Stabilization of sulfenyl(poly)selenide ions in N,N-dimethylacetamide

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Whereas redox processes resulted from the reactions $PhSe^{-}/S_8$ or $PhSe_2Ph/S_3^{\bullet-}$, mixed anions $RSSe_y^{-}$ (R = Ph, PhCH₂; y = 1-3) were obtained by the slow addition of solid selenium to thiolate ions in *N*,*N*-dimethylacetamide. The RS⁻ + *n* Se reactions, which were investigated by spectroelectrochemistry, led initially (n = 1) only to the formation of RSSe⁻ ions. These species oxidized into RS₂R faster than RS⁻ on a gold electrode, with the simultaneous electrodeposition of very reactive microcrystals of selenium. On a preparative scale, the substitution of RSSe⁻ ions (R = CH₃, Ph) on alkyl halides yielded RSSeR' compounds (R' = PhCH₂, CH₃, respectively) which greatly disproportionated. Further additions of Se (n = 2, 3) to RS⁻ ions led to RSSe₂⁻ and RSSe₃⁻ ions were calculated from the study of the backward reactions RS₂R + Se_x^{2⁻} (x = 4, 6).

We previously reported that solid selenium slowly reacts with RSe⁻ selenolate ions in *N*,*N*-dimethylacetamide (DMA), a dipolar aprotic medium, yielding successively RSe_y^- ions [eqn. (1); R = Ph, PhCH₂; y = 2-4].¹ RSe₃⁻ and RSe₄⁻ ions disproportionate [eqn. (2)] into diselanes and Se_x²⁻ polyselenide ions which had been characterized (x = 4, 6, 8):²

$$\mathbf{RSe}^- + (y-1) \ \mathbf{Se}(\mathbf{s}) \to \mathbf{RSe}_y^-$$
 (1)

$$2 \operatorname{RSe}_{v}^{-} \rightleftharpoons \operatorname{RSe}_{2} R + \operatorname{Se}_{x}^{2-}$$
(2)

Reactions (1) are similar to those observed between sulfur and thiolates leading to RS_y^- ions (R = alkyl, y = 2-5).³ However, very little is known about 'mixed anions' such as $RSSe_y^-$ or $RSeS_y^-$ ($y \ge 1$): a variety of selenenyl thiolates ($RSeS^-Li^+$) resulting from the addition of one sulfur unit to lithium alkyl selenolates (RSe^-Li^+) in THF were characterized *in situ* by ⁷⁷Se NMR at 193 K;⁴ however ' $RSeS^-$ readily underwent internal redox-reactions below room temperature' [eqn. (3)], and $RS^- + Se$ (or Te) processes were described as ineffective in THF.⁴

$$2 \operatorname{RSeS}^{-} \to \operatorname{RSe}_2 R + \operatorname{S}_2^{2-}$$
(3)

Using UV-visible absorption spectrophotometry, we recently showed that the stoichiometric addition of sulfur to selenolate ions 2-NO₂C₆H₄Se⁻ (ArSe⁻, $\lambda_{max} = 520$ nm; [S]_{ad}/ [ArSe⁻]₀ = 1) yielded $\simeq 85\%$ of ArSeS⁻ ions ($\lambda_{max} = 728$ nm);⁵ these species being partly oxidized in the presence of excess sulfur [eqn. (5)]:⁵

$$2 \operatorname{ArSe}^{-} + S_2 \rightleftharpoons 2 \operatorname{ArSeS}^{-}$$
(4)

$$2 \operatorname{ArSeS}^{-} + 3 \operatorname{S}_2 \rightleftharpoons \operatorname{Ar}_2 \operatorname{Se}_2 + \operatorname{S}_8^{2-}$$
(5)

While the formation of $ArSe_2^-$ as in eqn. (4) ($ArSe^- + Se$) was complete, the conversion of ArS^- into $ArSSe^-$ only reached 20%.⁵

It has now been established that RS_2^- ions oxidize into RS_2R faster than RS^- ions on a gold electrode, according to eqns. (6) and (7):^{3,6}

$$2 \text{ RS}^- + \text{S}_2 \rightleftharpoons 2 \text{ RS}_2^- \tag{6}$$

$$2 \operatorname{RS}_2^- - 2 \operatorname{e}^- \to \operatorname{RS}_2 \operatorname{R} + \operatorname{S}_2 \tag{7}$$

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Surprisingly, analogous anodic behaviours have been reported with RSe₂⁻ ¹ and ArSSe⁻ species,⁵ suggesting fast heterogeneous reactions between RSe⁻ or ArS⁻ ions and electrogenerated solid selenium. This hypothesis is reconsidered in the present paper which is mainly devoted to the expected stabilization of $RSSe_{\nu}^{-}$ ($\nu \ge 1$; R = Ph, PhCH₂) and PhSeS⁻ ions. The reactions RS^{-}/Se and $PhSe^{-}/S$, $RS_{2}R/Se_{x}^{2-}$ (x = 4, 6, 8) and $PhSe_2Ph/S_3^{\bullet-}$ were therefore followed by UV-visible spectrophotometry coupled with voltammetry (CV and rotating gold disc electrode). Natural selenium-containing compounds have been the subject of extensive studies because of their possible cancer chemopreventive properties.^{7,8} 'Selenenyl sulfides' RSSeR' identified in Allium volatiles from speciation experiments,⁹ are most frequently prepared by reactions between thiols (RSH) and selenenyl halides (R'SeX, X = Br, Cl).¹⁰ These species are also obtained by mixing the symmetrical products RS₂R and R'Se₂R' of the usual disproportionation (8):11

$$2 \operatorname{RSSeR}' \rightleftharpoons \operatorname{RS}_2 R + R' \operatorname{Se}_2 R' \tag{8}$$

Our spectroelectrochemical results on the stabilization of $RSSe^-$ ions were then applied on a preparative scale, to two typical alkylations of RS^- ($R = CH_3$, Ph) + Se solutions.

