

## A: Kinetics, Dynamics, Photochemistry, and Excited States

## Combined Experimental and Theoretical Studies on the Radical Nucleophile Addition Reaction for Sulfide and Selenide Centered Anions

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**Combined Experimental and Theoretical Studies** 

on the Radical Nucleophile Addition Reaction for

Sulfide and Selenide Centered Anions

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## ABSTRACT

The reactivity of sulfur and selenium centered nucleophiles towards 1-naphthyl radicals was studied in DMSO. The photostimulated reaction of sulfide anions,  $-SC(NH)C_6H_5$  (1),  $-SC(NH)NH_2$  (2), and  $-SC(NH)CH_3$  (3) renders, after the addition of MeI, methyl 1-naphthyl sulfide as a main product together with bis (1-naphthyl) sulfide and naphthalene under irradiation. Concordantly, the reaction of selenide anions,  $-SeC(NH)C_6H_5$  (4),  $-SeC(NH)NH_2$  (5), -SeCN (6), produces methyl 1-naphthyl selenide, bis (1-naphthyl) selenide and naphthalene in the presence of potassium *tert*-butoxide anion (*entrainment* conditions).

Absolute rate constants for the coupling of ions **1-6** to 1-naphthyl radicals were determined; as a general trend the selenide centered nucleophiles enhance in two times the reactivity of their sulfide analogues. From the mechanistic study it is proposed that the unstable radical anion produced by the addition of the nucleophile to 1-naphthyl radical affords, after fragmentation, 1-naphthylsulfide/selenide anion. In addition, experimental results are discussed in terms of DFT calculations. There is a general good agreement between the experimental and the calculated reactivity, being the spin density the main parameter to describe the difference found among the anions under study. Moreover, the calculations predict that anion -SeC(NH)CH<sub>3</sub> (**7**) would be a good candidate for the synthesis of selenide derivatives.

### INTRODUCTION

Among the variety of synthetic routes to obtain unsymmetrical diaryl or aryl chalcogenides, one of the most convenient methods involves the arylation of aryl chalcogenide anions RZ<sup>-</sup> (Z = S, Se, or Te) by the S<sub>RN</sub>1 mechanism.<sup>1-7</sup> Liquid ammonia was mainly used as solvent, owing to its low acidity and poor hydrogen donor ability towards aryl radicals. However, other solvents such as dimethylsulfoxide (DMSO) and acetonitrile (CH<sub>3</sub>CN) also give good results. The photoinduced aromatic radical nucleophilic substitution (S<sub>RN</sub>1) mechanism is a chain process with radicals and radical anions as intermediates, whose initiation step involves an electron transfer (ET) to the substrate. The general accepted pathways, for the propagation cycle, are out-lined in equations (1) – (3).

 $(ArX)^{-\bullet} \longrightarrow Ar^{\bullet} + X^{-} \qquad (1)$   $Ar^{\bullet} + RZ^{-} \longrightarrow (ArZR)^{-\bullet} \qquad (2)$   $(ArZR)^{-\bullet} + ArX \longrightarrow ArZR + (ArX)^{-\bullet} \qquad (3)$ 

Aryl selenide anions, ArSe<sup>-</sup>, which are important precursors of aromatic chalcogenide derivatives can be obtained by the  $S_{RN}$ 1 reactions, between aryl halides and Se<sup>2-</sup> or

Se<sub>2</sub><sup>2-</sup> anions. These anionic species are derived from reduction of elemental selenium with metallic sodium in liquid ammonia or its cathodic reduction in acetonitrile, respectively.<sup>8-12</sup> These methodologies demonstrate to be superior to the elemental selenium insertion with Grignard reagents or aryl lithium and synthesized ArSe<sup>-</sup> from aromatic diazonium salts,<sup>13-15</sup> especially when electron-withdrawing substituents like nitro, carbonyl and cyano groups are present in the molecule. However, these procedures involve the use of cryogenic solvents or electrochemical experimental setup, methodologies that are not accessible in many organic synthetic laboratories. Our first contribution to the chalcogenide chemistry overcomes this withdraw by the use of sulfur-centered nucleophiles such as thiourea,<sup>16</sup> thioacetate,<sup>17</sup> thiobenzamide and thioacetamide anions<sup>18</sup> for the synthesis aryl sulfide anions (ArS<sup>-</sup>) and several sulfur aromatic compounds from moderate to good yields. Later on, this methodology was extended to selenium using selenourea, selenobenzamide and selenocyanate ions in photoinduced S<sub>RN</sub>1 reactions as a "one-pot" method to obtain aryl selenide anions among other examples including a number of selenoethers.<sup>19</sup> The use of commercially available, easily handling thiobenzamide, thiourea, thioacetamide, selenourea, selenobenzamide, potassium selenocyanate and potassium tert-butoxide

