthalene (general procedure)

The photochemical reaction was carried out in a three-necked, 10-mL Schlenk tube equipped with a nitrogen gas inlet and a magnetic stirrer. The flask was dried under vacuum, filled with nitrogen and then charged with 10 mL of dried DMSO. Then 2.5 mmol of the nucleophile and 0.5 mmol of 1-bromonaphthalene (**13**) were added to the degassed solvent under nitrogen. After 1 h of irradiation with a medium pressure Hg lamp, the reaction was quenched by the addition of an excess of MeI (6 equiv) and 30 mL of water, and then the mixture was extracted with methylene chloride (3×20 mL). The organic extract was washed twice with water, dried and the products were quantified by GC with diphenyl disulphide as internal standard.

Cyclic voltammetry

The working electrode was a 3-mm-diameter glassy carbon electrode disk (Tokai) that was carefully polished and ultrasonically rinsed in absolute ethanol before use. The counter electrode was a platinum wire, and the peak potential values are referenced to NHE. All experiments have been done at 20 °C under N_2 atmosphere. Cyclic voltammetric data were recorded using a commercial computer controlled potentiostat (AUTOLAB PGSTAT20, ECO-Chemie).

Computational methods

DFT calculations were performed using the B3LYP^[8] hybrid GGA functional together with the standard 6-31 + G* basis set for carbon and hydrogen and 6-311 + G* for Br, Se and S atoms with full geometry optimization. The solvent effects on the mechanism have been

considered using a self-consistent reaction field (SCRf) method based on the Tomasi's polarizable continuum model (PCM). As the solvent used in the experimental work was DMSO, we have selected its dielectric constant $\epsilon = 46.7$. Thermodynamic calculations were made with the standard statistical thermodynamics at 298.15 K and 1 atm. All calculations were carried out with the Gaussian09 suite of programmes and include the zero point energy correction.^[9] The characterization of stationary points was done by Hessian matrix calculations, with all positive eigenvalues for a minimum.

RESULTS AND DISCUSSION

From our previous report it is demonstrated that only thiourea anion (**6**) is able to initiate the chain $\text{S}_{\text{RN}}1$ reaction toward 1-bromonaphthalene; none of the selenium centred nucleophiles, selenobenzamide (**1**), selenourea (**2**) and selenocyanate (**3**) are able to transfer one electron to aryl halides under photostimulation.^[3] Still, the reactivity of sulphur analogues thiobenzamide ($^-\text{SCNH}(\text{Ph})$, **5**), thioacetamide ($^-\text{SCNH}(\text{CH}_3)$, **8**) and thiourea derivatives *N*-phenylthiourea ($^-\text{SCNHPh}(\text{NH}_2)$, **11**) and *N,N'*-diphenylthiourea ($^-\text{SCNHPh}(\text{NHPh})$, **12**) anions have not been investigated yet. In order to achieve this knowledge, we carried out the preparative photolysis study of these anions in the presence of 1-bromonaphthalene as a model aryl halide compound.

Reaction of sulphur centred anions with 1-bromonaphthalene in DMSO

Bidentate nucleophiles derived from the thioamide derivatives (**5**, **8**, **11** and **12**) can be generated in DMSO under nitrogen atmosphere by deprotonation with *tert*-butoxide anion ($\text{pK}_a = 32.2$).^[10]

When a solution of these anions was stirred in the presence of 1-bromonaphthalene (**13**) under irradiation at $\lambda_{\text{max}} > 320$ nm and quenched with methyl iodide, the expected products coming from reduction, methylated substitution-fragmentation and double substitution, naphthalene (**14**), methyl-1-naphthylsulphide (**15**) and di-1-naphthylsulphide (**16**), respectively, were found (Eqn 1); the most relevant results are summarized in Table 1. Both anions derived from

Table 1. Reactions of anion **5**, **8**, **11** and **12** with 1-bromonaphthalene (**13**) in DMSO¹

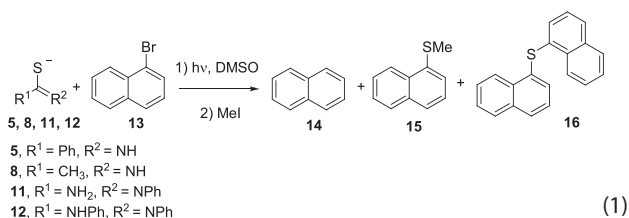
Entry	Anion	Conv'n	Product yield (%) ²		
			14	15	16
1 ²	8	86	12	68	6
2 ²	5	60	1	20	28
3 ³	11	43	6	25	11
4 ³	12	62	10	34	18

¹1-BrC₁₀H₇: .05 M, Anion: 0.25 M, irradiation under nitrogen atmosphere, reactions quenched with ICH₃. Reaction yields determined by CG using the internal method, error < 5.