Results and discussion

S_x^{2-} , Se_x^{2-} , RS^- and RSe^- ions in DMA

There is now general agreement concerning the nature of polysulfide ions in dipolar aprotic media.^{12,13} In *N*,*N*-dimethylacetamide, sulfur reduces in two bielectronic steps with respect to S₈ on a gold rotating electrode [waves R₁ and R₂, $E_{1/2}(R_1) = -0.40$ V vs. reference, $E_{1/2}(R_2) = -1.10$ V].¹³ The electrolysis at controlled potential on the plateau of R₁ occurs via the disproportionation (9) of red S₈²⁻ ions ($\lambda_{max1} = 515$ nm, $\varepsilon_{515}^8 = 3800$ dm³ mol⁻¹ cm⁻¹; $\lambda_{max2} = 360$ nm, $\varepsilon_{360}^8 = 9000$ dm³ mol⁻¹ cm⁻¹), up to the stable blue S₃^{•-} radical-anion ($\lambda_{max} = 617$ nm, $\varepsilon_{617}^3 = 4100$ dm³ mol⁻¹ cm⁻¹) in equilibrium with its dimer S₆²⁻ in a minor proportion. In our opinion cyclooctasulfur is in equilibrium with the reactive S₂ molecules, thus appearing in equations such as (9).¹³

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1433

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Redox process	Peaks ^a (potential/V)	
$8Se_{(s)} + 2e^{-} \Rightarrow Se_{8}^{2-}$ $3Se_{8}^{2-} + 2e^{-} \Rightarrow 4Se_{6}^{2-}$ $2Se_{6}^{2-} + 2e^{-} \Rightarrow 3Se_{4}^{2-}$ $3Se_{4}^{2-} + 2e^{-} \Rightarrow 4Se_{3}^{2-}(?)$ $2Se_{3}^{2-} + 2e^{-} \Rightarrow 3Se_{2}^{2-}(?)$	$\begin{array}{l} R_1 \ (-0.49) \\ R_2 \ (-0.62) \\ R_3 \ (-0.89) \\ R_4 \ (-1.28) \\ R_5 \ (-1.55) \end{array}$	$\begin{array}{c} O_1{}' \ (-0.33) \\ O_1{}' \ (-0.33) \\ O_2{}' \ (-0.65) \\ O_3{}' \ (-1.0) \end{array}$

^{*a*} $\mathbf{R} = \text{cathodic}; \mathbf{O} = \text{anodic}.$

$$\mathbf{S}_8^{2-} \rightleftharpoons 2 \ \mathbf{S}_3^{\bullet-} + \mathbf{S}_2 \tag{9}$$

$$3 S_8 + 8 e^- \rightarrow 8 S_3^{\bullet -}$$
 (10)

 S_8^{2-} and $S^{-1/3}$ ions $(S_3^{\bullet-} \rightleftharpoons S_6^{2-})$ oxidize (O_1) and reduce (R_2) at the same potentials $[E_{1/2}(O_1) = -0.20 \text{ V}; E_{1/2}(R_2) = -1.10 \text{ V}].$

Prior to this study, Se_x^{2-} ions (x = 8,6,4) were successively obtained by coulometric reduction (R_1-R_3 steps) of weighed amounts of grey selenium coating a large gold grid electrode.² Two further reduction steps detected on cyclic voltammograms (R_4 , R_5 , perhaps leading to Se_3^{2-} and Se_2^{2-} as in liquid ammonia)¹⁴ were not identifiable by our method because of passivation phenomena on the gold electrode surface. The redox processes summarized in Table 1 and the known UVvisible spectra² providing molar absorbance of the stable Se_x^{2-} ions (Fig. 1; x = 8, $\lambda_{max} = 648$, 453, 398 nm; x = 6, $\lambda_{max} = 598$, 440 nm; x = 4, $\lambda_{max} = 550$, 417 nm) were used

for quantitative data processing in this study. RY^- ions (Y = Se, R = Ph; Y = S, R = Ph, PhCH₂) were generated ([RY⁻]₀ $\leq 4 \times 10^{-3}$ mol dm⁻³) by electrolysis of

generated ([RY⁻]₀ $\leq 4 \times 10^{-3}$ mol dm⁻³) by electrolysis of RY₂R species at a controlled potential of a gold electrode on the plateau of their bielectronic waves (Y = Se,^{1,15} Y = S^{3,16}) according to previously described procedures [eqn. 11f]:

$$\mathbf{R}\mathbf{Y}_{2}\mathbf{R} + 2 \ \mathbf{e}^{-} \xleftarrow{\mathbf{f}}_{\mathbf{b}} 2 \ \mathbf{R}\mathbf{Y}^{-} \tag{11}$$

The electrochemical and spectrophotometric characteristics of RY_2R and RY^- species are summarized in Table 2.

PhSe₂Ph/S₃^{•-} and PhSe⁻/S₈ reactions

The addition of $PhSe_2Ph$ to $S_3^{\bullet-}$ ions resulted in instantaneous changes in voltammograms and spectra (Fig. 2) which agreed with equilibrium (12):

$$PhSe_2Ph + 8 S_3^{\bullet-} \rightleftharpoons 2 PhSe^- + 3 S_8^{2-}$$
(12)



Fig. 1 UV-visible absorption spectra $(\epsilon_i/dm^3 \text{ mol}^{-1} \text{ cm}^{-1})$ of Se₈^{2–} (1), Se₆^{2–} (2) and Se₄^{2–} (3) ions in dimethylacetamide.

