Preparation of selenoxides from the catalytic autoxidation of organoselenides with nitrogen oxides

Eric Bosch and Jay K. Kochi

Department of Chemistry, University of Houston, Houston, TX 77204-5641, USA

Various alkyl, aryl and benzyl selenides (RSeR') are readily converted in high yields to the corresponding selenoxide in the presence of dioxygen and catalytic amounts of either nitrogen dioxide, nitrosonium cation or nitric oxide in acetic acid. The selenoxides are initially isolated as the acetic acid adducts (from which the free selenoxides are readily liberated by treatment with base). Nitrogen dioxide is also capable of the stoichiometric oxidation of the selenoethers; and the electron donor–acceptor or EDA complex with nitrosonium, *i.e.* $[R_2Se \cdot NO^+]NO_3^-$ is formed as the first intermediate by the selenoether-induced disproportionation of NO_2. The critical role of the nitrosonium EDA complex is further demonstrated by the production of selenoxide by an alternative (low-temperature) photochemical procedure involving the deliberate irradiation of the charge-transfer absorption band of $[PhSeMe \cdot NO^+]NO_3^-$. A scheme is shown that presents the sequence of redox changes of the nitrogen oxides involved in the catalytic conversion of selenoethers to their selenoxides.

Introduction

The role of organoselenides in synthesis has increased dramatically since the early 1970s,[1-4] largely due to the discovery of two preparative transformations involving the corresponding selenoxides. Most commonly used is the spontaneous elimination of the selenoxide moiety at ambient temperatures to provide a facile route to olefins.[5-8] Allylic selenoxides, on the other hand, undergo a facile [2,3] sigmatropic rearrangement to allylic alcohols.[9-10] While the selenoxides in these rearrangements are themselves seldom isolated more stable selenoxides used in other transformations have been isolated.[11] The sporadic reports of the preparation and isolation of stable selenoxides from aryl-, benzyl- or methyl-substituted selenides (selenoethers) utilize stoichiometric amounts (or an excess) of common oxidants such as hydrogen peroxide,[12] ozone,[13] *tert*-butyl hydroperoxide[14] and sodium metaperiodate.[15]

We report here the selective aerial oxidation of selenoethers to their selenoxides, catalysed by nitrogen oxides. This provides an inexpensive, high yield alternative to the existing procedures. In this oxidation, a novel charge-transfer complexation plays a major role, and we demonstrate that electron donor–acceptor (EDA) complexes with nitrosonium are the first critical intermediates. Since the selenoxide products are strongly basic and readily form acetic acid adducts, they effectively prevent over-oxidation and thus render the overall transformation highly selective.

Results

Stoichiometric oxidation of selenoethers with nitrogen dioxide
When phenyl methyl selenide (1 mmol) was treated with nitrogen dioxide[16] (1 equiv.) in rigorously dried dichloromethane under an argon atmosphere at 0 °C, a vigorous reaction was accompanied by the copious evolution of nitric oxide which was identified by its characteristic IR stretching bands at 1904, 1876 and 1851 cm^{-1}.[17-19] Quantitative analysis of phenyl methyl selenoxide and nitric oxide established the 1:1 stoichiometry under anaerobic conditions, as shown in eqn. (1). The reaction

$$PhSeMe + NO_2 \xrightarrow[CH_2Cl_2]{0\,°C} PhSe(O)Me + NO \qquad (1)$$
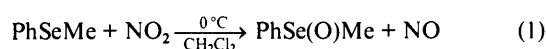
was rather capricious, and the reaction in dichloromethane

resulted in a colourless precipitate along with the selenoxide and unreacted selenoether. The solid was removed by filtration, recrystallized from acetonitrile, and identified as a nitric acid adduct by elemental analysis and ^1H and ^{13}C NMR spectroscopy.[20,21] Since the ^1H NMR spectrum of the initially formed solid only consisted of the methyl and aromatic resonances, the solid was presumed to be a dinitrogen tetraoxide adduct. However, the colourless solid was extremely hygroscopic and after recrystallization was transformed into the nitric acid adduct which exhibited an additional proton resonance at 12 ppm[22-25] [see eqn. (2)]. The selenoxide was recovered

$$PhSe(O)Me \cdot N_2O_4 + H_2O \longrightarrow PhSe(O)Me \cdot HNO_3, etc. \qquad (2)$$
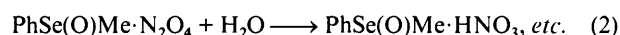
from the nitric acid adduct in quantitative yield simply on treatment with aqueous potassium carbonate. The oxidation of dibenzyl selenide with NO_2 (1.1 equiv.) in dichloromethane also yielded a mixture of products from which the nitric acid adduct of dibenzyl selenoxide[22,23] and unreacted dibenzyl selenide were isolated and identified.

In order to circumvent these problems and to perform the selenoether oxidation with NO_2 in a controlled, reproducible manner, we reasoned that reaction in acetic acid would result in the formation of the well-known (and soluble) acetic acid adducts of the selenoxides.[23,26] Indeed, the treatment of phenyl methyl selenide with 1 equiv. of NO_2 in acetic acid at 25 °C resulted in the quantitative formation of the acetic acid adduct of phenyl methyl selenoxide with the concomitant liberation of 1 equiv. of nitric oxide, as shown in eqn. (3). Treatment of the

$$PhSeMe + NO_2 \xrightarrow[CH_3CO_2H]{25\,°C} PhSe(O)Me \cdot HOAc + NO \qquad (3)$$
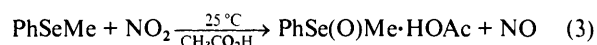
adduct with potassium carbonate (as described in the Experimental section) resulted in the evolution of CO_2, and the selenoxide was liberated in quantitative yield, as shown in eqn. (4). The oxidation of the various selenoethers in Table 1

$$2\,PhSe(O)Me \cdot HOAc + K_2CO_3 \xrightarrow{H_2O}$$
$$2\,PhSe(O)Me + 2\,KOAc + CO_2 \qquad (4)$$
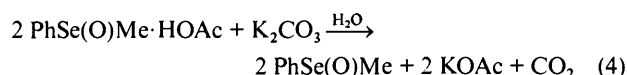
with stoichiometric amounts of NO_2 led to high yields of the corresponding selenoxides by the same procedure.[27,28]

Table 1 Stoichiometric oxidation of selenoethers with nitrogen dioxide[a]

| Selenoether	Amount/ mmol	Adduct yield[b]/ mmol	Selenoxide yield[c] (%)
Phenyl methyl selenide	0.66	0.63	94
Phenyl methyl selenide	1.05	—[d]	91
Phenyl isopropyl selenide	1.75	1.70	96
Benzyl phenyl selenide	2.01	1.97	97
Benzyl methyl selenide	1.25	1.25	93
Dibenzyl selenide	1.03	1.03	97

[a] With 1.1 equiv. of NO_2 in acetic solution at 25 °C under an argon atmosphere, unless stated otherwise (see Experimental section). [b] Isolated yield of the acetic acid adduct. [c] Isolated yield of selenoxide based on selenoether charged. [d] Reaction in dichloromethane solution.

