C. R. Chimie 17 (2014) 634–640

Contents lists available at ScienceDirect

Comptes Rendus Chimie

www.sciencedirect.com

Full paper/Mémoire

Solvent-induced dichotomy in the oxidation mechanism of alkyl aromatic selenoethers☆

La dichotomie du mécanisme d'oxydation des séléniures alkyl-aliphatiques induite par le solvant

Ioana Fechete [a], Viatcheslav Jouikov [b,*]

[a] *ICPEES, UMR 7515 CNRS, Université de Strasbourg, 67000 Strasbourg, France*
[b] *CPM, UMR 6226 ISCR, University of Rennes-1, 35042 Rennes, France*

ARTICLE INFO

Article history:
Received 3 December 2013
Accepted after revision 3 March 2014
Available online 29 April 2014

Keywords:
Solvent polarity
Selenoethers
Dichotomy
Oxidation mechanism

ABSTRACT

Changing solvent polarity (considered in terms of dielectric permittivity ε) is an easy experimental way for tuning the reactivity of electrogenerated cation radicals of alkyl aromatic selenoethers. First-order cleavage of Se–C_{sp^3} bond is favored in polar media, whereas bimolecular cation radical disproportionation becomes the main reaction in low-polar solvents. The key element of this dichotomy is the dielectric adjustment of specific transannular interactions between Se and C=O group in the cation radicals. A series of alkyl arylselenides with pending carboxy or acetamido substituents was studied by cyclic voltammetry, IR spectroscopy and DFT calculation in binary solvents covering the span of polarity $8 < \varepsilon < 85$. Different products were obtained from the same starting selenide in polar and low-polar media, 1,2-bis(acetamido)cyclohexane and *N*-cyclohexenylacetamide, respectively. In both cases, the final product carrying the PhSe moiety was Ph_2Se_2.
© 2014 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

Mots clés :
Polarité du solvant
Sélénoéthers
Dichotomie
Mécanisme d'oxydation

RÉSUMÉ

La modification de la polarité du solvant (considéré en termes de permittivité diélectrique ε) est un moyen expérimental facile de modulation de la réactivité de radicaux cations électrogénérés à partir de sélénoéthers alkyl-aromatiques. Le clivage de la liaison Se–C_{sp^3}, du premier ordre cinétique, est favorisé dans les milieux polaires, alors que la dismutation bimoléculaire des radicaux cations devient la réaction principale dans les solvants peu polaires. L'élément clé de cette dichotomie est l'ajustement diélectrique des interactions trans-annulaires spécifiques entre Se et le groupe C=O dans les radicaux cations. Une série d'alkylarylséléniures avec les substituants pendants (carboxy ou acétamido) a été étudiée par voltamétrie cyclique, spectroscopie IR et par le calcul DFT dans des solvants binaires couvrant la plage de polarité $8 < \varepsilon < 85$. Différents produits ont été obtenus, dans les milieux polaires et peu polaires, à partir du même séléniure, comme le 1,2-bis-(acétamido)cyclohexane et le *N*-cyclohexénylacetamide, respectivement. Dans les deux cas, le produit final portant le groupement PhSe est le Ph_2Se_2.
© 2014 Académie des sciences. Publié par Elsevier Masson SAS. Tous droits réservés.

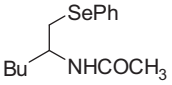
☆ Thematic issue dedicated to François Garin.

* Corresponding author.
E-mail address: vjouikov@univ-rennes1.fr (V. Jouikov).