Table 2 Electrochemical and spectrophotometric characteristics of RY₂R and RY⁻ species (Y = Se, S) in DMA— $E_{1/2}$ at a rotating gold disc electrode *vs.* reference

	$\frac{\mathbf{R}\mathbf{Y}_{2}\mathbf{R}}{E_{1/2}(\mathbf{R})/\mathbf{V}}$	RY ⁻			
R, Y		$E_{1/2}(O)/V$	$\lambda_{\rm max}/{\rm nm}$	$\varepsilon_{\max}{}^a$	
Ph, Se	-0.76	-0.36	318	12 700	
Ph, S	-1.25	+0.02	309	18 200	
PhCH ₂ , S	-1.55	-0.03	285^{b}	3850	
^{<i>a</i>} $\varepsilon_{\rm i}/{\rm dm^3}$ mol	l^{-1} cm ⁻¹ . ^b Shou	ılder.			

 $A_{617}(S_3^{\bullet-})$ decreased in favor of $A_{515}(S_8^{2-} \text{ and } A_{360}(S_8^{2-}, \text{ and } PhSe^- \text{ in part})$ according to calculated $\Delta[S_3^{\bullet-}]/\Delta[S_8^{2-}]$ values close to $-2.6 \simeq -8/3$, and through the same isosbestic point ($\lambda_{is} = 545 \text{ nm}$) as in the course of electrooxidation (13) of $S^{-1/3} \text{ ions}$:¹³

$$8 S_3^{\bullet -} \to 3 S_8^{2-} + 2 e^-$$
(13)

However, as shown by the growth of the reduction wave of PhSe₂Ph [$E_{1/2}(\mathbf{R}) = -0.76$ V] from the first additions of diphenyl diselenide, preceding the constant cathodic current of $\mathbf{S_3^{\bullet -}}/\mathbf{S_8^{2^-}}$ ions [$E_{1/2}(\mathbf{R}) = -1.10$ V] reaction (12) was not quantitative. At the stoichiometric value [PhSe₂Ph]_{ad}/[$\mathbf{S_3^{\bullet -}}$]₀ = 1/8 in the experimental conditions of Fig. 2, consumption of $\mathbf{S^{-1/3}}$ ions only reached 40%. $\mathbf{S_8^{2^-}}$ ions remained unreactive towards PhSe₂Ph since A_{515} always increased with addition of the substrate in excess. Conversely, sulfur quantitatively reacted with benzene selenolate ions in accordance with eqn. (14):

$$2 \operatorname{PhSe}^{-} + S_8 \to \operatorname{PhSe}_2\operatorname{Ph} + S_8^{2-}$$
(14)

With the addition of sulfur to PhSe⁻ ions the spectra were the same as those observed when S₈ was electrolyzed at 2 F mol⁻¹ S₈ for various [S₈]₀ concentrations,¹³ regardless of [S]_{ad}/ [PhSe⁻]₀ ratio values between 0 and 1: the increases of absorbances at 515 nm (S₈²⁻) and 617 nm (S₃^{•-}) because of the partial disproportionation (9) with a negligible sulfur proportion always confirmed ($\pm 6\%$) the conservation eqn. (15):

$$[\mathbf{S}_8]_0 = [\mathbf{S}_8^{2-}] + 1/2[\mathbf{S}_3^{\bullet-}]$$
(15)

At the same time, the reduction currents of PhSe₂Ph $[E_{1/2}(\mathbf{R}) = -0.76 \text{ V}]$ and of $S_3^{\bullet-}/S_8^{2-}$ ions $[E_{1/2}(\mathbf{R}) = -1.10 \text{ V}]$ increased, while the anodic wave of the latter $[E_{1/2}(\mathbf{O}) = -0.20 \text{ V}]$ progressively replaced that of PhSe⁻ ions $[E_{1/2}(\mathbf{O}) = -0.36 \text{ V}]$ up to stoichiometry (14).



Fig. 2 Dependence of the UV-visible spectra on the addition of diphenyl diselenide to a $[S_3^{\bullet-}]_0 = 6.06 \times 10^{-3}$ mol dm⁻³ solution. [PhSe₂Ph]_{ad}/[S₃^{$\bullet-$}]₀ = 0 (1); 0.063 (2); 0.12₅ (3); 0.23 (4); 0.32 (5); 0.50₃ (6); 0.96 (7). Thickness of the cell = 0.1 cm; scan rate = 500 nm min⁻¹.



Fig. 3 Changes in UV-visible spectra with the addition of selenium powder to a $[PhS^-]_0 = 2.87 \times 10^{-3} \text{ mol } dm^{-3} \text{ solution. } n = (Se)_{ad}/(RS^-)_0 = 0 (1); 0.99 (2); 1.98 (3); 2.99 (4); 4.0 (5); recordings at equilibrium except for <math>(1) \rightarrow (2)$, A = f(t), 0 < t < 95 min.

Thus, in contrast to the two successive steps which were evidenced in the course of the addition of sulfur to the least reducing $2\text{-NO}_2\text{C}_6\text{H}_4\text{Se}^-$ (ArSe⁻) species,⁵ formation (4) of ArSeS⁻, then reversible oxidation (5) into ArSe₂Ar, only redox processes (12) and (14) resulted from the reactions PhSe₂Ph/S₃^{•-} and PhSe⁻/S₈, respectively, without any observed stabilization of PhSeS⁻ ions.