Autoxidation of selenoethers catalysed by nitrogen oxides

A solution of phenyl methyl selenide in acetic acid remained unchanged under a dioxygen atmosphere (in the dark) for weeks at room temperature. However, the overall oxidation of selenoethers with nitrogen dioxide in acetic acid as depicted in eqns. (3) and (4), coupled with the well-known aerial (re)oxidation of the nitric oxide,[29] provided the basis for the catalysed aerial oxidation of selenoethers as follows. An acetic acid solution of phenyl methyl selenide (3.4 mmol) was saturated with O_2 and the flask connected to a gas-filled balloon to ensure a complete oxygen atmosphere. Small amounts of nitrogen dioxide (0.17 equiv.) were added, and the mixture stirred at 25 °C overnight. The solvent and unreacted nitrogen oxides were removed *in vacuo*, and the spectral analysis of the solvent mixture in the cold trap identified only unreacted NO_2 by its characteristic IR stretching bands at $\nu_{NO}/cm^{-1} = 1600$ and 1620.[30] The acetic acid adduct of phenyl methyl selenoxide was isolated in quantitative yield [eqn. (5)]. Treatment of the

$$PhSeMe + 0.5\ O_2 \xrightarrow{[NO_2]}_{CH_3CO_2H} PhSe(O)Me \cdot HOAc \quad (5)$$
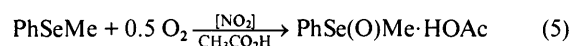
aqueous solution of the acetic acid adduct with potassium carbonate (0.5 equiv.) resulted in the copious evolution of CO_2. When the evolution of gas ceased, the selenoxide was isolated in quantitative yield by the work-up described in eqn. (4). The other selenoethers in Table 2 were also subjected to these conditions, and the corresponding selenoxides isolated in excellent yield. Indeed, even the labile isopropyl phenyl selenoxide was isolated in quantitative yield after treatment of the acetic acid adduct with base at 0 °C. (The selenoxide subsequently underwent slow decomposition at 25 °C.[27,28]) Moreover, the same autoxidation in acetic acid was catalysed by catalytic quantities of either a nitrosonium salt or nitric oxide [see eqn. (6)].

$$RSeR' + 0.5\ O_2 \xrightarrow{[NO^+]\ or\ [NO]}_{CH_3CO_2H} RSe(O)R' \cdot HOAc \quad (6)$$
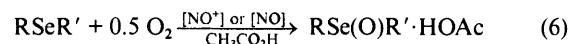
It should be noted that acetic acid solutions of phenyl methyl selenide were indefinitely stable in the presence of nitric oxide under anaerobic conditions.

The nitrogen dioxide-catalysed autoxidation was incomplete when carried out in dichloromethane solution (turnover numbers < 2) due to the formation of a colourless precipitate of the nitric acid adduct as described in the stoichiometric oxidation (*vide supra*). (Such a precipitation effectively removed the nitrogen oxide catalyst from the reaction mixture.)

In situ oxidation–elimination of selenoethers

A dichloromethane solution of α-phenylseleno-α-benzyl-butyrolactone[31] was cooled to −78 °C, treated with 3 equiv. of nitrogen dioxide, and then warmed to 25 °C. The red solution faded to yellow, and a white precipitate formed. After 2 h, the precipitate (containing the phenylselenyl moiety) was removed and washed with dichloromethane. The combined solutions were concentrated *in vacuo*, and the butenolide[32,33] isolated in 92% yield by preparative TLC [see eqn. (7)]. When the reaction was
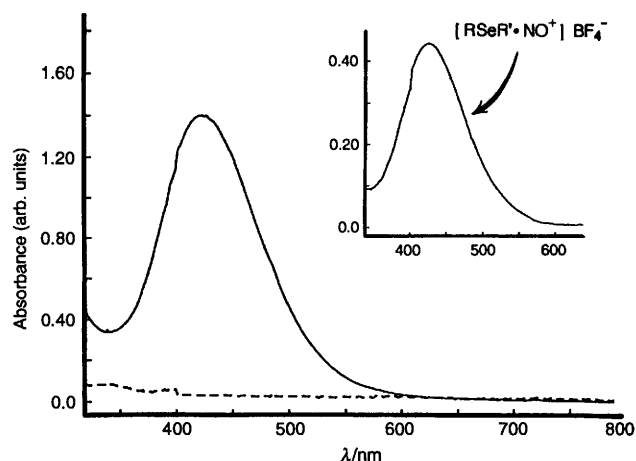
Fig. 1 Charge-transfer absorption spectrum (——) of 2×10^{-3} M benzyl methyl selenide and 6×10^{-4} M nitrogen dioxide in dichloromethane at −78 °C relative to the spectrum of NO_2 alone (– – –). Inset: Charge-transfer absorption spectrum of 2×10^{-3} M benzyl methyl selenide and $NO^+ BF_4^-$ in dichloromethane at −78 °C.

performed in acetic acid, 1 equiv. of NO_2 was sufficient to effect the transformation in quantitative yield. Alternatively, the same result was obtained with dioxygen in the presence of catalytic amounts of nitrogen oxides.

Visual and spectral changes during the catalytic and stoichiometric oxidation of selenoethers with nitrogen dioxide. Identification of nitrosonium complexes

The stoichiometric and catalytic oxidation of selenoethers with nitrogen dioxide were both characterized by a vivid series of characteristic colour changes particular to each selenoether. For example, immediately upon treatment of an acetic acid solution of phenyl methyl selenide with nitrogen dioxide (1 equiv.), the solution turned red. The colour rapidly faded and the solution became colourless after 5 min at 25 °C. The same colour changes were observed in dioxygen-saturated solutions in either acetic acid, dichloromethane–acetic acid mixtures or pure dichloromethane.