²1-h irradiation time.

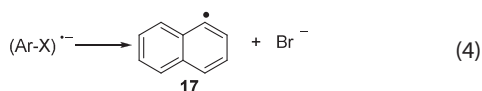
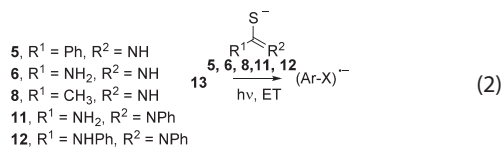
³3-h irradiation time.

thioacetamide and thiobenzamide, **5** and **8**, respectively, are reactive toward 1-bromonaphthalene affording 86 and 60% of conversion respectively (Table 1, entries 1 and 2). Thiourea derivatives **11** and **12** are also reactive, but longer irradiation time is necessary for a moderate conversion, 43 and 62% respectively, after 3 h of irradiation time (Table 1, entries 3 and 4). For all the anions under study, the substituted product **15** and **16** are formed in a significant amount, between 20 and 68% yield. These reactions do not proceed in the dark.

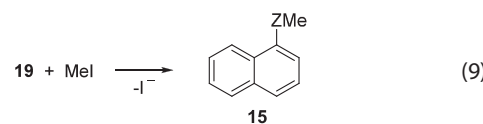
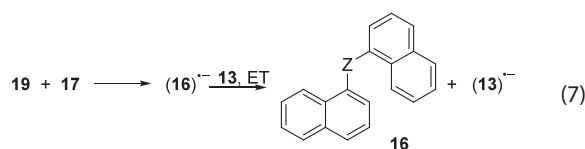
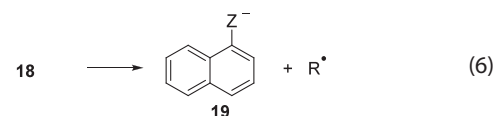
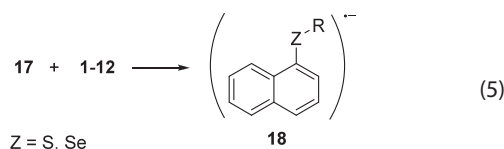


From literature it is known that thiobenzoate (**10**) and thioacetate (**9**) anions are not able to initiate the reaction; however, in the presence of potassium *tert*-butoxide, good yield of products **14**, **15** and **16** are formed.

Summing up, the photosubstitution reaction is initiated by a PET between photoexcited 1-bromonaphthalene and thiourea, thiobenzamide, thioacetamide anions, and in a lesser extent, thiourea derivatives **11** and **12** (Eqn 2). For selenium centred anions **1–3** and sulphur anions **9** and **10**, an entrainment reagent is necessary, in these reactions *tert*-butoxide anion is used to accomplish the initiation step (Eqn 3). Upon ET the unstable 1-bromonaphthalene radical anion is formed, which quickly fragments into 1-naphthyl radical and bromide anion (Eqn 4).^[11]



1-Naphthyl radical can follow three competitive pathways to account the product distribution observed as outcome of the reaction. Namely, addition to sulphur/selenium centred anions to afford **18** radical anion, this unstable intermediate fragments giving naphthyl selenide/sulphide anion (**19**) (Eqns 5 and 6). As the concentration of anion **19** increases the addition to 1-naphthyl radical becomes important to reach a point where efficiently competes with the anions under study. In this reaction di-1-naphthylselenide/sulphide is formed (Eqn 7). The formation of naphthalene as reduction product comes from the hydrogen atom abstraction probably from the solvent as indicated in Eqn 8. Finally, the remaining anion **19** is methylated by methyl iodide at the end of the reaction to give methyl-1-naphthylselenide/sulphide (Eqn 9).