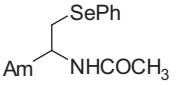
http://dx.doi.org/10.1016/j.crci.2014.03.003
1631-0748/© 2014 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

1. Introduction

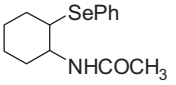
Two general types of interactions controlling the localization of the reaction site, the selectivity and the synthetic outcome are delimited within the perturbation theory of reactivity: orbital-controlled and charge-controlled interactions, depending on whether the orbital or the Coulombic contribution to the total interaction energy predominates [1,2]. While the orbital term arising from two-electron integral energy is a fundamental factor intrinsically related to the chemical structure of the reacting centers, charge interactions can be subjected to an external tuning. One of the possibilities for this is related to the media dielectric permittivity, given within Born model as:



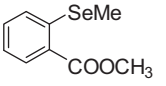
1



2



3



4

$PhSe(CH_2)_2$-COOMe
5

$PhSeCH_2COOEt$
6

$PhSeC_6H_{12}$
7

$$E_{charge} = (q^+q^-e^2)/4\pi\varepsilon_0\varepsilon l \quad (1)$$

(where q^+ and $q^-$are interacting charges, ε_o and ε are vacuum and solvent dielectric permittivities, l is the q^+–q^- distance [3]). In the electrochemical context, a modification of E_p (but not of the reaction mechanism) when changing the solvent polarity or the corresponding ion of the supporting electrolyte is well documented [4–7]. Reactions with charge-related alteration of reactivity are rare. This feature is expected to be best observable in first turn in the processes with compounds involving intramolecular neighboring group assistance.

To cite a few examples from such families, these are lowering the oxidation potentials of amines due to n_N–σ_{C-Si} hyperconjugation [8], the cases of thio- [9], seleno- [10] and telluroethers [11] showing abnormally low oxidation potentials, the through-space interactions of two sulfur or selenium atoms in mesocyclic dichalcogenido compounds [12–18] and macrocyclic bi-, tri- and tetraselenides [19]. Through-space interaction of the 2-(2-pyridyl) ethyl pending substituent with a selenium atom was reported to remarkably facilitate electron transfer from selenides [20].

We have previously shown that similar transannular interactions take place in the cation radicals of selenoethers bearing substituents with a C=O group whose oxygen can approach Se atom to a distance allowing substantial Coulombic interactions [21,22]. Usually, cation radicals resulting from the oxidation of dialkyl and alkyl arylselenides undergo monomolecular charge-controlled cleavage of bonds adjacent to selenium (hard acid center): Se–C_{sp^3} or (Se)C_{sp^3}–H [23–25]; this is in contrast with the cation radicals of diaromatic selenides, for which second-order (orbital-controlled) reactions are typical [26–28], like for parent aryl thioethers [29]. In case of the selenides with transannular Se···O interactions, similar orbital-controlled bimolecular interactions were observed [21] instead of the expected first-order reactivity.

In this communication, we aim at demonstrating how orbital- and charge-controlled reactivity of cation radicals can be simply switched by the dielectric effect of the reaction media. For this, the alkyl aromatic selenoethers **1–6** were studied by cyclic voltammetry, large-scale electrolysis and IR spectroscopy in binary mixtures of various polarities. The selenide **7**, in which such intramolecular interaction is absent, was considered as a test compound.

2. Experimental

Cyclic voltammetry and large-scale electrolyses were carried out using a PAR 2273 electronic potentiostat piloted with PowerSuite software (PAR). A standard three-electrode electrochemical cell was used with a 2-mm glassy carbon (GC) working electrode. The auxiliary electrode was a GC rod and the Ag/0.1 M $AgNO_3$ in CH_3CN system served as a reference electrode. The working electrode was carefully polished with Struers 4000 paper and washed in acetonitrile before each measurement.

DFT calculations were carried out using Gaussian 03 software [30].

Aryl selenide **4** was prepared by methylation of 2-methylselenobenzoic acid [31,32] by MeI in a methanol solution of NaOH. Compounds **1–3** were prepared by electrochemical oxidation of Ph_2Se_2 in an acetonitrile–$NaClO_4$ solution in the presence of cyclohexene, hex-1-ene and hept-1-ene, respectively [33]. Selenides **5** and **6** were prepared by the reaction of PhSeH with ethyl ethers of 3-chloropropionic and 2-chloroacetic acid, respectively [34]. Analytical-grade acetonitrile (AN) was purified by distillation from $KMnO_4$–P_2O_5 and kept over activated 4-Å molecular sieves. Bu_4NBF_4 (Aldrich) was kept over P_2O_5 and used without any additional purification.