salts, together with the mild reaction conditions, room temperature under nitrogen atmosphere in DMSO, makes this process a very convenient methodology for obtaining aryl chalcogenide anions and symmetrical or unsymmetrical diarylchalcogenides, (Scheme 1). These methodologies are comparable to other transition metal-free, photo-induced protocols<sup>20-22</sup> to produce biological relevant sulfides and selenides, which have antioxidant,<sup>23</sup> antibacterial,<sup>24</sup> antifungal and antiprotozoal properties.<sup>25</sup>



Scheme 1: General output for the reaction S<sub>RN</sub>1 reaction between sulfide and selenide

centered anions and aryl halides

The synthetic relevance of our reactions protocol for the chalcogenide installation in aromatic rings has been established,<sup>16-19</sup> still, scarce information on the dynamic and direct comparison between sulfur and selenium analogues is lacking. Therefore, the

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aim of the present work is to study the reactivity of sulfur and selenium centered nucleophiles, like  $-SC(NH)C_6H_5(1)$ ,  $-SC(NH)NH_2(2)$ ,  $-SC(NH)CH_3(3)$ ,  $-SeC(NH)C_6H_5(4)$ ,  $-SeC(NH)NH_2(5)$ , -SeCN(6), and  $-SeC(NH)CH_3(7)$ , towards 1-naphthyl radicals, as a model reaction. Furthermore, in order to obtain a deeper insight in the mechanistic aspects of this process, a comparative study of the reactivities of selenium and sulfur anions was carried out by DFT method at B3LYP/6-311+G\* level of theory. This study includes the analysis and comparison of the potential energy surfaces of the reaction, isolation of stationary points and evaluation of their energetics and spin densities.

#### METHODS

**General Procedures**. The general methods and procedure for the photoinduced reaction are the same as published before.<sup>16, 19</sup> <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 400 and 100 MHz respectively on a Bruker AC-400 spectrometer with CDCl<sub>3</sub> as solvent. Gas chromatographic analyses were performed on a Hewlett Packard 6890 A with a flame-ionization detector, on a HP-5 30 m capillary column of a 0.32 mm x 0.25 m film thickness. GS/MS analyses were carried out on a Shimadzu GC-MS QP 5050 spectrometer, employing a 25 m x 0.2 mm x 0.33 m HP-5 column.

**Materials:** *tert*-BuOK, selenourea, KSeCN, thiourea, thioacetamide, thiophenol, 1bromonaphthalene, naphthalene, were all high purity commercial samples which were used without further purification. Selenobenzamide was prepared by the addition of insitu generated H<sub>2</sub>Se to benzonitrile.<sup>26-27</sup> Thiobenzamide was prepared and purified according to previous reports.<sup>28</sup> DMSO was distilled under vacuum and stored over molecular sieves (4 Å). The anions **1-5** and PhS<sup>-</sup> were generated in situ by acid-base deprotonation using *tert*-BuOK.

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 <sup>1</sup>H and <sup>13</sup>C NMR and mass spectrometry.

Registry No.: 1-(methylthio)naphthalene<sup>29</sup> [10075-72-6]; bis-(1-naphthyl) sulfide<sup>30</sup> [607-53-4]; 1-naphthyl phenyl sulfide<sup>31</sup> [7570-98-1]; methyl 1-naphthyl selenide<sup>32</sup> [20613-85-8]; bis (1-naphthyl) selenide<sup>33</sup> [227010-30-2].

