Letter

Stabilisation of 2-nitrophenyl-selenosulfide, -diselenide and -thioselenide ions in *N*,*N*-dimethylacetamide

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The direct addition of sulfur or selenium to 2-nitrophenyl selenide ions ($ArSe^-$) in *N*,*N*-dimethylacetamide leads to the formation of $ArSeS^-$ or $ArSe_2{}^-$ species, which have been characterized by UV-vis spectrophotometry coupled with voltammetry. The nucleophilic substitution of benzyl bromide by $ArSeS^-$ ions yields selenenyl sulfide $ArSeSCH_2Ph$ as the major product.

Only a few synthetic preparations have been reported for selenenyl sulfides RSeSR′; these are based on the one hand, on the reactions between selenenyl bromides RSeBr and thiols R′SH,[1] and on the other hand, on the exchange reactions between diselenides RSe_2R and disulfides $R'S_2R'$.[2] Naturally occurring compounds of this class, which were recently identified in *Allium* volatiles[3] (R = Me; R′ = Me, allyl, prop-1-ene) attract considerable attention because of their possible anticarcinogenic properties.[3,4] An easier access would be provided from the precursor $RSeS^-$ or $R'SSe^-$ ions, whose generation can be conceived as a $RS_2{}^-$ one in aprotic dipolar media, from the direct addition of sulfur to thiolate ions.[5] In polar organic media insertions of S–S bonds in organic substrates notably result from cathodic[6] or anodic[7] activation of sulfur into $S_x{}^{2-}$ polysulfides and S^{2+} ions, respectively, whereas thiolates and selenolates are clearly obtained by electrochemical reduction of RS_2R[5] and RSe_2R[8] species.

We report here on a potential route to $RSeS^-$ and $RSe_2{}^-$ ions using the reactions of sulfur and selenium towards colored $2\text{-}NO_2C_6H_4Se^-$ ions ($ArSe^-$) as a model. The studies were carried out in *N*,*N*-dimethylacetamide (DMA) at 20 °C by UV-vis absorption spectrophotometry coupled with voltammetry at a gold rotating disc electrode.

In DMA sulfur reacts with RS^- ions in two parallel ways:[5] (*i*) preponderant and successive formation [eqn. (1)] of $RS_x{}^-$ ions (R = alkyl, x = 2–5; R = aryl, x = 2–4) by *S*-nucleophilic processes[5,9] and (*ii*) weak oxidation [eqn. (2)] leading to RS_2R and polysulfide ions:

$$2RS_{x-1} + S_2 \rightarrow 2RS_x{}^- \qquad (1)$$

$$2RS^- + S_8 \rightarrow RS_2R + S_8{}^{2-} \qquad (2)$$

We suggested that processes such as those in eqn. (1) could involve the reactive S_2 molecules in equilibrium with cyclic S_8.[5b,6] The addition of sulfur to the more stabilized 2-nitrophenyl sulfide ions (ArS^-, $\lambda_{max} = 502$ nm) led to the formation of $ArS_2{}^-$ ions only[5,10] ($\lambda_{max} = 681$ nm) [eqn. (3)], without significant oxidation, as in eqn. (2).

$$2ArS^- + S_2 \rightleftharpoons 2ArS_2{}^- \qquad (3)$$

Seventy-five percent $ArS_2{}^-$ ions were obtained at the stoichiometry $[ArS^-]_0 = 8[S_8]_0 = 2.0 \times 10^{-3}$ mol dm^{-3}. 2-Nitrophenyl selenolate anions were obtained at initial concentrations $[ArSe^-]_0 \leqslant 4.2 \times 10^{-3}$ mol dm^{-3} by controlled potential electrolysis[†] at a large gold grid electrode [$E = -1.0$ V *vs.* the reference Ag/AgCl, KCl sat. in $DMA/N(Et)_4ClO_4 = 0.1$ mol dm^{-3}] of the corresponding diselenide Ar_2Se_2 [half-wave potential $E_{1/2}(R) = -0.69$ V, $\lambda_{max} = 378$ nm, $\varepsilon_{378} = 7300$ dm^3 mol^{-1} cm^{-1}], which was prepared as previously reported.[11] Fig. 1 shows the dependence of the UV-vis spectrum on the addition of a concentrated solution of sulfur to an initial solution of 2-nitrophenyl selenolate ions at various ratios $y = [S]_{ad}/[ArSe^-]_0$, with added sulfur noted as $[S]_{ad} = 8[S_8]$. The maximal absorbances of red $ArSe^-$ ions at 520 nm ($\varepsilon_{520} = 1200$ dm^3 mol^{-1} cm^{-1}) and 315 nm ($\varepsilon_{315} = 14500$ dm^3 mol^{-1} cm^{-1}) decrease to the benefit of two new bands ($ArSeS^-$, $\lambda_{max1} = 728$ nm, $\lambda_{max2} = 340$ nm) with the occurrence of three isosbestic points (λ_{is} = 565, 418 and 347 nm). For $y < 0.70$ (curves 1–6), the consumption of $ArSe^-$ ions, $\Delta[ArSe^-]/[S]_{ad}$, remains in a proportion of $-1:1$, and then progressively slows down (curves 7,8) in agreement with eqn. (4) and as observed in the course of reaction (3) leading to $ArS_2{}^-$ ions:[10]