Stabilization and electrocatalytic oxidation of RSSe⁻ ions

When grey selenium powder (pellets, diameter *ca.* 10–30 µm) was added to stirred solutions of PhS⁻ and PhCH₂S⁻ ions at a ratio $n = (\text{Se})_{\text{ad}}/(\text{RS}^-)_0 = 1$, the changes in UV-visible spectra and cyclic voltammograms were similar in both cases, as illustrated in Figs. 3 and 4 (R = Ph). In the course of the Se consumption which required about 1.5 h up to n = 1, two absorption bands regularly increased with time: R = Ph (see Fig. 3, curves $1 \rightarrow 2$), $\lambda_{\text{max1}} = 403$ nm, $\lambda_{\text{max2}} = 260$ nm, isosbestic point $\lambda_{\text{is}} = 272$ nm; R = PhCH₂, $\lambda_{\text{max1}} = 430$ nm, $\lambda_{\text{max2}} = 260$ nm, $\lambda_{\text{is1}} = 324$ nm, $\lambda_{\text{is2}} = 298$ nm), in agreement with the formation of only RSSe⁻ ions:

$$\mathbf{RS}^- + \mathbf{Se}(\mathbf{s}) \to \mathbf{RSSe}^-$$
 (16)

As soon as solid Se was added, and before any growth of absorbance at about 400 nm, the oxidation current of RS^-



Fig. 4 Cyclic voltammograms of a $[PhS^-]_0 = 3.52 \times 10^{-3} \text{ mol dm}^{-3}$ (0.14 mmol) solution (1) added with selenium powder (11 mg, 0.14 mmol); $\Delta t = 2 \text{ min } (2)$; 92 min (3). *E vs.* Ag/AgCl, KCl sat. in DMA-NEt₄ClO₄ 0.1 mol dm⁻³. Scan rate = 50 mV s⁻¹.

Table 3 $\Delta E_{1/2}(O)/V$ variation of anodic half-wave potentials^{*a*} related to the oxidations of RYZ⁻ and RY⁻ ions into RY₂R species

	R = Ph	$R = PhCH_2$	$\mathbf{R} = \mathbf{A}\mathbf{r}^b$		
Y, Z = S, S	-0.23	-0.46	-0.50		
Y, Z = Se, Se	-0.08	-0.06	-0.41		
Y, Z = S, Se	-0.47	-0.35	-0.68		
^{<i>a</i>} $\Delta E_{1/2}(O) = E_{1/2}(RYZ^{-}) - E_{1/2}(RY^{-})$. ^{<i>b</i>} Ar = 2-NO ₂ C ₆ H ₄ .					

ions into RS₂R [Fig. 4, curve 1, $Ep^a = +0.04$ V, $Ep^c = -1.40$ -1.40 V] totally shifted towards less anodic potentials (curve 2, $Ep^a = -0.37$ V). At the end of reaction (16) PhSSe⁻ had an oxidation peak at -0.44 V (curve 3), and reversal of the voltage scan direction resulted in the appearance of the sharp reduction peak of electrodeposited Se $[Ep^c(1) = -0.49 \text{ V}]^2$ followed by the subsequent cathodic peaks 2–5 of the polyselenide ions (Table 1), then associated anodic peaks (3', 2'). This electrochemical behavior of RS⁻ ions in the presence of selenium complies with the following electrocatalytic mechanism [eqns. (16)–(18)], which is analogous to those previously reported for RS⁻/RS₂^{-3,6} and RSe⁻/RSe₂⁻ species:¹

$$2 \mathbf{R} \mathbf{S}^{-} - 2\mathbf{e}^{-} \to \mathbf{R} \mathbf{S}_2 \mathbf{R} \tag{17}$$

$$\mathbf{RS}^- + \mathbf{Se}(\mathbf{s}) \to \mathbf{RSSe}^-$$
 (16)

$$2 \operatorname{RSSe}^{-} - 2e^{-} \to \operatorname{RS}_2 R + 2 \operatorname{Se}(s)$$
(18)

Thus, RS₂⁻, RSe₂⁻ and RSSe⁻ ions oxidize into RY₂R (Y = S, Se) on a gold electrode, at a greater rate than RY⁻ ions, as shown by the differences between their respective half-wave potentials of oxidation listed in Table 3. The occurrence of the catalytic processes from the addition of insoluble selenium to RY⁻ ions (Y = S, Se) implies fast heterogeneous reactions such as in eqn. (16) between RY⁻ and the released Se in the course of electrooxidation [*e.g.*, eqn. (18)], although RSe₂⁻ or RSSe⁻ were only obtained by direct addition (1) or (16) after 1.5 hour. The same schemes were tested on quantitative electrolysis at a controlled potential of a large gold grid electrode (*E* = -0.10 V), of a solution containing ArSe⁻ [Ar = 2-NO₂Ph, *E*_{1/2}(O) = +0.16 V, $\lambda_{max} = 520$ nm, $\varepsilon_{max} = 1200$ dm³ mol⁻¹ cm⁻¹]⁵ and ArSe₂⁻ [*E*_{1/2}(O) = -0.25 V, $\lambda_{max} = 728$ nm, $\varepsilon_{max} = 3450$ dm³ mol⁻¹ cm⁻¹]⁵ ions: [ArSe⁻]₀ = 3.40 × 10⁻³ mol dm⁻³, [ArSe₂⁻]₀ = 2.25 × 10⁻³ mol dm⁻³ [spectral changes in Fig. 5 as a function of *z* F mol⁻¹ (ArSe⁻)₀ + (ArSe⁻)₀]. As long as ArSe⁻ ions were in greater



Fig. 5 Spectral changes in the course of the electrooxidation at E = -0.10 V vs. reference of a $[ArSe^-]_0 = 3.40 \times 10^{-3}$ mol dm⁻³ + $[ArSe_2^-]_0 = 2.25 \times 10^{-3}$ mol dm⁻³ solution (Ar = 2-NO₂Ph): z F mol⁻¹ (ArSe⁻)_0 + (ArSe⁻)_0 = 0 (1)-0.58 (6); 0.65 (7); 0.75 (8); 0.85 (9).