Theoretical calculations, proton affinities (PA) basicity (B) and frontier molecular orbitals (FMO) evaluation

With the aim to study the initiation step, a theoretical and experimental study of the anions **1–12** was performed. The geometry

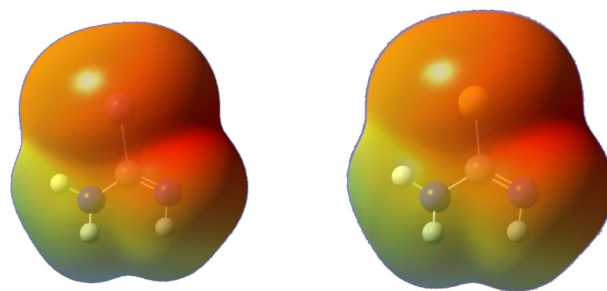
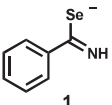



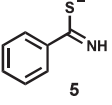






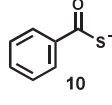
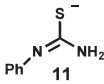
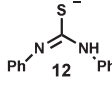
Figure 1. Optimized geometry and molecular electrostatic potential: positive/negative isosurfaces coloured from blue (positive) to red (negative), left: selenourea anion (**2**), Right: thiourea anion (**6**). Gray: carbon; white: hydrogen; blue: nitrogen; violet: selenium; gold: sulphur

Table 2. Calculated proton affinities, pKa and oxidation potential of anions **1–12**

Entry	Anion	B ¹	pKa ²	E _{ox} ³	ΔG _{TE} ⁰	E _{ox} ⁴	ΔG _{TE} ⁰ ⁴
1		288.7	—	0.204	-12.5	0.458	3.0
2		275.8	—	0.275	-10.9	0.414	1.9
3		258.3	—	0.652	-2	1.098	17.7
4		289.7	—	nd		nd	nd
5		291.5	16.9	0.208	-12.5	0.649	7.4
6		295.6	21.1	0.065	-16	0.509	4.2
7		257.9	4	0.947	4	1.286	22.1
8		293.6	18.5	0.087	-15	0.519	4.4
9		276.1	—	0.436	-7	0.664	7.7

(Continues)

Table 2. (Continued)

Entry	Anion	B ¹	pKa ²	E _{ox} ³	ΔG _{TE} ⁰	E _{ox} ⁴	ΔG _{TE} ⁰ ⁴
10		275.7	5.2	0.611	-3	0.671	7.9
11		293.1	—	0.05	-16		
12		292.6	—	0.189	-13		

¹Basicity calculated at B3LYP/6-311 + G(d) (for Se and S) level of theory.²From literature reference 10.³Oxidation peak potential at 0.1 Vs⁻¹ versus NHE with 0.1 M of TBATFB as supporting electrolyte in DMSO, anions were generated by acid–base reaction.⁴Calculated values at the B3LYP/6-311+ G(d) (for Se and S) level of theory, solvent effect considered under the PCM approximation.

optimization of the anions and their conjugated acids was done at the B3LYP level of theory and the basis set indicated in the Computational Section. Representatively, the molecular electrostatic potential fitted to the charge density distribution of selenourea and thiourea anions are illustrated in Fig. 1 where is possible to observe that upon N–H deprotonation the negative charge is delocalized at the nitrogen and sulphur/selenium atoms. However, only the chalcogenide atom is the reactive site in the radical-nucleophile addition step (Eqn 5). As expected, the thiobenzoic and thioacetate acids with the proton bonded to the sulphur atom show the lower energies. For *N*-phenylthiourea, the more acidic proton at the PhNH moiety forms the more stable anion **11** when compared to the anion derived from deprotonation of the NH₂ group.

Once all the geometries were computed, the proton affinities (PA) were calculated according to Eqns 10–11, these values give a good approximation to the basicity of the anions under study. Evidently, the larger the value of the PA is, the stronger the basicity of anion A⁻ is.^[12] The results of calculated PA are summarized in Table S1 (see Supporting Information). In all cases the proton loss in AH is an endothermic process. As the PA is a property defined in the gas phase, we also estimated the basicity (B) of the anions as basicity: -ΔG of the deprotonation reaction with inclusion of solvent effect under the PCM approximation with the dielectric constant of DMSO, see Table 2. As a general trend, the basicity values are lower than the PA values, which indicates that both the AH and A⁻ are stabilized by the solvent. In a few cases, the experimental pKa values of the studied anions are available; for these anions, a good correlation with calculated B was found.^[10] In Table 2 entries 5, 6 and 8, the B order is the following **6** > **8** > **5**, which is in agreement with the pKa order **6** > **8** > **5** and in perfect agreement with the expected stability of the anion formed, where the phenyl group in **5** exerts a higher stabilization

of the negative charge than a methyl group in **8** and even better than electron donor groups such as the amino group in anion **6**.