Since the visual changes were particular to each selenoether, a common origin of the colours to NO_2 was sought. Accordingly, the quantitative effects of the colour change arising from the interaction of selenoethers with NO_2 was monitored by UV–VIS spectroscopy at low temperatures where the thermal oxidation in eqn. (1) was too slow to compete. Fig. 1 shows the well-resolved absorption band with $\lambda_{max} = 515$ nm of the red solution resulting from the addition of NO_2 to a solution of benzyl methyl selenide in dichloromethane at −78 °C. At this low temperature, the absorption band was persistent over the course of several hours (when protected from adventitious room light); and the benzyl methyl selenide could be recovered intact when the cold solution was rapidly quenched. Since the positions of the new absorption bands (in Table 3, column 3) for each of the selenoethers underwent progressive bathochromic shifts to lower energies with increasing donor strengths (as evaluated by the oxidation potentials in Table 3, column 2). they were ascribed to the charge-transfer (CT) absorption bands in the same manner as that which we previously described for the corresponding thioether–NO_2 interactions.[34] Indeed, the colours of the electron donor–acceptor (EDA) complexes derived from the selenoethers and NO_2 were identical to those obtained on mixing the pure nitrosonium salt ($NO^+ BF_4^+$) with the various selenoethers at −78 °C.[35] Table 3

Table 2 Catalytic autoxidation of selenoethers with nitrogen oxides[a]

| Selenoether	Amount/mmol	Nitrogen oxide	Amount/mmol	Selenoxide yield[b] (%)
Phenyl methyl selenide	3.42	NO_2	0.5	96
Phenyl isopropyl selenide	2.97	NO_2	0.5	96
Benzyl phenyl selenide	4.85	NO_2	0.5	93
Benzyl methyl selenide	3.85	NO_2	0.33	82
Benzyl methyl selenide	3.05	NO^+	0.50	74[c]
Benzyl methyl selenide	2.10	NO	0.50	97
Dibenzyl selenide	1.8	NO_2	0.5	92

[a] In acetic acid solution under 1 atm of dioxygen at 25 °C, unless stated otherwise (see Experimental section). [b] Isolated yield of selenoxide. [c] The other products were not identified.

Table 3 Charge-transfer spectra of selenoether EDA complexes prepared from nitrogen dioxide and nitrosonium salt[a]

Selenoether donor	E_p/V (vs. SCE)[b]	NO_2		NO^+	
		λ_{CT}[c]/nm	FWHM[d]/10^{-2} cm^{-1}	λ_{CT}[c]/nm	FWHM[d]/10^{-2} cm^{-1}
Benzyl methyl selenide	—	424	62	426	50
Benzyl selenide	1.41	444	79	452	59
Isopropyl phenyl selenide	1.29	496	50	500	58
Phenyl methyl selenide	1.16	498	46	494	55
Benzyl phenyl selenide	—	506	57	508	51

[a] In dichloromethane solution at -78 °C with 2×10^{-3} M selenoether and 6×10^{-4} M nitrogen oxide (see Experimental section). [b] Peak potential of irreversible anodic wave by cyclic voltammetry at $v = 0.1$ V s^{-1} recorded in dichloromethane solution containing 0.3 M Bu$_4$N$^+$ PF$_6^-$. [c] Maximum of the CT absorption band (± 3 nm). [d] Full width at half maximum.

establishes the direct correspondence of the charge-transfer absorption maxima (λ_{CT}) and transition probabilities [full width at half maximum (FWHM)] of the selenoether complexes with NO_2 (columns 3 and 4) and those derived from NO^+ (columns 5 and 6). The latter were obtained merely by the addition of the crystalline NO^+ BF$_4^-$ to a solution of the selenoether in dichloromethane at -78 °C. On stirring the heterogeneous mixture at this low temperature for a few minutes, the mixture took on a bright (orange-red) colouration as the nitrosonium salt slowly dissolved to afford the EDA complex. The resultant formation of the EDA complex is described in eqn. (8), where

$$RSeR' + NO^+ BF_4^- \underset{}{\overset{K_{EDA}}{\rightleftharpoons}} [RSeR' \cdot NO^+]BF_4^- \qquad (8)$$
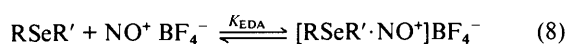
RSeR' is the generic representation of the selenoethers.[36] The selenoethers were recovered intact following rapid work-up of the coloured solutions.

On the basis of the essential identity of the two series of charge-transfer absorption bands in Table 3, we concluded that the CT colourations of selenoether solutions with nitrogen dioxide involved the same nitrosonium moiety. Since the latter was known to derive from the reversible disproportionation of NO_2,[37-40] the most convenient formulation for the relevant CT interaction of selenoethers with nitrogen dioxide is given by eqn. (9). Indirect support for this ionic disproportionation was

$$2 NO_2 \underset{}{\overset{}{\rightleftharpoons}} NO^+ NO_3^- \underset{}{\overset{RSeR'}{\rightleftharpoons}} [RSeR' \cdot NO^+] + NO_3^- \qquad (9)$$
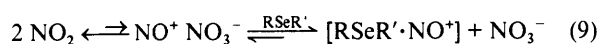
obtained by readily shifting the equilibrium to the right (observed as the increased intensity of the CT absorption band) by the addition of SbCl$_5$ as the Lewis acid[41] [eqn. (10)].

$$2 NO_2 + RSeR' \xrightarrow{SbCl_5} [RSeR' \cdot NO^+]SbCl_5NO_3^- \qquad (10)$$

Conversely, the equilibrium was readily shifted to the left (reduced intensity of the CT absorption band) by the addition of nitrate as the PPN salt,[42,43] [eqn. (11)].

$$2 NO_2 + RSeR' \xleftarrow{NO_3^-} [RSeR', NO^+] + NO_3^- \qquad (11)$$

Charge-transfer oxidation of selenoethers with nitrogen dioxide by selective photo-activation of the EDA complex

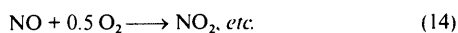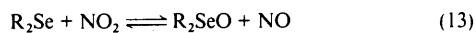The critical role of the nitrosonium complex [eqn. (9)] in the

selenoether oxidations with NO_2 was further probed by its selective photo-activation (via its charge-transfer absorption band) at -78 °C, where the thermal process (Tables 1 and 2) was too slow to compete. Experimentally, the brightly coloured solutions were held at this low temperature and continuously exposed to actinic radiation from a 250 W mercury lamp equipped with a sharp cut-off filter so that only light with $\lambda_{exc} > 410$ nm was transmitted. Under these controlled conditions, the results in Fig. 1 ensured the selective excitation of the charge-transfer absorption band of the EDA complex. (Any adventitious activation of either the uncomplexed selenoether or nitrogen dioxide was thus precluded.)