$$2ArSe^- + S_2 \rightleftharpoons 2ArSeS^- \qquad (4)$$

At the stoichiometric value $y = 1$, 85% of $ArSe^-$ ions have been converted into blue $ArSeS^-$ ions. Subsequent additions of sulfur (curves 9,10) result in a small oxidation of $ArSe^-/ArSeS^-$ ions [eqn. (5)] with the appearance of $S_8{}^{2-}$ ions (increase of their maximal visible absorbance at 515 nm[6] at the expense of A_{728}, $\lambda_{is} = 600$ nm) and of S_8 in excess, which is detected by its first bielectronic reduction (R) wave[6] [$E_{1/2}(R) = -0.40$ V]:

$$2\ ArSe^- + S_8 \rightleftharpoons Ar_2Se_2 + S_8{}^{2-} \qquad (5)$$

Despite its insolubility in DMA, elemental selenium reacts with $ArSe^-$ ions in a way similar to sulfur. The progressive

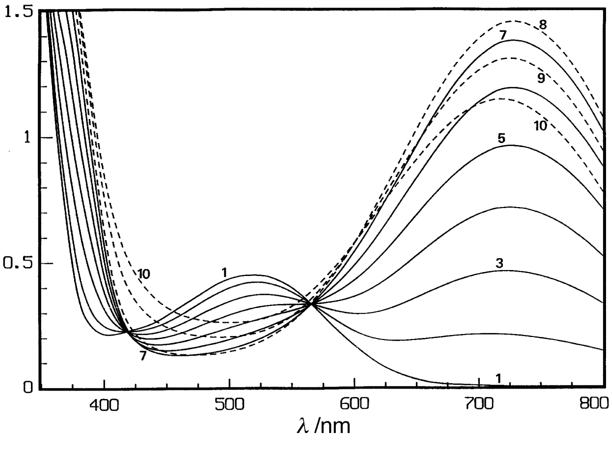

Fig. 1 Dependence of the UV-vis spectrum on the addition of sulfur (8.6×10^{-3} mol dm^{-3}) to a solution (40 cm^3) of 2-nitrophenyl selenolate ions $[ArSe^-]_0 = 3.60 \times 10^{-3}$ mol dm^{-3}: $y = [S]_{ad}/[ArSe^-]_0$ = 0 (1), 0.12 (2), 0.26 (3), 0.40 (4), 0.55 (5), 0.69 (6), 0.84 (7), 0.99 (8), 1.22 (9), 1.70 (10). Thickness of the cell = 0.1 cm, scan rate = 1000 nm min^{-1}.

addition of definite quantities of Se powder (Aldrich, 100 mesh) to ArSe$^-$ solutions entails the quantitative formation [eqn. (6)] of ArSe$_2{}^-$ ($\mathit{\Delta}$[ArSe$^-$]/[Se$_{ad}$] = 1 : 1 up to $y = 1$). A_{520} (ArSe$^-$) evolves into A_{728} and A_{354} (ArSe$_2^-$) through two isosbestic points at 565 and 442 nm:

$$\mathrm{ArSe^- + Se \rightarrow ArSe_2{}^-} \qquad (6)$$

The rate of this process is that of the dissolution of reacting Se (see below), which occurs within 3 h for the initial conditions $[\mathrm{ArSe^-}]_0 = [\mathrm{Se}]_0 = 4.25 \times 10^{-3}$ mol dm^{-3}, without any observed oxidation of ArSe$_2{}^-$.