Photoinduced Reactions of anion 1-6 (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 different concentrations

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of the nucleophile 1-6 (see Table 1), 0.125 mM of PhS- and 0.5 mmol of 1bromonaphthalene were added to the degassed solvent under nitrogen. After irradiation with a medium pressure Hg lamp, the reaction was quenched by the addition of MeI (6 equiv) in excess and 30 mL of water, and then the mixture was extracted with methylene chloride (3x20mL). The organic extract was washed twice with water, dried and the products were quantified by GC with diphenyl disulfide as internal standard. Computational methods : DFT calculations were performed using the B3LYP34-35 hybrid GGA functional together with the standard 6-31 + G\* basis set for carbon, nitrogen and hydrogen and 6-311 + G\* 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  $\varepsilon$  = 46.7. All calculations were carried out with the Gaussian 09 suite of programs and include the zero-point energy correction.<sup>36</sup> The characterization of stationary points was done by Hessian matrix calculations, with all positive eigenvalues for a minimum and one negative value for a transition state, in all cases zero-point energies correction were included. From a methodological point of view, in order to

calculate the reaction coordinate, we began optimizing the structure of the radical anion intermediate in solution. Intrinsic reaction coordinates (IRCs) were not calculated, and the following procedure was carried out. Once the minimum energy structure was obtained, the bond between the heteroatom (Z = Se or S) and the carbon of the aromatic ring (CA) of the radical anion was stretched towards reactants, to obtain the structure of the transition state (TS1). Furthermore, the maximum nature of the structure was confirmed by TS and Force calculations. In the same way, the bond between the heteroatom and the carbon B (CB) of the radical anion intermediate was stretched towards products to obtain the structure of the second transition state (TS2). The structures obtained for TS2 also corresponded to a maximum (see below, Scheme 3). In both cases the imaginary frequency corresponded to the stretching of the CA-Z and CB-Z bonds for TS1 and TS2 respectively, which confirms the connectivity of the stationary points along the PES reaction. Finally, the energies of the reactants and the products were obtained by calculating each of the compounds separately, considering their energy at an infinite distance.

## **RESULTS AND DISCUSSION**

Determination of the Rate Constant for the Nucleophilic Addition to 1-Naphthyl Radical

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According to previous results and considering only the overall product yield distribution, thiobenzamide, thiourea, thioacetamide, 17-18, 37 selenobenzamide, selenourea, and selenocyanate anions,<sup>19</sup> have similar reactivities towards 1-naphthyl radical, which is formed by photoinduced electron transfer followed by C-Br fragmentation (equation 1), Considering that the S<sub>RN</sub>1 reaction comprises initiation, propagation and termination steps, it is of interest to evaluate the relative reactivity of the different sulfur and selenium anions towards 1-naphthyl radical in competitive experiments. Benzene thiolate anion (PhS<sup>-</sup>) was chosen as reference to carry out the kinetic competition reactions, thus the outcome of our research study can be straightforward compared with reported data in the literature. In addition, both short irradiation times and the presence of a good nucleophile as PhS<sup>-</sup>, inhibit secondary products coming from ArS<sup>-</sup> and ArSe-, namely ArSAr and ArSeAr, respectively, which becomes important at longer reaction times. As a result, the absolute rate constants for the addition  $(k_c)$  of 1-naphthyl radical with the anions under study (1-6) can be determined in DMSO using the addition reaction of PhS<sup>-</sup>, towards 1-naphthyl radical (k<sub>cPhS-</sub>) as a competitive reaction, whose reported value,  $(6 \pm 2) \times 10^9$  M<sup>-1</sup>s<sup>-1</sup>, is obtained from the literature.<sup>38</sup>

The competitive reaction pathways of aryl radicals that account for the observed products (namely path a, b and c) are shown in Scheme 2 and are described as follows: a) coupling reaction with the anions **1-6** to give the substitution products **10** or **11**, from the sulfur and selenide anions respectively, after fragmentation of the radical anion intermediate (**8**) and subsequent reaction with CH<sub>3</sub>I; b) hydrogen atom abstraction from the solvent to yield the reduction product **12**; and c) coupling with the PhS<sup>-</sup> anion to generate the substitution product 1-naphthyl phenyl sulfide (**13**) after electron transfer to the substrate (Scheme 2).



Scheme 2: Competitive pathways for 1-naphthyl radical

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The relative reactivity of nucleophiles 1-6 was obtained after determining products 10

or 11 and 13 yields, using equation 4:

$$\frac{k_{cPhS}}{k_{c1-6}} = \frac{[C_6H_5SAr]_t[Nu^-]_0}{[ArZCH_3]_t[C_6H_5S^-]_0}$$
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where  $[Nu_{]_0}$  and  $[PhS_{]_0}$  are the initial concentrations of the nucleophiles and  $[ArZCH_3]_t$  and  $[C_6H_5SAr]_t$  are the concentrations of the substitution products at a given time (t). In this equation, it is assumed that the coupling of the aryl radical with the different nucleophiles follows a pseudo first order reaction kinetics and the nucleophiles concentrations remain constant along the reaction. Both requirements are fulfilled at short reaction times. In addition,  $k_c$  was estimated by considering the reported  $k_{cPhS}$  value<sup>38</sup> and the data are collected in Table 1.