The photoactivation of the EDA complex of phenyl methyl selenide and nitrogen dioxide in an 8:1 v/v mixture of dichloromethane and acetic acid at -78 °C resulted in the monotonic bleaching of the charge-transfer colour,[44] that occurred concomitantly with the selective formation of phenyl methyl selenoxide, as in eqn. (12).

$$[PhSeMe \cdot NO^+] NO_3^- \xrightarrow[ii\ K_2CO_3]{i\ h\nu_{CT}\ -78\ °C} PhSe(O)Me,\ etc. \qquad (12)$$
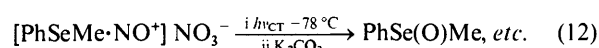
Discussion

Nitrogen dioxide is a unique reagent that can be employed both as an oxidant in the stoichiometric oxidation of selenoethers and as a catalyst for the autoxidation of selenoethers with equal efficacy (see Tables 1 and 2).[45] The reactions are best performed in acetic acid to allow the basic selenoxides[23] to be trapped as their acetic acid adducts. (In the absence of such an acid, insoluble nitrogen oxide adducts are formed which inhibit the catalytic process by removing the active catalyst from the system.) Since dioxygen alone is incapable of oxidizing selenoethers at ambient temperatures and atmospheric pressures (in the dark), one of the nitrogen oxide species must be the active agent in the catalytic oxidations. Indeed, the stoichiometric oxidation of selenoethers by NO_2 described in eqns. (1) and (3), coupled with the well known aerial (re)oxidation of the nitric oxide,[29] provides the basis for the catalytic process, as shown in Scheme 1. However, this simple scheme does not adequately account for various facets of the selenoether oxidations such as (a) the vivid colour changes that accompany the oxidations, and (b) the ready replacement of NO_2 with either NO^+ or NO in the

$$R_2Se + NO_2 \rightleftharpoons R_2SeO + NO \qquad (13)$$

$$NO + 0.5\,O_2 \longrightarrow NO_2, \; etc. \qquad (14)$$

$$R_2SeO + HOAc \longrightarrow R_2SeO\cdot HOAc \qquad (15)$$

Scheme 1

catalytic process [eqn. (6)]. Furthermore, any mechanistic formulation must be consistent with the results in Tables 1 and 2 as well as the charge-transfer oxidation described in eqn. (12). Accordingly, let us first address the stoichiometric thermal and photochemical (charge-transfer) oxidation of selenoethers with NO_2, and then relate these conclusions to the catalytic oxidations.

Spectral changes accompanying the stoichiometric oxidation of selenoethers with NO_2

The UV–VIS absorption spectra in Fig. 1, together with the spectral parameters in Table 3, provide definitive identification of the nitrosonium EDA complexes as the first (observable) intermediate formed from selenoethers and NO_2. In order to understand how the chromophoric moiety $[R_2Se\cdot NO^+]$ is formed from NO_2, we recall that earlier dimerization studies[46] identified the existence of trace amounts of the unsymmetric nitrito–nitro dimer in equilibrium with the prevalent nitro–nitro dimer,[47–50] as shown in eqn. (16). Although the heterolytic

$$O_2NNO_2 \rightleftharpoons 2\,NO_2 \rightleftharpoons ONONO_2 \qquad (16)$$
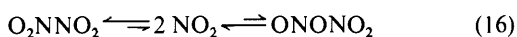
disproportionation of the nitrito–nitro dimer to the nitrosonium nitrate ion pair is negligible in dichloromethane, we previously demonstrated that complexation of NO^+ to strong organic donors such as electron-rich arenes[40] and thioethers[51] can shift the mobile equilibrium to the ionic EDA complex. We thus propose that the selenoethers which are significantly better donors than the corresponding thioethers[52] promote an analogous disproportionation, as in eqn. (17). Indeed, the formation

$$O_2NONO \rightleftharpoons NO^+NO_3^- \xrightarrow{R_2Se} [R_2Se\cdot NO^+]NO_3^- \qquad (17)$$
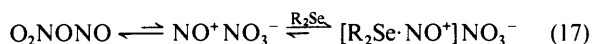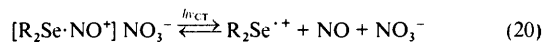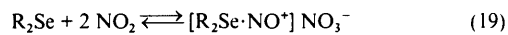
of highly coloured solutions even in the presence of very dilute concentrations of NO_2 (see Fig. 1) suggests that the formation constant for the nitrosonium selenoethers EDA complexes as shown in eqn. (8) is comparable to that previously determined for dibutyl sulfide[51] and hexamethylbenzene[35] ($K_{EDA} \approx 10^5$ dm^3 mol^{-1}).

Nitrosonium EDA complex as the critical intermediate in selenoether oxidation

The vivid colour of the nitrosonium EDA complex during the reaction of selenoethers with NO_2 is a hallmark of the oxidations. However, the most compelling evidence for the critical role of the nitrosonium complex comes from the direct photochemical activation of the $[R_2Se\cdot NO^+]$ EDA complex. Thus, the selective irradiation of the charge-transfer absorption band ($h\nu_{CT}$) of the nitrosonium EDA complex yields the selenoxide in high yield at temperatures too low ($-78\,^\circ C$) to effect the thermal oxidation of the selenoethers. It follows from Mulliken theory[53] that the selenoether cation radical is the reactive intermediate in the charge-transfer oxidation, see eqn. (18). The

$$[R_2Se\cdot NO^+]\,NO_3^- \xrightarrow{h\nu_{CT}} R_2Se^{\cdot+} + NO + NO_3^- \qquad (18)$$

further conversion of the selenoether cation radical to the selenoxide can proceed by ion-pair collapse with the nitrate counterion, as previously established for corresponding thioether cation radicals.[51,54,55] As such, the complete sequence for the photoinduced conversion of selenoethers to selenoxides is best described by the charge-transfer cycle in Scheme 2.[56]
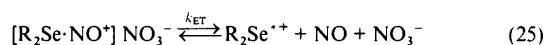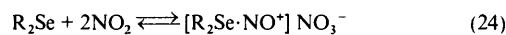
$$R_2Se + 2\,NO_2 \rightleftharpoons [R_2Se\cdot NO^+]\,NO_3^- \qquad (19)$$

$$[R_2Se\cdot NO^+]\,NO_3^- \xrightleftharpoons{h\nu_{CT}} R_2Se^{\cdot+} + NO + NO_3^- \qquad (20)$$

$$R_2Se^{\cdot+} + NO_3^- \longrightarrow R_2SeO + NO_2 \qquad (21)$$

$$R_2SeO + HOAc \longrightarrow R_2SeO\cdot HOAc \qquad (22)$$

Scheme 2

Electron-transfer mechanism for the thermal oxidation of selenoethers with nitrogen dioxide

The strong similarity of the colour changes accompanying both the stoichiometric thermal oxidation and the photoinduced oxidation suggests that the same series of intermediates are involved. If so, the formation of selenoether cation radicals via the electron-transfer (adiabatic) activation of the nitrosonium EDA complex represents the thermal counterpart to the charge-transfer activation in eqn. (19), as shown in eqn. (23).