$$\Delta E = E_{(AH)} - E_{(A^-)} - E_{(H^+)} \quad (11)$$

Even the pKa values of selenium derivatives are not available; the method is good at predicting the more acidic selenamides when compared with the parent sulphide derivatives. Accordingly, it is well established that sulphur anions are more basic than their selenium equivalents; as an example reported pKa values for thiophenol and benzeneselenol are 10.3 and 7.1 respectively.^[10] A similar trend was observed from our calculated basicity values; where B of selenourea is 20.3 kcal mol⁻¹ lower than the B of thio-urea anion. In a small magnitude this behaviour is repeated in anions **1** and **5**, and anions **4** and **8**, where the B of the selenium anions are around 3 kcal mol⁻¹ below in energy. This difference in stabilities becomes almost zero when very stable anions are compared such as selenocyanate and thiocyanate anions (see Table 2).

From Fig. 2 it is clear that more basic sulphur anions **5**, **6**, **8**, **11** and **12** with basicity values over 290 kcal mol⁻¹ were able to transfer one electron to 1-bromonaphthalene triggering the S_{RN}1 reaction. While for the more stable anions **1–3**, **7**, **9** and **10** the presence of *tert*-butoxide anion as entrainment reagent is required.^[3] Even there is no experimental reported data for selenoacetamide anion (**4**), from its calculated B value we expect to be reactive in the initiation step. Finally, thiocyanate anion (**7**)

is not able to transfer one electron to 1-bromonaphthalene under photostimulation, nor to add to 1-naphthyl radicals.^[13]

Evaluation of the FMO

The HOMO and LUMO energies involved in the ET reaction between the anions as electron donors and 1-bromonaphthalene as an electron acceptor were calculated. Despite the controversies, it has been shown that the LUMO energies, determined by B3LYP and standard basis set, can be used as a fast hand-rule estimation of experimental vertical electron affinities.^[14] A LUMO level of energy of -1.6411 and -1.6728 eV for the acceptor in vacuum and DMSO solution, under the PCM approximation, were calculated, respectively. The HOMO and LUMO energies of anions **1–12** and **13** gathered in Table 3. Considering only the energy of the reactants in the gas phase all the anions have HOMO energies above the LUMO of 1-bromonaphthalene, which indicates from the energetic point of view that all the anions can initiate the reaction. In a more realistic scenario, the computed HOMO energies of anions **1–12** notably reduce in solvent under the PCM approximation; these values are between -5 and -5.9 eV, and the transfer of one electron to the LUMO of **13** (-1.67 eV) is energetically unfavourable being this process quite unlikely. This result is in agreement with the experimental results where all the anions need photostimulation to accelerate the ET process. The nature of the PET (initiation step) was already studied by means of UV-spectroscopy and laser flash photolysis (LFP) for thiourea, thioacetate and thioacetate anions. Quenching studies by LFP clearly indicate that the triplet state of **13** is responsible