In DMA, RSe$^-$ ions (R = $C_6H_5CH_2$, C_6H_5) mainly reduce sulfur into polysulfide ions (results to be published) whereas RS$^-$ ions mainly yield RS$_x{}^-$ species,[5] according to the competing reactions (1) and (2). The formation of ArSeS$^-$ and ArSe$_2{}^-$ ions can be explained by a lowered redox reactivity of 2-nitrophenylselenide ions with respect to RSe$^-$ ones, due to a higher stabilization of the former anionic species. RS$^-$ ions are less reactive species than RSe$^-$ towards alkyl halides;[12] analogously, the conversion of 2-NO$_2$C$_6$H$_4$S$^-$ ions (λ_{max} = 502 nm) into ArSSe$^-$ ions (λ_{max} = 666 nm, λ_{is} = 548 nm) in the presence of excess selenium only attains 20%.

From the addition of traces of sulfur to ArSe$^-$ ions, the oxidation (O) wave of the latter [$E_{1/2}$(O) = +0.16 V] totally shifts to less anodic potentials without change in its limiting current, as shown with thiolate ions;[5] as an example $\Delta E_{1/2}$(O) = −0.25 V for $y = [\mathrm{S}]_{ad}/[\mathrm{ArSe^-}]_0 = 1$. This is explained by the electrocatalytic mechanism in reactions (7)–(9), which implies the fast formation of ArSeS$^-$ ions [eqn. (8)] and their electrooxidation [eqn. (9)] into Ar$_2$Se$_2$ (with release of sulfur) at a rate greater than that of ArSe$^-$ ions [eqn. (7)]:

$$\mathrm{2ArSe^- - 2e^- \rightarrow Ar_2Se_2} \qquad (7)$$

$$\mathrm{2ArSe^- + S_2 \rightarrow 2ArSeS^-} \qquad (8)$$

$$\mathrm{2ArSeS^- - 2e^- \rightarrow Ar_2Se_2 + S_2} \qquad (9)$$

This scheme is confirmed by the exhaustive oxidation of ArSeS$^-$ solutions at controlled potential (E = +0.2 V), affording recovery of the initially added sulfur [$E_{1/2}$(R) = −0.40 V] and of Ar$_2$Se$_2$ [$E_{1/2}$(R) = −0.69 V; λ_{max} = 378 nm]. Although 3 h are required to quantitatively obtain ArSe$_2{}^-$ according to eqn. (6), the shift of the oxidation wave of ArSe$_2{}^-$ is immediately observed after the addition of solid selenium, as soon as traces of ArSe$_2{}^-$ have been generated. The electrocatalytic process, which is analogous to that of eqns. (7)–(9), leads to Ar$_2$Se$_2$ by electrolysis of ArSe$_2{}^-$ (E = 0.0 V), with deposition of Se on the large gold grid electrode. The spectroelectrochemical characteristics of ArSeS$^-$, ArSe$_2{}^-$ and ArSSe$^-$ ions have been summarized in Table 1.

ArS$_2{}^-$ ions are better nucleophilic agents than the corresponding thiolates towards alkyl halides.[13] This α-effect[14] could be connected with the enhanced rate of electronic exchange with the electrode material for reducing ions ArS$_2{}^-$, ArSSe$^-$, ArSe$_2{}^-$ and ArSeS$^-$ with respect to ArS$^-$ and ArSe$^-$. Here again, the addition of alkyl iodides or bromides to the previous dilute solutions of ArSeS$^-$ or ArSe$_2{}^-$ readily yields the presumed species ArSeSR and ArSe$_2$R, without any recovery of sulfur or solid selenium. The products are distinguished by their bielectronic reduction waves and their maximal absorbances: ArSeSPr: $E_{1/2}$(R) = −0.76 V, λ_{max} = 385 nm, ε_{385} = 3400 dm^3 mol^{-1} cm^{-1}; ArSe$_2$Pr: $E_{1/2}$(R) = −0.77 V, λ_{max} = 380 nm, ε_{382} = 4600 dm^3 mol^{-1} cm^{-1}.