$$[R_2Se\cdot NO^+]\,NO_3^- \xrightleftharpoons[k_{bet}]{k_{ET}} R_2Se^{\cdot+} + NO + NO_3^- \qquad (23)$$
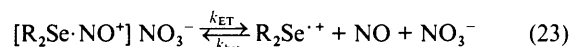
The driving force for electron-transfer is given by: $-\Delta G = F[E^\circ_{ox}(R_2Se) + E^\circ_{red}(NO^+)]$ where F is the Faraday constant and E° is the appropriate redox potential. On this basis, the electron-transfer described in eqn. (23) is predicted to be mildly exergonic, since the reduction potential of NO^+ is 1.50 V vs. SCE in dichloromethane[57] and the peak potentials for representative selenoethers in Table 3 are in the range $1.1–1.5$ V vs. SCE. Under the reaction conditions, the selenoether cation radicals are unlikely to be observed owing to their low steady-state concentration arising from the rapid reaction with nitrate to generate the selenoxide. The corresponding mechanism for the thermal oxidation can thus be represented as shown in Scheme 3.
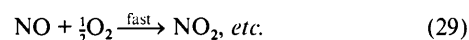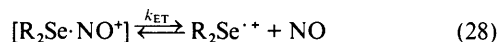
$$R_2Se + 2NO_2 \rightleftharpoons [R_2Se\cdot NO^+]\,NO_3^- \qquad (24)$$

$$[R_2Se\cdot NO^+]\,NO_3^- \xrightleftharpoons{k_{ET}} R_2Se^{\cdot+} + NO + NO_3^- \qquad (25)$$

$$R_2Se^{\cdot+} + NO_3^- \xrightarrow{fast} R_2SeO + NO_2 \qquad (26)$$

$$R_2SeO + HOAc \xrightarrow{fast} R_2SeO\cdot HOAc \qquad (27)$$

Scheme 3

The complexation of the selenoxide by acetic acid effectively removes the selenoxide from any further reactions.

Mechanism of the nitrogen oxide-catalysed autoxidation of selenoethers

Since catalytic amounts of different nitrogen oxides either NO, NO^+ or NO_2 catalyse the oxidation of selenoethers in Table 2, any mechanistic scheme must take cognizance of the interchangeability among this diverse group of catalysts. Initially, we note that electron transfer to the nitrosonium cation generates the selenoether cation radical together with nitric oxide. The rapid aerial oxidation of the latter to nitrogen dioxide[29] is then tantamount to the equilibration of NO^+, NO and NO_2 as shown in eqns. (28) and (29). The comprehensive mechanism

$$[R_2Se\cdot NO^+] \xrightleftharpoons{k_{ET}} R_2Se^{\cdot+} + NO \qquad (28)$$

$$NO + \tfrac{1}{2}O_2 \xrightarrow{fast} NO_2, \; etc. \qquad (29)$$

for the thermal, photochemical and catalytic oxidations of selenoethers is summarized in Scheme 4.[58] The catalytic cycle in Scheme 4 underscores the facile interconversion of the various nitrogen oxides during the oxidation of selenoethers. The induced disproportionation of NO_2 generates the critical nitrosonium cation from NO_2 and the aerial oxidation regenerates NO_2 from the reduced nitric oxide.

Scheme 4
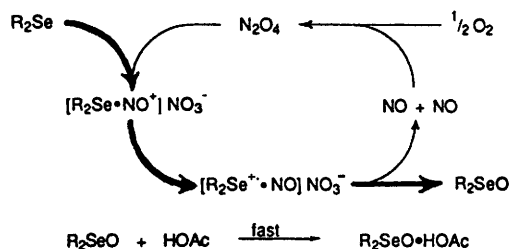
Summary and conclusions

The nitrogen oxide-catalysed autoxidation of selenoethers in acetic acid provides a mild and inexpensive route to the selenoxides. The use of acetic acid as solvent is critical to the success of the autoxidation owing to the efficient trapping of very basic selenoxides as the acetic acid adducts. Based on the stoichiometric and photoinduced oxidations with NO_2 the catalytic process is shown to proceed via a series of equilibria involving the formation of the nitrosonium EDA complex as the first intermediate formed by selenoether-induced disproportionation of NO_2. Electron-transfer within the EDA complex generates the selenoether cation radical which subsequently undergoes a facile oxygen atom transfer from the nitrate counterion to yield the selenoxide. Aerial reoxidation of the nitric oxide to NO_2, and the rapid complexation of the selenoxide with acetic acid completes the catalytic cycle.

Experimental

Materials

Nitrogen dioxide and nitric oxide (>99%, Matheson) were purified by published procedures.[54,59] Nitrosonium tetrafluoroborate (Strem) was stored in a vacuum atmosphere HE-493 dry box free from traces of oxygen, moisture and solvent vapours. Glacial acetic acid (Merck) was used as received. The UV–VIS spectroscopic studies were performed in dry oxygen-free dichloromethane purified as previously described.[60] Benzyl bromide, 2-bromopropane, dimethyl sulfate (Aldrich), diphenyl diselenide and dimethyl diselenide (Strem) were used as received and dibenzyl diselenide was available from a previous study. Treatment of the diselenoethers with sodium tetrafluoroborate in ethanol yielded the corresponding sodium selenoethers which were alkylated with either benzyl bromide, 2-bromopropane or dimethyl sulfate to form: benzyl methyl selenide, phenyl isopropyl selenide, phenyl methyl selenide, benzyl phenyl selenide and dibenzyl selenide, respectively, in high yield.[28] α-Benzyl-γ-butyrolactone was prepared by the treatment of γ-butyrolactone with 1.1 equiv. of LDA in THF at −78 °C and 1.2 equiv. of benzyl bromide.

Instrumentation

^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively in [^2H]chloroform, unless stated otherwise, on a General Electric QE-300 NMR spectrometer and the chemical shifts are reported in ppm units downfield from tetramethylsilane. Coupling constants J are given in Hz. UV–VIS absorption spectra were recorded on a Hewlett-Packard 8450A diode-array spectrometer. Infrared spectra were recorded on a Nicolet 10DX FT spectrometer. Gas chromatography was performed on a Hewlett-Packard 5790 series gas chromatograph equipped with a 3392 integrator. GC–MS analyses were carried out on a Hewlett-Packard 5890 chromatograph interfaced to a HP 5970 mass spectrometer (EI, 70 eV). Melting points were measured with a Mel-Temp (Laboratory Devices) apparatus and are uncorrected. Cyclic voltammetry (CV) was performed on a BAS-100A Electrochemical Analyzer. The CV cell was of an airtight design with high vacuum Teflon valves and Viton

O-ring seals to allow an inert atmosphere to be maintained without contamination by grease. The working electrode consisted of an adjustable platinum disc embedded in a glass seal to allow periodic polishing (with a fine emery cloth) without changing the surface area (ca. 1 mm^2) significantly. The saturated calomel reference electrode (SCE) and its salt bridge was separated from the catholyte by a sintered glass frit. The counter electrode consisted of a platinum gauze that was separated from the working electrode by ca. 3 mm.