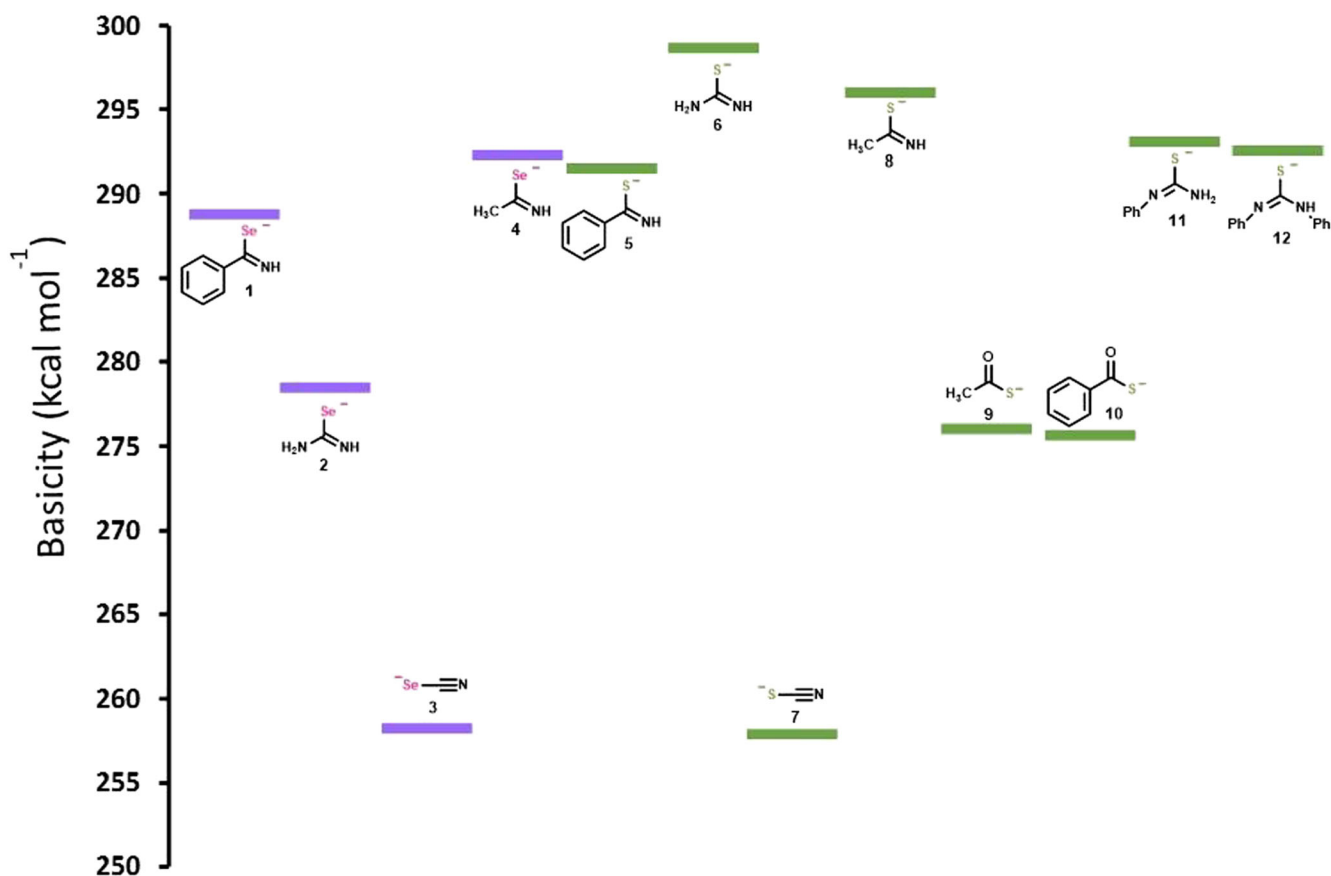


Figure 2. Calculated basicity of anions 1–12

Table 3. Calculated HOMO and LUMO frontier orbital energies of anions **1–12**¹

Entry	Anion	Gas phase		Solution (DMSO)	
		HOMO	LUMO	HOMO	LUMO
1	1	-0.6487	2.5372	-5.0997	-1.0753
2	2	-0.4533	3.2659	-5.1728	-0.0939
3	3	-0.7992	3.5606	-5.7176	-0.1048
4	4	—	—	-5.0698	-0.0218
5	5	-0.7929	2.5769	-5.2861	-0.9928
6	6	-0.5197	3.4071	-5.3879	0.0597
7	7	-1.0855	4.1104	-5.9066	0.1141
8	8	—	—	-5.2812	0.1639
9	9	-0.5695	3.6716	-5.4147	-0.0761
10	10	-0.9861	2.3609	-5.4323	-1.3553
11	11	-1.2041	2.9465	-5.3274	-0.3192
12	12	-1.6561	2.4036	-5.2052	-0.6850
13	13	-6.2132	-1.6411	-6.2657	-1.6728

¹B3LYP/6-311 + G(d) (for S, Se and Br) level of theory.