(a)

(b)

$$2 \operatorname{ArSe}_2^{-} - 2 e^{-} \rightarrow \operatorname{ArSe}_2 \operatorname{Ar} + 2 \operatorname{Se}(s)$$
(19)

Simultaneously A_{728} (ArSe₂⁻) remained at a constant value because of the 'instantaneous' reaction between ArSe⁻ and Se which was generated at the electrode surface. Then (z > 0.60), curves 7–9), the consumption of ArSe₂⁻ (decrease in A_{728}) resulted in the deposition of solid selenium on the gold grid, and the recovery of ArSe₂Ar ($z \simeq 1.05$) according to its characteristic absorption at 378 nm ($\varepsilon_{max} = 7300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).⁵

Similarly, a gold foil $(1 \times 1 \text{ cm})$ was coated with grey selenium by electrolysis (E = -0.25 V) of PhSSe⁻ ions (about 0.076 mmol), and then observed by scanning electron microscopy (SEM). The SEM images shown in Figs. 6a–6b revealed an epicentric crystallization with small dendrites, mostly 1 to 2 µm in length, which could explain the high reactivity of 'Se-nucleophiles' such as RY⁻ species (Y = S, Se) towards electrogenerated selenium.

The recent interest in biochemistry of RSSeR' species^{7–9} led us to examine the alkylation of two RSSe⁻ solutions on a preparative scale as examples: CH₃SSe⁻ + PhCH₂Br and PhSSe⁻ + CH₃I. The compositions of the mixtures of products RSSeR', RS₂R, R'Se₂R' which were analyzed by ¹H NMR and GC/MS (see Experimental) corresponded to significant disproportionation of the expected selenenyl sulfides CH₃SSeCH₂Ph (\simeq 80%) and PhSSeCH₃ (\simeq 70%), as previously reported for this class of rather unstable compounds [eqn. (8)].¹¹



Fig. 6 Scanning electron micrographs of electrodeposited selenium on a gold foil from the oxidation of PhSSe⁻ ions (E = -0.25 V). (a) ×1000; (b) ×5000.

Formation of $RSSe_{\nu}^{-}$ ions

Further additions of solid selenium to $RSSe^-$ ions [R = Ph,PhCH₂, $n = (Se)_{ad}/(RSe^{-})_0$ greater than 1] resulted in its total consumption within 2 h (n = 2), then 2.5 h (n = 3), whereas traces of solid Se remained unreactive for n = 4 beyond 4 h. The partial oxidation of the anionic solutions was shown by the appearance of Se_x^{2-} ions ($x \ge 4$). Mixtures of these species were detected by the simultaneous increase in their absorption at around 625 nm ($\text{Se}_6^{2-}/\text{Se}_8^{2-}$, R = Ph, Fig. 3, curves 3–5) or 590–620 nm ($\text{Se}_4^{2-}/\text{Se}_6^{2-}$ or $\text{Se}_6^{2-}/\text{Se}_8^{2-}$, R = PhCH₂), and in their reduction waves (RDE, $x = 8, 6, 4; E_{1/2} = -0.55, -0.83,$ -1.20 V),² with greater currents at potentials close to those of RS₂R (R = Ph, $E_{1/2} \simeq -1.25$ V; R = PhCH₂, $E_{1/2} \simeq$ -1.55 V). At the same time another absorption band increased at about 405 nm (R = Ph) or 380 nm (R = PhCH₂) which could not be related to Se_x^{2-} ions from the shape of their own spectra (Fig. 1). Moreover, spectra and voltammograms were the same when equilibrium was attained for the respective stoichiometries: $RS^{-}+2$ Se (R = Ph, Fig. 3, curve 3) and $RS_2R + Se_4^{2-}$; $RS^- + 3$ Se (Fig. 3, curve 4) and $RS_2R + Se_6^{2-}$ (see below Fig. 7, curve 5). All of these observations were analogous to those occurring in the course of the RSe⁻ + *n* Se(s) $(n \ge 2)$ and RSe₂R + Se_x²⁻ (x = 4, 6) reactions, which yielded RSe_{v}^{-} ions (v = 3, 4, maximal absorbances at 400–420 nm) in equilibrium with RSe₂R and mixtures of polyselenide ions [eqn. (2)].¹ Here again, the fast reactions $RS_2R + Se_x^2$ $(R = Ph, PhCH_2; x = 4, 6)$ were followed by calculations first of the polyselenide concentrations as a function of $m = [RS_2R]_{ad}/[Se_x^{2-}]_0$: $[Se_6^{2-}]$ and $[Se_8^{2-}]$ (598 < λ_{max} < 648 nm), or $[Se_4^{2-}]$ and $[Se_6^{2-}]$ (550 < λ_{max} < 598 nm), were deduced from experimental values of A598 and A648 or A598 and A_{550} , respectively, by the use of the known ε_i molar absorptivity (Fig. 1), *e.g.* eqn. (20), ε_i (dm³ mol⁻¹ cm⁻¹, $\pm 4\%$): $\varepsilon_{598}^6 = 1750$, $\varepsilon_{598}^8 = 2150$; $\varepsilon_{648}^8 = 2500$, $\varepsilon_{648}^6 = 1450$.¹

$$A_{\rm i} = \varepsilon_{\rm i}({\rm Se_6}^{2-})[{\rm Se_6}^{2-}] + \varepsilon_{\rm i}({\rm Se_8}^{2-})[{\rm Se_8}^{2-}]$$
(20)

The other concentrations $[RS_2R]$ and $[RSSe_y^-]$, as well as the average number \bar{y} of Se units in $RSSe_y^-$ chains, were then calculated by solving the conservation equations from $[RS_2R]_{ad}$ and $[Se_x^{2-}]_0$ values. As an example, Fig. 7 shows the changes in spectra for the reaction $PhS_2Ph + Se_6^{2-}$. Two steps can be distinguished:

(*i*) for $0 < m \le 0.42$ (curves 1–2), the maximal absorbance of Se₆^{2–} ions (A_{440} , A_{598}) evolved towards that of Se₈^{2–} (A_{398} , A_{453} , A_{648}) through three isosbestic points ($\lambda_{is} = 398$, 474 and 545 nm), according to the rough stoichiometry of eqn. (21):

$$PhS_2Ph + 2.4 Se_6^{2-} \rightarrow 2 PhSSe_{1.6}^{-} + 1.4 Se_8^{2-}$$
 (21)



Fig. 7 Changes in UV-visible spectra with the addition of diphenyl disulfide to a $[\text{Se}_6^{2-}]_0 = 1.15 \times 10^{-3} \text{ mol } \text{dm}^{-3} \text{ solution:}$ $m = [\text{RS}_2\text{R}]_{\text{ad}}/[\text{Se}_6^{2-}]_0 = 0$ (1); 0.42 (2); 0.66 (3); 0.90 (4); 1.02 (5).

Table 4 Calculated compositions of solutions at equilibrium for the reactions $RS_2R + Se_x^{2-}$ (x = 4, 6) and $RS^- + n$ Se (n = 2, 3) depending on initial conditions^{*a*}

Initial cond. ^{<i>a</i>}	[Se4 ²⁻]	[Se ₆ ²⁻]	[Se ₈ ^{2–}]	[(RS) ₂]	$[(RSSe_y^{-})]$	\bar{y}
$[(PhS)_2]_0 = 2.70 + [Se_4^{2-}]_0 = 2.74$		0.42	0.21	0.60	4.20	1.6
$[PhS^{-}]_{0} = 2.87 + [Se]_{0} = 5.70$		0.23	0.15	0.38	2.11	1.5
$[(PhS)_2]_0 = 1.12 + [Se_6^{2-}]_0 = 1.10$		0.35	0.17	0.54	1.16	2.7
$[PhS^{-}]_{0} = 2.87 + [Se]_{0} = 8.58$		0.37	0.22	0.59	1.69	2.7
$[(PhCH_2S)_2]_0 = 2.54 + [Se_4^{2-}]_0 = 2.66$	0.54	0.22		0.64	3.80	1.9
$[PhCH_2S^-]_0 = 2.90 + [Se]_0 = 5.70$	0.40_{5}	0.105		0.51	1.88	1.85
$[(PhCH_2S)_2]_0 = 1.59 + [Se_6^{2-}]_0 = 1.54$	_	0.475	0.20	0.72	1.74	2.75
$[PhCH_2S^-]_0 = 2.90 + [Se]_0 = 8.60$	_	0.445	0.225	0.67	1.56	2.65
^{<i>a</i>} All concentrations are in mmol dm^{-3} .						

(*ii*) for $0.42 < m \le 1.0$ (curves 2–5), the progressive displacement $A_{648} \rightarrow A_{618}$ agreed with a partial recovery of Se₆²⁻ ions, and with the formation at the same time of RSSe_y⁻ ions of higher \bar{y} rank (Table 4, m = 1, $\bar{y} = 2.7$), giving a maximum absorbance at about 412 nm. These results can be explained by eqns. (22)–(24):

$$\mathbf{RS}_{2}\mathbf{R} + \mathbf{Se}_{6}^{2-} \rightleftharpoons \mathbf{2} \ \mathbf{RSSe}_{3}^{-} \tag{22}$$

$$2 \operatorname{RSSe}_{3}^{-} + \operatorname{Se}_{6}^{2-} - \xrightarrow[b]{f}{b} 2 \operatorname{RSSe}_{2}^{-} + \operatorname{Se}_{8}^{2-}$$
(23)

$$2 \operatorname{RSSe}_{2}^{-} + \operatorname{Se}_{6}^{2-} \xrightarrow{f}{b} 2 \operatorname{RSSe}^{-} + \operatorname{Se}_{8}^{2-}$$
(24)

In the presence of Se₆²⁻ ions in excess (m < 0.42), reactions (22) and (23) totally shift to the right, leading to a mixture of RSSe⁻ and RSSe₂⁻ ions by equilibrium (24) ($\bar{y} \simeq 1.6$). With further additions of RS₂R, the consumption of Se₆²⁻ displaces equilibria (23) and (24) in reverse, increasing the \bar{y} value to 2.7 (mixture RSSe₂⁻/RSSe₃⁻).

Similarly, three steps were observed from progressive changes in $A = f(\lambda)$ curves during the addition of PhS₂Ph to the more reducing Se₄²⁻ ions: (*i*) $0 < m \le 0.35$, $A_{550} \rightarrow A_{598}$ and $A_{417} \rightarrow A_{440}$, and thus Se₄²⁻ \rightarrow Se₆²⁻ according to the nearly quantitative redox process (25).

$$PhS_2Ph + 3 Se_4^{2-} \rightarrow 2 PhS^- + 2 Se_6^{2-}$$
 (25)

(*ii*) $0.35 < m \le 0.67$, $A_{598} \rightarrow A_{645}$ and $A_{440} \rightarrow A_{450}/A_{400}$ due to further reaction of Se₆²⁻ ions which provided Se₈²⁻ ions in accordance with the overall eqn. (26).

$$PhS_2Ph + 1.5 Se_4^{2-} \rightarrow 2 PhSSe^- + 0.5 Se_8^{2-}$$
 (26)

(*iii*) $0.67 < m < 1.0_2$, $A_{645} \rightarrow A_{615}$ and $A_{450}/A_{400} \rightarrow A_{407}$; the reactions of $\text{Se}_6^{2^-}/\text{Se}_8^{2^-}$ ions finally led to $\bar{y} \simeq 1.6$ (m = 1) by 'Se-exchanges' as in eqn. (24).