**Table 1**. Rate constant ( $k_c$ ) for the reaction of 1-naphthyl radical with selenium and sulfur-centered nucleophiles in DMSO at 25°C.<sup>a</sup>

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Entry	Nu <sup>-</sup> [concentration]	k <sub>C6H5S</sub> ./k <sub>c</sub>	Average k <sub>C6H5S</sub> ./k <sub>c</sub>	k <sub>c</sub> k <sub>c</sub> (M <sup>-1</sup> s <sup>-1</sup> )		
<b>1</b> b, c	<b>1</b> [0.125] M	2.95				
2 <sup>b, c</sup>	<b>1</b> [0.25] M	1.52	2.1±0.7	(3±1) x 10 <sup>9</sup>		
<b>3</b> b, c	<b>1</b> [0.5] M	1.82				
<b>4</b> <sup>d</sup>	<b>2</b> [0.125] M	2.63				
5 <sup>d</sup>	<b>2</b> [0.25] M	2.84	2.8±0.2	(2.1±0.2) x 10 <sup>9</sup>		
<b>6</b> <sup>d</sup>	<b>2</b> [0.5] M	3.01				
<b>7</b> <sup>d</sup>	<b>3</b> [0.125] M	1.81				
<b>8</b> d	<b>3</b> [0.25] M	1.52	1.8±0.3	(3.3±0.6) x 10 <sup>9</sup>		
<b>9</b> d	<b>3</b> [0.5] M	2.07				
10 <sup>b, e</sup>	<b>4</b> [0.062] M	0.97				
11 <sup>b, e</sup>	<b>4</b> [0.125] M	0.82	0.9±0.2	(7±1) x 10 <sup>9</sup>		
12 <sup>b, e</sup>	<b>4</b> [0.25] M	0.79				
13 <sup>b, e</sup>	<b>4</b> [0.5] M	1.18				
14 <sup>b, c</sup>	<b>5</b> [0.125] M	1.46				

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15 <sup>b, c</sup>	<b>5</b> [0.25] M	1.14	1.2±0.2	(5±1) x 10 <sup>9</sup>
16 <sup>b, c</sup>	<b>5</b> [0.5] M	1.08		
<b>17</b> <sup>b, c</sup>	<b>6</b> [0.125] M	3.31		
18 <sup>b, c</sup>	<b>6</b> [0.25] M	2.50	2.8±0.4	(2.1±0.3) x 10 <sup>9</sup>
19 <sup>b, c</sup>	<b>6</b> [0.5] M	2.50		

**a** Photostimulation with high-pressure Hg lamp in 10 mL of DMSO.  $[1-BrC_{10}H_7] = 0.05$  M and  $[C_6H_5S^2] = 0.125$ M. Products yield determined by GC using the internal standard method, error < 5%. From triplicated experiments. **b** Together with *t*-BuOK in excess. **c** 1 h reaction time. **d** 15 minutes reaction time. **e** 1 h reaction time.

Competition experiments between different concentrations of anion **1** and  $C_6H_5S^-$ (0.125 M) in the presence of 1-bromonaphthalene (0.05 M) were performed in DMSO ([1] ranges 0.125 – 0.5 M see Table 1 entries 1-3). After the indicated reaction time, products **10** and **13** were quantified and the relative reactivity k <sub>C6H5S</sub>/k<sub>c1</sub> was determined. From the k<sub>C6H5S</sub>/k<sub>c1</sub> average value and using the reported value of k<sub>C6H5S</sub>-, then k<sub>c1</sub> was obtained (merged value from entries 1-3 in Table 1). The same methodology was applied for all nucleophiles (**1-6**) obtaining as a result the following