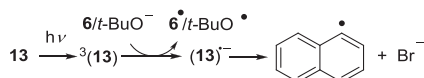
for the ET reaction with anions **6** and *tert*-butoxide giving **13**⁻ as a reactive intermediate. Fragmentation of the latter renders the 1-naphthyl radical and bromide ion (Scheme 2).^[15]

The triplet state of **13** was calculated giving a value of -4.234 eV for its lowest SOMO orbital. Considering that the HOMO orbitals of anions **1–12** are below the SOMO of the triplet excited 1-bromonaphthalene, all the anions are still not reactive, which is not the case according to the experimental results. We conclude that the model of considering only the FMO of the reactant is not reproducing the experimental results or other MOs are involved in the reactivity of nucleophiles toward **13**. Most likely, the consideration of both, reactant and product energy balance must be evaluated in order to explain the different reactivity observed for the anions in the PET toward aryl halides. For this purpose, the electrochemical properties of the anions were studied experimentally in order to evaluate the initiation PET step under thermodynamic grounds.

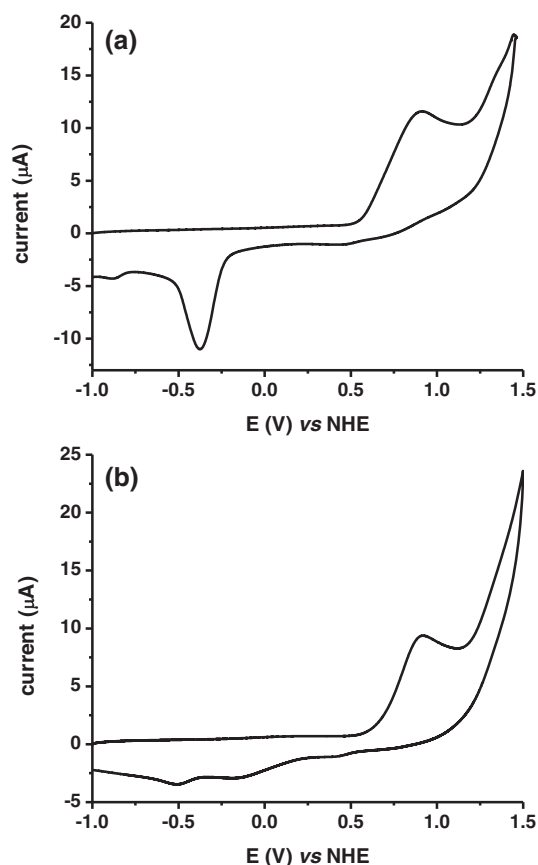
Cyclic voltammetry study, experimental and theoretical evaluation of the free Gibbs energy associated to the PET step.

Electrochemical behaviour of thioamides, selenamides and their corresponding anions

Electrochemical investigations have been carried out in DMSO at room temperature; both neutral and anion molecules were investigated by means of cyclic voltammetry. The results obtained for the oxidation of the anions are summarized in Table 2. The electrochemical oxidation of thiocarbonyl compounds, such as diarylthioketones and thioureas, has been previously reported by Blanckespoor *et al.*^[16] A stepwise electron-transfer oxidation of the thiocarbonyl

**Scheme 2.** PET initiation step

compounds to their corresponding monomeric radical cations, followed by addition to a neutral thiocarbonyl compound and further one-electron oxidation of the resultant dimer radical cation to finally afford dimer dication with disulphide linkage (Eqn 12), has been established.^[16,17] Because dimer dication are very reactive intermediates, frequently follow-up reactions with the formation of the carbonyl compound are found as electrolysis products; however, in the reverse scan, the dimeric cation's reduction wave is present (Eqn 13). The electrochemical behaviour of the thio/selenourea derivatives explored in this work is similar. Figure 3 shows the voltamperometric profiles of N-phenylthiourea (a) and selenobenzamide (b). By analogy, the anodic wave merged at 0.9 V and the cathodic peak observed at -0.5 V are because of the oxidation/reduction of the dimeric compounds. Moreover, when the corresponding anions are formed by the addition of one strong base such as the dimsyl anion, the oxidation of the corresponding anions is observed at lower potential value than the neutral species. Figure 4 shows the voltamperometric profiles observed for sulphur and selenium centred anions in the presence of BuLi.^[18] Anions **1** and **5** exhibit an oxidation peak at ca. 0.25 V (Eqn 14); thus, a large shift of the anodic peak potential values can be observed between the neutral and the corresponding anions. For example, selenobenzamide anion (**1**) and thiobenzamide anion (**5**) show shifts of 700 and 1100 mV respectively. The cyclic voltammograms for the rest of the anions listed in Chart 1 can be found in the Supporting Information. An irreversible process is observed for the oxidation of all the anions under study, and the corresponding anodic peak