The calculated concentrations and average \bar{y} numbers at the end of slow reactions $[RS^-]_0 + n$ (Se)_{ad} (R = Ph, PhCH₂; n = 2, 3) and of the equivalent fast reactions $[RS_2R]_0 + [Se_x^{2^-}]_0$ (m = 1; x = 4, 6) are given in Table 4. Based on $[RS_2R]$ values at equilibrium compared with $[RS^-]_0$ or $[RS_2R]_0$ (Table 4, R = Ph and PhCH₂), the disproportionations of $RSSe_y^-$ ions could therefore be roughly situated at *ca*. 25% (y = 2) and 45% (y = 3). These levels meet those of RSe_3^- (30%) and RSe_4^- (~45%) ions [eqn. (2)].¹ Furthermore, the spectra of $RSSe_y^-$ ions (y = 2, 3) were obtained over the wavelength range 350–600 nm as previously obtained for RSe_3^- and RSe_4^- ions:¹ (*i*) $RSSe^-/RSSe_2^-$ and $RSSe_2^-/RSSe_3^-$ mixtures were assumed to give $1 < \bar{y} < 2$ and $2 < \bar{y} < 3$ respectively, with definite compositions linked to \bar{y} values (*e.g.* $\bar{y} = 1.6$, 40% RSSe⁻ and 60% RSSe₂⁻); (*ii*) for the most accurate conditions $[RS_2R]_0 = [Se_x^{2^-}]_0$, the absorbances of $Se_x^{2^-}$ ions (x = 6, 8 or 4, 6) calculated by the use of concentrations in Table 4 and characteristics in Fig. 1 were subtracted from the experimental A values, 10 nm apart; (*iii*) the known spectra of RSSe⁻ ions (RS⁻ + 1 Se, $\varepsilon_i \pm 5\%$) led firstly to those of RSSe⁻₂ (x = 4), then RSSe⁻₃ (x = 6). The $A = f(\lambda)$ curves are reported in Fig. 8 for R = Ph, whereas Table 5 summarizes the spectrophotometric characteristics of RSSe⁻_y ions (R = Ph, PhCH₂; y = 1-3). λ_{max} wavelengths of RSSe⁻_y ions were lower by $\simeq 25$ nm than those of homologous RSeSe⁻_y species (y = 1-3), with close ε_y values in both cases.¹ The formation of RSSe⁻₄ ions could not be proved from the addition of RS₂R disulfides to Se²⁻₈ ions, because of the detection of solid selenium within the solutions in the course of the reactions which entailed at first the shift A_{648} (Se²⁻₈) $\rightarrow A_{630}$ (Se²⁻/Se²⁻).

Conclusions

Whereas selenolate ions undergo redox exchanges to RSe_2R diselenides with sulfur in *N*,*N*-dimethylacetamide, selenium adds to thiolates with the formation of the sulfur–selenium bond in $RSSe^-$ species. The latter reactions, and those leading to RSe_2^- ($RSe^- + Se$) which we recently reported, are analogous to the well known 'S-nucleophilic processes' affording RS_2^- ions from thiolates and sulfur.

In mixtures $RS^- + RSSe^-$, $RSSe^-$ ions oxidize into RS_2R faster than RS^- ions on a gold electrode, with a fast heterogeneous reaction between selenolate ions and electrogenerated selenium. RSSeR' alkylated selenenyl sulfides disproportionate to a large extent into symmetrical RS_2R and $R'Se_2R'$ compounds.

 $RSSe_y^-$ ions (y = 2, 3), which partly disproportionate into RS_2R and Se_x^{2-} ions, result from the slow addition of solid Se to $RSSe^-$ ions. The same equilibria are readily obtained by the reactions between RS_2R and Se_x^{2-} ions.



Fig. 8 Calculated spectra ($\varepsilon_i/dm^3 mol^{-1} cm^{-1}$) of PhSSe_y⁻ ions. y = 1-3, (1)–(3).

R		RSSe ⁻	$RSSe_2^-$	RSSe ₃ ⁻
Ph	λ_{\max}^{a}/nm	403	400	405
	ε _{max} ^{b c}	900	3000	3600
PhCH ₂	λ_{\max}^{a}/nm	430	375	375
-	$\epsilon_{\max}^{b\ c}$	400	2600	3000
^{<i>a</i>} $\lambda_{\max}(y =$	2, 3) \pm 4 nm. ^{<i>b</i>} ε_{1}	$dm^3 mol^{-1} c$	m^{-1} . ^c $\varepsilon_{\mathrm{i}}(y=2,$	3) ± 15%.

Experimental

Materials and equipment

N,N-Dimethylacetamide, grey selenium (99.999%, 100 mesh), and all the organic compounds were purchased from Aldrich except for diphenyl diselenide and dibenzyl mono-and di-selenide (Acros Organics). Solvent purification and storage after addition of NEt_4ClO_4 (Fluka, 0.1 mol dm⁻³) as supporting electrolyte have been reported elsewhere.¹⁷ Spectroelectrochemical equipments and electrodes,¹ as well as the thermostatted $(20.0 \pm 0.50 \,^{\circ}\text{C})$ flow-through cell¹⁷ have previously been described. All the potentials were referenced to Ag/AgCl, KCl saturated in DMA-NEt₄ClO₄ (0.1 mol dm⁻³) electrode. The Se-coated gold foil was observed by Scanning Electron Microscopy (SEM FEG Gemini 982 Leo Microscope). The micrographs were obtained in secondary electron image mode (accelerating voltage of 2 kV). The synthesized mixtures were analyzed by ¹H NMR spectroscopy (200.132 MHz, Bruker AC 200) with CDCl₃ as the solvent (Me₄ Si as standard) and GC-MS (Hewlett-Packard 5989 A, EI 70 eV).