Table 1 Spectrophotometric and electrochemical characteristics of ArSeS$^-$, ArSe$_2{}^-$, ArSSe$^-$ and ArS$_2{}^-$ ions (Ar = 2-NO$_2$C$_6$H$_4$) in *N*,*N*-dimethylacetamide at 20 °C. $E_{1/2}$ at a rotating gold disc electrode *vs.* reference Ag/AgCl, KCl sat. in DMA/N(Et)$_4$ClO$_4$ 0.1 mol dm^{-3}

ArXY$^-$	λ_{max}/nm	ε_{max}/dm^3 mol^{-1} cm^{-1}	$-\Delta E_{1/2}$(O)/V^a
ArSeS$^-$	728	4900	0.25
	340	6100	
ArSe$_2{}^-$	728	3200	0.41
	354	5800	
ArSSe$^-$	666	5000	0.68
ArS$_2{}^{-b}$	681	5200	0.50
	362	6000	

^{a} $\Delta E_{1/2}$(O) = $E_{1/2}$(ArXY$^-$) − $E_{1/2}$(ArX$^-$) for $y = 1$ with $E_{1/2}$ (ArSe$^-$) = +0.16 V and $E_{1/2}$ (ArS$^-$) = +0.55 V. ^{b} Values determined previously.

The alkylation of a blue solution of ArSeS$^-$ ions with benzyl bromide was run at a preparative scale.‡ RSeSR′ species are known to be unstable compounds that evolve by disproportionation [eqn. (10)]:[1b,2]

$$\mathrm{2RSeSR' \rightleftharpoons RSe_2R + R'S_2R'} \qquad (10)$$

The crude solid product was thus immediately analyzed by ^{1}H NMR and GC/MS. The composition of the mixture: ArSeSCH$_2$Ph (60%), (PhCH$_2$S)$_2$ (12%), Ar$_2$Se$_2$ (12%) and ArSeCH$_2$Ph (16%, close to the initial proportion ArSe$^-$: ArSeS$^-$ = 0.15) was determined from δ_H (s, CH$_2$) by comparison with those of commercial dibenzyl disulfide (δ_H = 3.59) and of a synthetic sample of ArSeCH$_2$Ph (ArSe$^-$ + PhCH$_2$Br). Thus the nucleophilic reaction of ArSeS$^-$ ions with benzyl bromide yields the expected selenenyl sulfide ArSeSCH$_2$Ph, which partly disproportionates (30%) according to eqn. (10).

Studies are currently being extended to the formation of RSSe$_x{}^-$ (R = alkyl, $1 \leqslant x \leqslant 3$) and RSe$_y{}^-$ ($2 \leqslant y \leqslant 4$) ions, from alkane thiolates or selenolates and selenium in dipolar aprotic medium.

Notes and references

† All of the equipment and the flow-through cell have been previously described.[6] The spectroelectrochemical experiments were carried out with 0.1 mol dm^{-3} tetraethylammonium perchlorate as supporting electrolyte.

‡ Ar$_2$Se$_2$ (1.12 g, 2.78 mmol) in DMA (120 cm^3) was reduced into aryl selenolate ions by controlled potential coulometry (E = −1.1 V) in a two-compartment cell in the presence of 0.5 mol dm^{-3} N(Et)$_4$ClO$_4$. The ArSe$^-$ solution (electrical yield 88%) was stirred with solid sulfur (0.135 g, 4.2 mmol S; S : ArSe$^-$ = 0.85) at 40 °C for 15 min. PhCH$_2$Br (4.9 mmol) in DMA (10 cm^3) was then added dropwise at room temperature up to the decoloration of the solution. The products (1.18 g) were extracted with diethyl ether. Recovered Ar$_2$Se$_2$ (0.23 g), which gave no GC signal, was separated in the last fraction to be obtained by column chromatography of the mixture (silica gel, CH$_2$Cl$_2$–Et$_2$O = 1 : 1).

ArSeSCH$_2$Ph: m/z 324 (M$^+$, 4%) and 91 (100); δ_H (200 MHz, CDCl$_3$) 4.03 (s, 2H).

ArSeCH$_2$Ph: mp 95–96 °C: m/z 292 (M$^+$, 4%) and 91 (100); δ_H (200 MHz, CDCl$_3$) 4.20 (s, 2H), 7.27–7.68 (m, 8H), 8.36 (dd, 1H, J 8.3 and 1.3 Hz).

Ar$_2$Se$_2$: mp 215–216 °C (lit.[11] 220 °C); δ_H (200 MHz, CDCl$_3$) 7.35–7.55 (m, 4H), 7.89 (dd, 2H, J 8 and 1.6 Hz), 8.34 (dd, 2H, J 8 and 1.8 Hz).

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Letter 9/034540