**Figure 3.** Cyclic voltammograms recorded at a glassy carbon disk electrode at a sweep rate of 0.1 Vs⁻¹ in 0.1 M TBATFB/DMSO of (a) selenobenzamide 1 mM and (b) N-phenylthiourea 1 mM

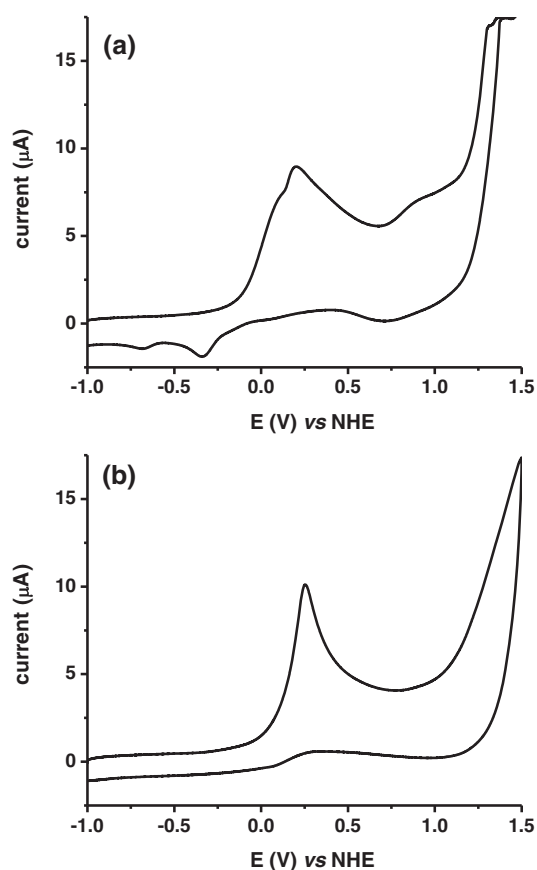
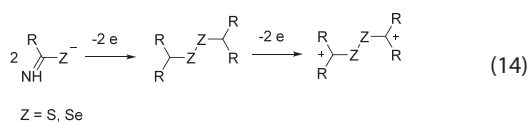
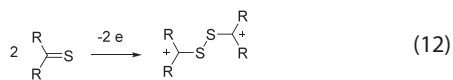


Figure 4. Cyclic voltammograms recorded at a glassy carbon disk electrode at a sweep rate of 0.1 Vs^{-1} in $0.1 \text{ M TBATFB/DMSO}$ of (a) selenobenzamide 1 mM (**1**) and (b) thiobenzamide 1 mM (**5**) in the presence of BuLi

potential values are summarized in Table 2. Our experimental findings are also in good agreement with the previously reported data for thiocyanate^[19] and selenocyanate anions.^[20]



Although the E^0 values for the oxidation of the anions **1–12** cannot be directly extracted from the CV experiments, qualitative information on the driving force of the initiation step can be achieved, and the free energy changes associated with ET from anions **1–12** to the triplet excited states can be estimated using the Weller equation (Eqn 15).^[21]

$$\Delta G_{ET}^0 (\text{kcal mol}^{-1}) = 23.06 [E^0(\text{A}/\text{A}^-) - E^0(\mathbf{13}/\mathbf{13}^-) + \Delta E_{\text{Coul}}] - E_{0-0} \quad (15)$$

The anodic peak potential values of the anions **1–12** were measured from CV, and these values were collected in Table 2. A reduction potential of -1.81 V versus NHE for 1-bromonaphthalene was taken from the literature.^[11] The coulombic interaction (ΔE_{Coul}) required to separate oppositely charged fragments is not considered because no opposite charges emerged upon ET. The triplet energy (E_{0-0}) of 59 kcal mol^{-1} was extracted from the literature.^[22] Thus, ΔG_{ET}^0 values were calculated and also collected in Table 2. In exergonic order, it is possible to differentiate three zones. First, the reactive anions **6**, **11**, **8**, **12**, **5** with large negative ΔG_{ET}^0 values (between -16 and $-12.5 \text{ kcal mol}^{-1}$) and basicity over $290 \text{ kcal mol}^{-1}$. For these largely negative exergonic values, a very fast ET kinetic is expected. For example, the triplet quenching value for thiourea anions was reported as $8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.^[15a] In the particular case of selenobenzamide anion (**1**), the estimated thermodynamic value predicts it to be reactive in a PET reaction toward 1-bromonaphthalene, but its lack of reactivity can be easily understood from the calculated basicity. Second, the non-reactive anions **2**, **9**, **10** and **3** present negative ΔG_{ET}^0 values (between -11 and -2 kcal mol^{-1}) and basicity below $290 \text{ kcal mol}^{-1}$. For these small exergonic values, a slow ET kinetic is expected which is not able to compete with the fast kinetic decay of the reactive triplet excited state of 1-bromonaphthalene having a life time of $8 \mu\text{s}$ in DMSO at room temperature, which corresponds to a unimolecular decay rate constant of $1.2 \times 10^5 \text{ s}^{-1}$.^[15a] Finally, thiocyanate anion (**7**) with an estimated positive ΔG_{ET}^0 value is clearly not reactive.