addition rate constant values:, 3 x 10<sup>9</sup> M<sup>-1</sup>s<sup>-1</sup> for 1, 2.1 x 10<sup>9</sup> M<sup>-1</sup>s<sup>-1</sup> for 2, 3.3 x 10<sup>9</sup> M<sup>-</sup>  $^{1}$ s<sup>-1</sup> for **3**, 7 x 10<sup>9</sup> M<sup>-1</sup>s<sup>-1</sup> for **4**, 5.0 x 10<sup>9</sup> M<sup>-1</sup>s<sup>-1</sup> for **5**, and 2.1 x 10<sup>9</sup> M<sup>-1</sup>s<sup>-1</sup> for **6**. In all cases, the estimated absolute rate constants measured range from 2.1 to 6.7 x 10<sup>9</sup> M<sup>-1</sup>s<sup>-1</sup> which are consistent with a fast coupling reaction between chalcogenide nucleophiles and 1-naphthyl radical.<sup>39</sup> Thus, the rate constant values estimated for the sulfur centered nucleophiles follow the reactivity order  $k_{c3} \ge k_{c1} > k_{c2}$ . Moreover, among the selenium centered nucleophiles the order  $k_{c4} > k_{c5} > k_{c6}$  was found. As a general trend, selenium anions have higher coupling rate constants towards 1-naphthyl radical in comparison with their sulfur-centered analogs, which agree with the greater polarizability of the selenium atom. Furthermore, this trend is also observed in the previously reported relative reactivity between sulfur and selenium nucleophiles. For example, the reactivity order in the radical-nucleophile addition reaction is  $C_6H_5Te^- >$  $C_6H_5Se^- > C_6H_5S^-$  for 2-quinolyl radical in liquid NH<sub>3</sub>; where the ratio kC<sub>6</sub>H<sub>5</sub>Se<sup>-</sup>/kC<sub>6</sub>H<sub>5</sub>S<sup>-</sup> is 5.8 and kC<sub>6</sub>H<sub>5</sub>Te<sup>-</sup>/kC<sub>6</sub>H<sub>5</sub>Se<sup>-</sup> is 4.8.<sup>40</sup> However, the ratio drops to 2.7 for kC<sub>6</sub>H<sub>5</sub>Se<sup>-</sup>/kC<sub>6</sub>H<sub>5</sub>S<sup>-</sup> when CH<sub>3</sub>CN is used as solvent.<sup>41</sup> This decrease in the relative reactivity by changing the solvent can be easily understood just considering the effect of the temperature, -33°C in liquid NH<sub>3</sub> and 25°C in CH<sub>3</sub>CN, which would

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increase the reactivity with the consequent diminution in the selectivity of the addition reaction. Nevertheless, some other specific interactions in polar protic and aprotic solvents cannot be disregarded.

Absolute rate constants for the radical addition to chalcogenide nucleophiles can be obtained using electrochemical techniques. Thus, by means of cyclic voltammetry, the value of  $kC_6H_5Se^{-}/kC_6H_5S^{-}$  is 1.23 for the coupling with 9-anthracenyl radical in acetonitrile at room temperature. For the more electrophilic, 4-acethylphenyl radical, there is no discrimination between PhSe<sup>-</sup> and PhS<sup>-</sup> where the addition reaction is under the diffusion time regime, reaching the maximum value of 2x10<sup>10</sup> M<sup>-1</sup>s<sup>-1,42</sup> Although in most cases selenium anions are more reactive in the radical-nucleophilic coupling step, if the global reactivity is considered, the sulfur centered nucleophiles are more reactive. The latter is evidenced from the fact that sulfur derivatives give similar yields at shorter reaction times. This difference can be explained considering that the overall reactivity comprises both, initiation and propagation steps, where the lower efficiency of the selenium anions lies on a poor electron donor capacity (initiation step) and/or shorter propagation chain.<sup>18</sup>

To get a deeper insight into the reaction mechanism and molecular properties that accounts for the different addition efficiencies of anions 1-5 and selenoacetamide anion (7) against 1-naphthyl radical, a topographic exploration of the potential energy surface for the radical-nucleophilic coupling reaction was modeled.