Generation of Se_x^{2-} ions

Accurate concentrations of Se_x^{2-} ions were obtained by the same method as recently reported:^{1,2} selenium was initially deposited on a large gold grid electrode [25 < w(Se)/mg < 40] by the electrooxidation (E = 0.0 V) of Se_x^{2-} solutions ($\bar{x} \simeq 6$) which were themselves chemically generated in DMA from the reduction of Se with hydrazine and sodium methoxide:¹⁸

$$12 \text{ Se}(s) + 4 \text{ MeO}^- + N_2 H_4 \rightarrow 2 \text{ Se}_6^{2-} + 4 \text{ MeOH} + N_2$$
(27)

The cathodic polarization of the Se-coated grid in DMA (40 cm³) was then kept until the spectra and the related maximal absorbances of Se_x²⁻ (Fig. 1; x = 8, E = -0.55 V; x = 6, E = -0.75 V; x = 4, E = -1.10 V) were attained. Concentrated solutions of RS₂R substrates in DMA (R = Ph, PhCH₂; $v_{max} = 4$ cm³) were progressively added to Se_x²⁻ ions. In all cases, absorbances reached equilibrium within 1 min.

Syntheses of RSSeR' compounds

The CH₃SSe⁻ + PhCH₂Br and PhSSe⁻ + CH₃I reactions were carried out according to the same procedure on a preparative scale: solid sodium thiomethoxide (95%) and lithium thiophenoxide (1 mol dm⁻³ in THF) of commercial origin were dissolved in 80 cm³ of deaerated DMA under an N₂ atmosphere. The RS⁻ solutions were stirred at 50 °C with selenium powder (Se:RS⁻ = 1:1) which reacted within 3 hours. Stoichiometric amounts of alkyl halides dissolved in DMA (20 cm³) were then added dropwise (20 min) at room temperature to the yellow RSSe⁻ solutions. After filtration (0 °C) of the medium and addition of water (300 cm³), the products were extracted with diethyl ether. The organic phase was thoroughly washed with water (elimination of residual DMA) and dried over MgSO₄. After evaporation *in vacuo*, the mixtures were rapidly analyzed without attempting to separate the individual compounds because of the poor stability of the RSSeR' species.^{10,11}

Reaction of CH₃SSe⁻ ions with PhCH₂Br. CH₃S⁻Na⁺ (0.814 g, 11.6 mmol), Se (0.909 g, 11.5 mmol), PhCH₂Br (1.40 cm³, 11.5 mmol). The composition of the mixture of products (1.97 g): CH₃SSeCH₂Ph (29%), (PhCH₂)₂Se₂ (57%), $(CH_3S)_2$ (14%), was determined from δ_H (s, 2H) and δ_H (s, 3H); (CH₃S)₂ and (PhCH₂)₂Se₂ were identified by the use of commercial samples which were added to the synthesized mixture. Volatile $(CH_3S)_2$ was assumed to have been greatly reduced in the course of the solvent evaporation. The disproportionation level of CH₃SSeCH₂Ph (~80%) was thus calculated by reference to the only (PhCH₂)₂Se₂ proportion. (PhCH₂)₂Se, which gave no ¹H NMR signal, was detected in the mass spectra as a result of the known selenium extrusion from benzylic diselenide under thermal conditions.¹⁹ CH₃SSeCH₂Ph: $\delta_{\rm H}$ 2.24₅ (s, 3H), 4.08 (s, 2H); m/z 218 (⁸⁰Se, M^+ , 4%), 91 (100), 65(16) and 39 (9). (PhCH₂)₂S₂: δ_H 3.80 (s, 4H); m/z 342 (⁸⁰Se, M⁺, 2%), 91 (100). (CH₃S)₂: $\delta_{\rm H}$ 2.39₅ (6H, s; m/z 96 (M⁺ + 2, 11), 94 (M⁺, 100%). (PhCH₂)₂Se: m/z 262 (⁸⁰Se, M⁺, 7%), 91 (100).

Reaction of PhSSe⁻ with CH₃I. PhS⁻Li⁺ in THF (11 cm³, 11 mmol), Se (0.792 g, 10.0 mmol), CH₃I (0.80 cm³, 12.8 mmol). The products were identified both by ¹H NMR with the use of commercial samples of (PhS)2, (CH3Se)2 and PhSCH3 compounds, and by GC-MS. The composition of the mixture (1.79 g): PhSSeCH₃ (32%), (PhS)₂ (35%), (CH₃Se)₂ (22%) PhSCH₃ (11%, close to the initial and ratio $PhS^{-}:PhSSe^{-} = 1:10$), was determined by combining the integrals of $\delta_{\rm H}$ (s, 3H) with those of aromatic $\delta_{\rm H}$, (PhS)₂ (4 Ho) and PhSSeCH₃ (2Ho). It was in good agreement with the integration of the GC peaks. Here again, the disproportionation of PhSSeCH₃ (\simeq 70%) was evaluated from the respective proportions of PhSSeCH₃ and (PhS)₂ in the mixture. PhSSeCH₃: $\delta_{\rm H}$ 2.46 (s, 3H), 7.51 (1Ho, Ar), 7.55 (1Ho, Ar); m/z 204 (⁸⁰Se, M⁺, 87%), 189 (57), 109 (100), 77 (51), 69 (37), 65 (76), 51 (43), 39 (49). (PhS)₂: $\delta_{\rm H}$ 7.45 (2Ho, Ar), 7.49 (2Ho, Ar); m/z218 (M⁺, 76%). (CH₃Se)₂: $\delta_{\rm H}$ 2.67₅ (s, 6H); m/z 190 (⁸ ⁰Se. M⁺, 88%). PhSCH₃: $\delta_{\rm H}$ 2.44₇ (s, 3H); m/z 124 (M⁺, 100%).

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