Theoretical evaluation of the ΔG_{ET}^0

The good correlation between experimental reactivity and calculated basicity encourages us to calculate thermodynamic oxidation half reaction potential and free energies for PET values in DMSO. The oxidation potentials were calculated according to the thermodynamic cycle for the half reaction indicated in Eqn 16 for which the radicals of anions **1–10** were evaluated. In order to compare the calculated value with the experimental results, the IUPAC recommended absolute standard potential of the saturated hydrogen electrode (SHE) was added.^[23]



As a general trend calculated oxidation potentials are between 0.06 and 0.45 V over estimated; however, a very good correlation between experimental versus calculated data was obtained (see Figure S13 in Supporting Information).

The thermodynamics of the PET step were also evaluated on quantum chemical calculation grounds; 1-bromonaphthalene and its radical anion were calculated; a value of -2.36 V was thus obtained for the reduction potential of **13**. The energy to reach the triplet state of the former was calculated by TD-DFT to be 62 kcal mol^{-1} , slightly higher than the experimental value (59 kcal mol^{-1}). The ΔG_{ET}^0 was evaluated by using Eqn 16, with fully calculated data; the values thus obtained are collected in Table 2. As can be seen, in all cases, the values obtained are more endergonic than the experimental ones. However, the relative reactivity order is well predicted within the family of sulphur

anions where thiourea, thioacetamide and thiobenzamide with ΔG_{ET}^0 lower than $7.4 \text{ kcal mol}^{-1}$ are reactive at the initiation step, and unreactive thioacetate, thiobenzoate and selenocyanate anions with ΔG_{ET}^0 over $7.7 \text{ kcal mol}^{-1}$ (see Figure S14 in Supporting Information).

The employment of long range and dispersion corrected DFT functional as well as the inclusion of discrete solvent molecules, of relevance in the evaluation of anions, could improve the agreement between calculated and experimental values. Nevertheless, a good correlation between experimental and theoretical E_{ox} and ΔG_{ET} was achieved having important predictive scope.

Summing up, the calculated basicity and E_{ox} and the estimated ΔG_{ET}^0 obtained from the cyclic voltamperograms are in good agreement with the observed experimental reactivity of anions. These results are reasonable from the pioneer work of Bordwell *et al.*^[24] who reported a linear correlation between experimental pKa and the oxidation potentials of a family of SET reactive nucleophiles. Taking into account that the easily calculated basicity can predict the reactivity in the ET reactions, from the basicity value of the selenoacetamide anion (**4**) ($292.4 \text{ kcal mol}^{-1}$), we predict that the ET toward 1-bromonaphthalene under photostimulation is likely although it has not been yet experimentally explored.

CONCLUSIONS

The basicity was calculated for a number of selenium and sulphur anions that demonstrated to be useful in organic synthesis for incorporating a chalcogen substituent by $S_{\text{RN}}1$ reaction. The basicity values are in good agreement with available experimental pKa values. In addition, it was found that nucleophiles with basicity values higher than $290 \text{ kcal mol}^{-1}$ are able to initiate the reaction, which is in agreement with the fact that the more basic the anions are the best electron donors. Not a clear reactivity order could be found by exploring the frontier molecular orbital energies. The oxidation peak potentials for the sulphur and selenium centred anions were measured by means of cyclic voltammetry. A good correlation between the reactivity order and experimental estimated ΔG_{ET}^0 values were found. Finally, because there is a close relationship between basicity and ET ability, we conclude that molecular modelling proved to be a solid tool for reproducing and predicting the reactivity within a family of compounds, in this case the PET reaction toward aryl halides.

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