# Theoretical evaluation of frontier molecular orbitals (FMO) and charge density distribution

In all cases the HOMO coefficients and the charge densities for the bidentate nucleophiles were calculated. These properties give information about the reactive position in the anion that can be compared with the experimental results. Even experimental data for 7 are lacking, this anion was also included in our calculation for comparative reasons since thioacetamide anion (3) shows the highest reactivity among sulfur centered nucleophiles. The calculations were made at the B3LYP level of theory and the basis set 6-311+G\* for the atoms of S and Se and 6-31+G\* for the rest of the atoms. Previous reports have demonstrated the ability of this methodology for suitable description of reactions dynamics involving the formation and fragmentation of radical anions.<sup>43-46</sup> Recently, results from Pierini's research group <sup>45</sup> have demonstrated that B3LYP reproduce electron affinity values within mean absolute deviation close to

0.1eV in comparison with other 23 DFT methods. Also, for calculated reduction potentials PW91, BPW91, and M06-L are functionals that give the best results in correlation with measured values. Nevertheless, the popular functionals B3LYP and PBE0 showed a correct behavior in such report. Furthermore, an excellent correlation was reported employing B3LYP and M06-2X for the calculation of oxidation and reduction potentials.<sup>46</sup> Based on these previous reports, B3LYP DFT method of calculation was selected as a complement to our experimental findings. Likewise, the experimental setup, DMSO was used as solvent under PCM model aproximation.47-49 In all cases the charge density is located mainly on the sulfur atom for anions 1-3, on the selenium atom for anions 4, 5 and 7, and to a lesser extent on the nitrogen atom (Table S1). Since these anions react with 1-naphthyl radical, their HOMO coefficient rules the reactive position in the reaction under study. It was observed for sulfur centered anions that the HOMO coefficient is high on the chalcogenide atom, whereas it is very small on the nitrogen atom. Likewise, for selenium anions it was also observed that the HOMO coefficients are mainly on the Se atom (Table S1, Figure S1). These results are in good agreement with the experimental results, where the anions react only through S or Se atoms, and no nitrogen substitution products were detected under

any condition. However, when analogous S and Se anions are compared, 2 and 5 for

example, no difference was observed in the HOMO coefficient between both chalcogenide atoms, the same trend was observed when comparing anions 1 and 4, 3 and 7. As a consequence, analysis of both negative charge density and HOMO coefficient of the anions are not good parameters to describe the observed experimental reactivity. For a deeper inside into the reaction mechanism, full exploration of the potential energy surface was necessary. Potential energy surface exploration for formation and fragmentation of the radical anion intermediate in carbon-chalcogenide addition reaction **Reaction pathways and geometries of the stationary points.** Based on the previous experimental evidences,<sup>19, 38</sup> we proposed that selenium and sulfur centered anions react with the 1-naphthyl radical to form a radical anion intermediate (8) which fragments into anion 9 (Scheme 3). Subsequently, this anion can react with methyl iodide or another 1-naphthyl radical to account for the observed products.



Scheme 3: Reaction intermediates along de PES

Considering this mechanism, the corresponding energies for the formation and the fragmentation of the intermediate radical anion **8** were analyzed starting from the reactants proposed in Scheme 3. Two consecutive reaction pathways (reaction coordinates) were considered along the potential energy surface (PES) exploration: firstly, the coupling reaction between anions **1-5** and **7** with 1-naphthyl radical, to obtain the radical anion intermediate **8**, passing through a transition state on the potential energy surface (**TS1**) where the bond between  $C_A$  and Z is been formed. Secondly, fragmentation reaction of radical anion **8** to form anion **9** and the radical  $\cdot C(NH)Y$  as products, going through a second transition state **TS2**, where  $C_B$  and Z is broken. In all cases, the energies presented are relative to reactants, so their energies are

considered as zero and to simplify the discussion, only reactive centers  $C_A$ , Z and  $C_B$  are considered (Scheme 3).

For comparison, Figure 1, Figures 2 and S2, shows structures, unpaired spin densities and potential energy topography including stationary points TS1, 8 and TS2 found for the reaction between 1-naphthyl radical and thiourea (2) or selenourea (5) anions. In the first reaction pathway, the attack to the 1-naphthyl radical is perpendicular to the naphthalene  $\pi$  system for both nucleophiles. The distances C<sub>A</sub>-Z in **TS1** are 2.21 Å and 2.25 Å for sulfur and selenium anions, respectively (Table S2, entries 2 and 5). In the radical anion intermediate the bonds  $C_A$ -Z is fully formed (distances  $C_A$ -S = 1.76 Å and  $C_A$ -Se = 1.91 Å, see Table S2 entries 2 and 5). The difference found in the bond distances of these two radical anions agrees with the atomic radius of both chalcogenide atoms. The second reaction pathway where C<sub>B</sub>-Z fragmentation occurs through TS2, shows a C<sub>B</sub>-Z distances of 2.30 Å and 2.34 Å for thiourea and selenourea anions, respectively (Table S2, entries 2 and 5). Along both pathways, the C(NH)NH<sub>2</sub> residue is perpendicular to the naphthalene  $\pi$  system, which is consistent with a perpendicular attachment of the nucleophile to 1-naphthyl radical in order to avoid steric hindrance between NH and NH<sub>2</sub> of the nucleophiles and C<sup>2</sup>-H/C<sup>8</sup>-H in the