Stoichiometric oxidation of selenoethers with nitrogen dioxide

General procedure. A solution of phenyl methyl selenide (113 mg, 0.66 mmol) in acetic acid (2 ml) was prepared under an argon atmosphere in a 10 ml flask fitted with a Schlenk adaptor. The flask was capped with a rubber septum and nitrogen dioxide (22 µl, 0.72 mmol) added with the aid of a hypodermic syringe. The resulting red-brown solution quickly faded to yellow and became colourless after 3 min. The head gases were transferred to an evacuated gas IR cell (5 cm path length). The IR spectrum showed the characteristic stretching frequencies at 1904, 1876 and 1851 cm^{-1} of nitric oxide[17] as the only nitrogen oxide. When a trace of oxygen was introduced these absorbances diminished with the concomitant appearance of the intense absorbances of NO_2 at $v = 1620$ and 1601 cm^{-1}.[30] Removal of the solvent and nitric oxide under reduced pressure led to a quantitative yield of the acetic acid adduct of phenyl methyl selenoxide (156 mg, 0.63 mmol) as a clear oil: v(film, NaCl)/cm^{-1} 1710; $δ_H$ 2.00 (s, 3 H), 2.88 (s, 3 H), 7.53–7.55 (m, 3 H), 7.77–7.81 (m, 2 H), 13.02 (s, 1 H); $δ_C$ 21.1, 35.9, 126.2, 129.7, 131.6, 174.6. The acetic acid adduct was diluted with water (2 ml), K_2CO_3 (0.35 mmol) was added and there was immediate evolution of gas. The mixture was extracted with dichloromethane after gas evolution ceased. The dichloromethane layer was separated, dried, and the solvent removed in vacuo to yield phenyl methyl selenoxide (614 mg, 3.28 mmol) as low melting colourless crystals: mp 50 °C (lit.,[61] 53–54 °C); $δ_H$ 2.54 (s, 3 H), 7.42–7.45 (m, 3 H), 7.64–7.67 (m, 2 H); $δ_C$ 36.9, 124.9, 129.2, 130.7, 141.3. The oxidations of the other selenoethers in Table 1 were performed with the same procedure with the quantities and yields listed. The characteristic spectral data of the products were as follows.

Benzyl methyl selenide.—Colourless oil; $δ_H$ 1.89 (s, 3 H), 3.73 (s, 2 H), 7.20–7.35 (m, 5 H); $δ_C$ 4.0, 28.1, 126.6, 128.3, 128.7, 139.2.

Benzyl methyl selenoxide acetic acid adduct.—Colourless oil; v(film, NaCl)/cm^{-1} 1710; $δ_H$ 2.02 (s, 3 H), 2.55 (s, 3 H), 4.44 (s, 2 H), 7.36 (m, 5 H), 12.44 (s, 1 H); $δ_C$ 21.1, 29.6, 52.7, 128.7, 129.2, 130.2, 174.9 (Calc. for $C_{10}H_{14}O_3Se$: C, 45.99; H, 5.40. Found: C, 45.71; H, 5.45%).

Benzyl methyl selenoxide.[62]—White crystals; mp 110–111 °C; $δ_H$ 2.32 (s, 3 H), 4.08 (AB quartet, J_{AB} 11.7, $Δv_{AB}$ 50.3, 2 H), 7.23–7.40 (m, 5 H); $δ_C$ 30.6, 54.1, 127.9, 128.6, 129.2, 129.9.

Dibenzyl selenoxide, acetic acid, adduct.—Viscous oil; v(film, NaCl)/cm^{-1} 1710; $δ_H$ 2.02 (s, 3 H), 4.26 (s, 2 H), 4.70 (s, 2 H), 7.16–7.32 (m, 10 H), 12.19 (s, 1 H); $δ_C$ 61.4, 129.1, 130.8, 131.0, 148.5.

Dibenzyl selenoxide.—Colourless crystals; mp 130–131 °C (lit.,[63] 134–135 °C); $δ_H$ 3.94 (AB quartet, J_{AB} 11.7, $Δv_{AB}$ 24.1, 4 H), 7.21–7.35 (m, 10 H); $δ_C$ 52.8, 128.1, 128.8, 129.5, 130.4.

Isopropyl phenyl selenide.—Colourless oil; $δ_H$ 1.40 (d, J 6.9, 6 H), 3.44 (septet, J 6.9, 1 H), 7.42–7.53 (m, 3 H), 7.65–7.68 (m, 2 H); $δ_C$ 24.1, 33.7, 127.2, 128.8, 129.5, 134.7.

Isopropyl phenyl selenoxide, acetic acid adduct.—Pale yellow oil; v(film, NaCl)/cm^{-1} 1710; $δ_H$ 1.30 (d, J 7.2, 3 H), 1.28 (d, J 7.2, 3 H), 3.40 (septet, J 7.2, 1 H), 7.32–7.57 (m, 3 H), 7.67–7.73 (m, 2 H), 10.68 (s, 1 H); $δ_C$ 15.6, 16.1, 21.0, 53.6, 126.8, 129.5, 131.7, 134.9, 174.7.

Isopropyl phenyl selenoxide.[28]—Pale yellow oil analysed by quantitative ^1H NMR immediately after treatment with K_2CO_3 in acetone–water solvent at 0 °C; $δ_H$ 1.23 (d, J 6.9, 3 H), 1.28

(d, *J* 6.9, 3 H), 3.01 (septet, *J* 6.9, 1 H), 7.24–7.27 (m, 3 H), 7.52–7.60 (m, 2 H); δ_C 14.6, 15.5, 51.8, 125.6, 128.5, 130.4, 137.4.

Benzyl phenyl selenide.—Colourless crystals; δ_H 4.08 (s, 2 H), 7.16–7.25 (m, 8 H), 7.41–7.48 (m, 2 H); δ_C 32.1, 126.8, 127.2, 128.3, 128.7, 128.9, 130.3, 133.4, 138.5.

Benzyl phenyl selenoxide, acetic acid adduct.—Colourless crystals; *v*(Nujol)/cm⁻¹ 1710; δ_H 2.04 (s, 3 H), 4.43 (br d, *J* 12.6, 2 H), 6.99 (br d, *J* 7.2, 2 H), 7.16–7.29 (m, 3 H), 7.37–7.50 (m, 5 H), 12.35 (s, 1 H); δ_C 20.8, 57.2, 126.8, 128.3, 128.5, 129.3, 130.2, 131.8, 135.6, 135.7, 175.6.

Benzyl phenyl selenoxide.—Colourless crystals; mp 132–133 °C (lit.,[64] 135–136 °C); δ_H 3.97 (AB quartet, J_{AB} 11.1, Δv_{AB} 64.6, 2 H), 6.83–6.86 (m, 2 H), 7.08–7.16 (m, 3 H), 7.28–7.36 (m, 5 H); δ_C 58.4, 125.7, 128.1, 128.8, 129.3, 129.4, 130.9, 139.1.

Reaction in dichloromethane solvent. The oxidation of phenyl methyl selenide was performed as described in the general procedure with rigorously dried dichloromethane as solvent. A dichloromethane solution of phenyl methyl selenide (184 mg, 1.08 mmol) was prepared under an argon atmosphere and cooled to −45 °C. One equiv. NO₂ was added with the aid of a hypodermic syringe and the dark red solution was allowed to warm to 25 °C over 1 h during which time the solution became colourless. The head gases were transferred to an evacuated cell and the IR spectrum indicated that nitric oxide was the only nitrogen oxide present. The nitric oxide and the solvent were removed under reduced pressure and phenyl methyl selenoxide isolated in excellent yield. The reaction in dichloromethane solution was however capricious and in the presence of an excess of nitrogen dioxide the selenoxide was contaminated by the formation of a colourless precipitate which was assigned to the phenyl methyl selenoxide·N₂O₄ adduct: δ_H(CD₃CN) 3.14 (s, 3 H), 7.6–7.7 (m, 3 H), 7.8–7.9 (m, 2 H); δ_C 34.2, 129.1, 131.2, 134.2, 136.3. Furthermore reaction in dichloromethane which was not rigorously dried resulted in higher yields of a colourless precipitate and reduced yields of phenyl methyl selenoxide. The supernatant liquid was carefully removed with a syringe and the colourless residue recrystallized from acetonitrile and identified as the nitric acid adduct.

Phenyl methyl selenoxide, nitric acid adduct.—Colourless crystals; mp 95–96 °C (lit.,[25] 97 °C); δ_H(CD₂Cl₂) 3.32 (s, 3 H), 7.58–7.68 (m, 3 H), 7.86–7.91 (m, 2 H), 12.63 (s, 1 H); δ_C(CD₃CN) 34.2, 129.1, 131.2, 134.2, 136.3 (Calc. for C₇H₉NO₄Se: C, 33.62; H, 3.63. Found: CV, 33.77; H, 3.64%). Recrystallization of the N₂O₄ adduct from acetonitrile yielded the same nitric acid adduct presumably by reaction with traces of moisture.[22,23] The oxidation of dibenzyl selenide with 1 equiv. of NO₂ in reagent grade dichloromethane similarly resulted in the formation of a colourless solid along with un-reacted selenide. The solid was similarly recrystallized from acetonitrile and identified as the nitric acid adduct.

Dibenzyl selenoxide, nitric acid adduct.—Colourless crystals; mp 104–105 °C (lit.,[21] 104–105 °C); δ_H 4.35 (AB quartet, J_{AB} 12.0, Δv_{AB} 136.6, 4 H), 7.26–7.40 (m, 10 H); δ_C 61.4, 129.1, 130.8, 131.0, 148.5 (Calc. for C₁₄H₁₅NO₄Se: C, 49.42; H, 4.44. Found: C, 49.30; H, 4.53%). In both cases the selenoxide was liberated from the nitric acid adduct on treatment with potassium carbonate as described for the acetic acid adduct.

Nitrogen oxide-catalysed oxidation of selenoethers: general procedure

Nitrogen dioxide. A solution of phenyl methyl selenide (585 mg, 3.42 mmol) in acetic acid (5 ml) was prepared in a 25 ml flask fitted with a side arm. Dry oxygen was bubbled through the solution for several minutes. The flask was capped with a rubber septum and an oxygen-filled balloon fitted to the side arm of the flask to ensure an oxygen atmosphere. Nitrogen dioxide (15 µl, 0.5 mmol) was added directly to the stirred solution with the aid of a hypodermic syringe. The dark red-brown solution was stirred at 25 °C overnight. The solvent and

nitrogen oxides were removed *in vacuo* to yield the acetic acid adduct of phenyl methyl selenoxide as a colourless oil. The acetic acid adduct was diluted with water (2 ml) and K₂CO₃ (2 mmol) added. After the evolution of gas ceased the solution was extracted with dichloromethane. The dichloromethane layer was separated, dried, and the solvent removed *in vacuo* to yield essentially pure phenyl methyl selenoxide (614 mg, 3.28 mmol) as low melting colourless crystals.

Nitric oxide. The same procedure was used in nitric oxide-catalysed oxidations with the exception that gaseous nitric oxide was added with the aid of a gas-tight syringe. In a separate reaction an acetic acid solution of phenyl methyl selenide was treated with NO (1 equiv.) under an argon atmosphere for 1 h. The selenide was recovered intact after removal of the nitric oxide and solvent under reduced pressure.

Nitrosonium cation. Autoxidations catalysed by nitrosonium salts were performed in a similar manner although the flask was initially charged with a weighed amount of NO⁺BF₄⁻ in the dry box. In this reaction, the product contained traces of contaminants which were not isolated or characterized.

Preparation of α-phenylseleno-α-benzylbutyrolactone

A THF solution of lithium diisopropylamide (4.3 mmol) was added dropwise to a cold (−78 °C) THF solution of α-benzyl-butyrolactone (4.0 mmol, 20 ml) under an argon atmosphere. The mixture was stirred at −78 °C for 30 min and a solution of phenyl selenium bromide (4.4 mmol, 3 ml) in THF was added dropwise. The mixture was allowed to warm to 25 °C over 1 h and then poured into dilute aqueous HCl. The mixture was extracted with dichloromethane and the organic layer washed with water, saturated aqueous sodium chloride and dried. The solvent was removed under reduced pressure and the crude product subjected to flash chromatography with hexane–ethyl acetate (20:1) as eluent to give the title compound;[31] δ_H 1.98 (dd, *J* 6.3, 14.1, 1 H), 2.30 (dt, *J* 14.1, 9.6, 1 H), 3.87 (AB quartet, J_{AB} 14.1, Δv_{AB} 72.1, 2 H), 3.87 (t, *J* 8.9, 1 H), 3.96–4.50 (m, 1 H), 7.06–7.37 (m, 8 H), 7.55–7.58 (m, 2 H).