aromatic ring. As a result, the distances  $C_A$ -S,  $C_A$ -Se in **TS1** and  $C_B$ -S,  $C_B$ -Se in **TS2**, are not significantly different in agreement with the exothermic character of the reaction and the earlier nature of both transition states (Figure 2). Thus, the geometries and bond distances cannot fully explain the observed reactivity. Similar results were found for anions **1**, **3**, **4** and **7** (see Figures S2 and Table S2).



Figure 1. Unpair spin densities of TS1, radical anion (8) and TS2 for the addition reaction of anion thiourea (2) and selenourea (5) with 1-naphthyl radical.

Table 2 summarizes the results obtained for the energy profiles and spin densities at the main reactive centers ( $C_A$ , Z and  $C_B$ ) of the anions studied when they react with 1-

naphthyl radical. For both reaction coordinates, formation and fragmentation of the

radical anion intermediate **8**, the process is exothermic for all the anions under study. This illustrates the irreversible nature of the overall processes that agree with the experimental results, where only methylated anion **9** is found as main product and no traces of neutral **8** were ever observed. Furthermore, according to quantum chemical calculation results, **8** formation is the rate determining step since in all cases the energy of **TS1** is higher than **TS2**, then relative reactivity can be easily extracted from **TS1** relative energies.

Table 2. Stationary Points Including Solvent Effect and spin densities for the reaction between Selenium and Sulfur anions with 1-

naphthyl radical.<sup>a</sup>

TS1				Radical Anion			TS2				Products		
Anion	(ΔE <sub>TS1</sub> )	δĊΑ	δΖ	δC <sub>B</sub>	(∆E <sub>8</sub> )	δር <sub>Α</sub>	δΖ	δC <sub>B</sub>	(ΔE <sub>TS2</sub> )	δĊΑ	δΖ	δС <sub>в</sub>	(ΔE <sub>p</sub> )
1	8.7	0.50	0.35	-0.14	-5.3	0.18	0.002	0.03	-0.3	0.07	0.05	0.73	-5.7
2	9.2	0.53	0.28	-0.02	-3.4	0.19	0.004	0.19	3.7	0.11	0.09	0.44	-5.1
3	8.3	0.48	0.34	-0.12	-5.1	0.19	0.006	0.02	4.3	-0.12	0.002	0.54	-1.5
4	6.5	0.42	0.41	-0.48	-2.4	0.20	0.15	0.04	-1.1	0.11	0.14	0.67	-6.5
5	7.1	0.44	0.43	-0.03	0.03	0.23	0.02	0.04	3.0	0.19	0.10	0.49	-5.3
7	6.3	0.41	0.44	-0.15	-1.5	0.25	0.01	0.03	3.5	0.10	0.10	0.51	-2.02

a Calculated values at the B3LYP/6-311+ G(d) (for Se and S) level of theory, solvent effect considered under the PCM approximation with the dielectric constant of DMSO.<sup>47-49</sup> Energies are expressed

in kcal mol<sup>-1</sup> including zero point energy correction. Z = S for anions **1-3** and Z = Se for anions **4**, **5** and **7**.  $\delta$  = spin densities.