Oxidation of α-phenylseleno-α-benzylbutyrolactone with NO₂

A dichloromethane solution of α-phenylseleno-α-benzylbutyro-lactone (1.2 mmol, 2 ml) was cooled at −78 °C under an argon atmosphere and NO₂ (110 µl, 3.6 mmol) added with the aid of a hypodermic syringe. The solution immediately took on a dark red colour which faded to pale yellow over the course of 3 h during which time a white precipitate formed.[65] The solution was further diluted with dichloromethane and the precipitate filtered off, the solvent was removed under reduced pressure and the crude residue separated by preparative thin layer chromatography with hexane–ethyl acetate (6:1) as eluent. 3-Benzylfuran-2(3*H*)-one[32] was isolated as a colourless oil (192 mg, 1.10 mmol); δ_H 3.54 (d, *J* 2, 2 H), 4.69 (d, *J* 2, 2 H), 6.86 (m, 1 H), 7.16–7.29 (m, 5 H); along with (10 mg, 0.06 mmol) of (*E*)-3-phenylmethylenedihydrofuran-2(3*H*)-one;[33] δ_H 3.20 (dt, *J* 2.7, 7.2, 2 H), 4.41 (t, *J* 7.2, 2 H), 7.25–7.46 (m, 5 H), 7.52 (t, *J* 2.7, 1 H).

Spectral characterization of the precursor EDA complex formed with selenoethers and nitrogen oxides

General procedure—nitrogen dioxide. A solution of NO₂ in dichloromethane (6 × 10⁻⁴ M) was cooled to −78 °C and (3 ml) transferred under a flow of argon into a quartz curvette equipped with a Teflon stopcock. The cuvette was cooled in a dry ice–acetone bath and allowed to equilibrate for several minutes. The UV–VIS absorption spectrum of the solution of NO₂ was recorded at −78 °C, and phenyl methyl selenide (1.0 µl) added. After mixing thoroughly (while cold), the UV–VIS absorption spectrum of the resultant red solution was recorded at −78 °C. The former spectrum was subtracted from the latter and the difference was referred to as the charge-transfer spectrum with λ_{max} = 498 nm. (After recording each of

the absorption spectra the coloured solution was rapidly transferred, with the aid of a Teflon cannula, into a vigorously stirred slurry of diethyl ether and saturated aqueous $NaHCO_3$. The organic layer was separated, dried and analysed by quantitative HPLC. After each measurement the selenoether was recovered quantitatively.) Similar concentrations of the other selenoethers in Table 3 also resulted in the formation of well-resolved charge-transfer absorption bands with optical densities between 0.5 and 1.

Nitrosonium cation. A Schlenk tube was charged with $NO^+BF_4^-$ (11.8 mg, 0.1 mmol) in the dry box. Dichloromethane (3 ml) was added under a flow of argon and the heterogeneous mixture cooled to $-78\,^\circ C$, when the UV–VIS absorption spectrum was recorded. Phenyl methyl selenide (3 μl) was added, and the slurry stirred at $-78\,^\circ C$ until the solution took on a red colouration. The UV–VIS absorption spectrum was recorded at $-78\,^\circ C$. The initial spectrum was digitally subtracted from the final spectrum and the difference was considered to be the charge-transfer absorption spectrum. The absorption maxima and the full width at half maximum of the charge-transfer bands with NO_2 and NO^+ are compared in Table 3.

Photochemical oxidation of selenoethers with nitrogen dioxide via the selective activation of the EDA complex

General procedure. A solution of NO_2 (0.035 M, 7 ml) in dichloromethane–acetic acid (8:1) was prepared under an argon atmosphere in a Schlenk tube fitted with a Teflon stopcock. The solution was cooled to $-78\,^\circ C$ in a dry ice–acetone bath and phenyl methyl selenide (50 μl, 0.3 mmol) was added to the cold colourless solution with the aid of a hypodermic syringe. The solution immediately became dark red. The reaction tube was then placed in a clear Dewar flask cooled to $-78\,^\circ C$ with dry ice in acetone. The reaction tube was irradiated with a medium pressure 250 W Hg lamp fitted with an aqueous IR filter and an ESCO 410 nm cut-off filter. After 1 h, the dark red colour was partially bleached and the photosylate was rapidly transferred with the aid of a cannula, under argon pressure, to a slurry of aqueous K_2CO_3 and dichloromethane. Quantitative ^1H NMR analysis indicated that the photosylate contained phenyl methyl selenide (0.26 mmol) and phenyl methyl selenoxide (0.03 mmol). Work-up and analysis of an identical 'dark' control reaction mixture stored at $-78\,^\circ C$ in the dark for 1 h indicated that the selenoether was recovered intact.

Acknowledgements

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52 For comparison: $E_p(PhCH_2SCH_2Ph) = 1.81$ V and $E_p(PhCH_2\text{-}SeCH_2Ph) = 1.41$ V *vs.* SCE at $v = 0.1$ V s^{-1} in dichloromethane with $Bu_4N^+PF_6^+$ (0.3 M) as electrolyte.

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54 E. Bosch and J. K. Kochi, *J. Chem. Soc., Perkin Trans. 1*, 1995, 1057.

55 Since nitrogen dioxide is also present in the reaction mixture, some of the selenoxide may derive from the reaction of the selenoether cation radical with NO_2. This reaction has been demonstrated for the analogous thioether cation radicals: $R_2S^{\cdot+} + NO_2 \rightarrow R_2SO + NO^+$ (see refs. 51 and 54). In this case the overall stoichiometry remains unchanged because the nitrosonium cation formed may react with the remaining nitrate anion to form N_2O_4. For the purposes of clarity the possible reaction of the selenoether cation radical with NO_2 is not included in the schemes.

56 Note that the diffusive separation of the triad formed in eqn. (20) is not included for the sake of clarity.

57 K. Y. Lee, D. J. Kuchynka and J. K. Kochi, *Inorg. Chem.*, 1990, **29**, 4196.

58 As noted before, the possible formation of some selenoxide by reaction of the selenoether cation radical with NO_2 (or NO_2^-) is not included for the sake of clarity. Furthermore, since the aerial oxidation of NO to NO_2 is a multistep process (S. Goldstein and G. Czapski, *J. Am. Chem. Soc.*, 1995, **117**, 12078) other radicals such as peroxynitrite ($\cdot OONO$), may also enter separately into the catalytic process in indeterminate amounts.

59 C. C. Addison, *Chemistry in Liquid Dinitrogen Tetraoxide*, Vieweg, Braunschweig, 1967.

60 E. Bosch, R. Rathore and J. K. Kochi, *J. Org. Chem.*, 1994, **59**, 2529.

61 D. G. Foster, *Rec. Trav. Chim. Pays-Bas*, 1935, **45**, 447.

62 E. Fromm and K. Martin, *Liebigs Ann. Chem.*, 1913. **401**. 177.

63 See Cinquini *et al.* in ref. 15.

64 M. Oki and H. Iwamura, *Tetrahedron Lett.*, 1966, 2917.

65 The precipitate presumably contains the '$PhSe$' moiety bound to nitrogen oxides, but it was not analysed.