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Spin contribution analysis. Comparative analysis of the atomic spin densities of the stationary points (Figure 1 for anions 2, 5 and Figure S3 for anions 1, 3, 5 and 7) shows differences in spin distribution along the reaction pathways (Scheme 3). Firstly, the spin density is concentrated at  $C_A$  of the 1-naphthyl radical. Along the PES, the spin density migrates finally to  $C_{\rm B}$  in residue  $\cdot C(\rm NH)Y$  going throw TS1, 8 and TS2 (Figure S3). Spin densities on reaction centers C<sub>A</sub>, Z and C<sub>B</sub> are depicted in Table 2, moreover unpair total spin distribution are plotted in Figure 1. While, for TS1 a significantly different contribution of sulfur and selenium (0.28 and 0.43 respectively) to total spin density is observed; in intermediate 8 the contribution is very small for both chalcogenide atoms (0.004 for S and 0.02 for Se), where in intermediate 8 the spin is concentrated only in the aromatic ring. Ultimately, similar contribution of both C<sub>B</sub> atoms, 0.44 for thiourea and 0.49 for selenourea, were computed in TS2 (Table 2, entries 2 and 5). Therefore, the spin concentration at the chalcogenides in TS1 is the main parameter to describe the difference experimentally found in reactivity between sulfur and selenium centered anions. Similar trend in spin distribution for TS1, 8 and TS2 along PES was calculated for pairs of anions (1 and 4, 3 and 7, see Figures S3 and Table 2).

From the energies computed in the PES of thiourea to selenourea anions (Figure 2), it was found that the activation energy necessary for the formation of the radical anion of the sulfur compound is 2.1 kcal mol<sup>-1</sup> ( $\Delta\Delta E_{TS1}$ ) higher than selenourea, consequently with the higher spin density supported by selenium atom in TS1. These results agree with experimental rate constants measured where  $k_{c5}>k_{c2}$ . The same trend was found when comparing the other pair of nucleophiles (1 to 4 and 3 to 7).



**Figure 2**. Stationary points along PES for thiourea and selenourea anions with 1naphthyl radical. Energies in kcal mol<sup>-1</sup>.

Among the sulfur-centered nucleophiles family, anion **3** has the lowest activation energy to from the radical anion, followed by **1** and finally **2**, which possesses the

highest  $\Delta E_{TS1}$  (Figure 3). These results correlate with the rate constants for coupling to the 1-naphthyl radical experimentally measured ( $k_{c3} \ge k_{c1} > k_{c2}$ ). The energy difference found, for the formation of the radical anion, between anions 1 and 3, is only 0.4 kcal mol<sup>-1</sup>, which is in accordance with the minimum difference found between the coupling rate constants for these anions.



Figure 3. Stationary points along PES for sulfur centered anions (1, 2 and 3) with 1-

naphthyl radical. Energies in kcal mol<sup>-1</sup>.

In the case of selenium centered nucleophiles (Figure 4), the same tendency was observed as for sulfur nucleophiles. Anion 7 has the lowest activation energy for the coupling reaction with 1-naphthyl radical, followed by 4 and 5 with the highest activation energy. For the case of 4 and 5, calculated  $\Delta\Delta E_{TS1}$  is in good agreement with experimental founding ( $k_{c4} > k_{c5}$ ). According to the results obtained by means of quantum chemical calculations anion 7 has the lowest activation energy for the coupling reaction towards 1-naphthyl radical. This makes anion 7 a good candidate to carry out the synthesis of alkyl aryl selenides.



**Figure 4**. Stationary points along PES for selenium centered anions (**4**, **5** and **7**) with 1-naphthyl radical. Energies in kcal mol<sup>-1</sup>.

### CONCLUSION

The relative rate constants of the photoinduced reactions of 1-bromonaphthalene with the different nucleophiles were determined. The order found for the sulfur nucleophiles is  $-SC(NH)CH_3 \ge -SC(NH)C_6H_5 > -SC(NH)NH_2$  and  $-SeC(NH)C_6H_5 > -SeC(NH)NH_2 >$ -SeCN for selenium nucleophiles. In all cases, it was observed that anions derived from selenium are approximately 2 times more reactive than their sulfur analogues. This can be explained in terms of the greater polarizability of selenium compared to sulfur atoms. In addition, we were able to explore the potential energy profile for the different nucleophiles where intermediates and transition states structures were located and characterized for the first time. As a result, it was found that the calculated reactivity order for the selenium compounds was 7 > 4 > 5, the same trend was also found for sulfur compounds (3 > 1 > 2). Sulfur compounds have higher activation energy than their selenium analogues, this difference is mainly given by the higher spin density supported by the selenium atom in **TS1**, which correlate with the coupling constant order found experimentally.

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Supporting Information Available. HOMO coefficient's for anions 1-5 and 7 (Table S1

and Figure S1), bond distances (Table S2), transition state and intermediate structures

(Figure S2) and spin densities (Figure S3) for the reaction between 1-naphthyl radical

and anions 1-4 and 7, and Cartesian Coordinates for stationary points.

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