N-Cyclohexenylacetamide. M_p 99 °C (white needles from hexane). ^1H NMR (CCl_4, TMS) δ: 5.76 (s H), 3.7 (s H), 1.9 (s 3H), 1.16–1.66 (m 8H). IR (solid): 3300 cm^{-1}; $\nu_{C=O}$ 1650 cm^{-1} (amide I), ν_{N-H} 1560 cm^{-1}, δ_{C-H} 725 cm^{-1}. Calcd, %: C 69.56, H 8.69, N 10.14; Found ($C_8H_{12}O$) %: C 69.72; H 8.75; N 10.05.

1,2-Bis(acetamido)cyclohexane. M_p 268 °C (white powder from ethanol). ^1H NMR ($CDCl_3$, TMS): 6.12 (s

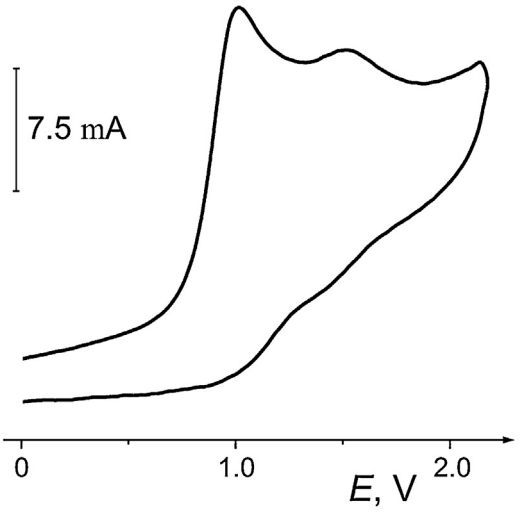


Fig. 1. Voltammogram of oxidation of **2** (2×10^{-3} mol L^{-1}) in AN/Bu_4NBF_4 at a GC microdisk electrode; scan rate $v = 2$ V s^{-1}, T = 295 K.

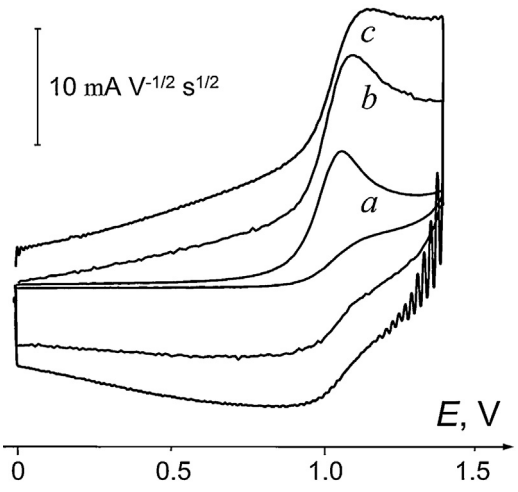


Fig. 2. Current-normalized voltammograms of **3** (2×10^{-3} mol L^{-1}) at different scan rates: (a) 0.5 V s^{-1}; (b) 25 V s^{-1}; (c) 100 V s^{-1}.

2H), 3.61–3.75 (m 2H), 2.1 (m 4H), 1.9 (s 6H), 1.7–1.8 (m 4H). IR: 3290 cm^{-1}, $\nu_{C=O}$ 1645 cm^{-1} (amide I), ν_{N-H} 1555 cm^{-1}, δ_{C-H} 725 cm^{-1}. Calcd, %: C 60.58; H 9.15; N 14.13; Found ($C_{10}H_{18}N_2O_2$) %: C 60.73; H 9.07; N 14.21.

Diphenyldiselenid. M_p 62 °C (yellow fibers from ethanol). ^{1}H NMR (CCl_4, TMS): 7.6, 7.13 (10H). IR: ν_{C-H} 690 cm^{-1}, ν_{C-H} 735 cm^{-1}. Calcd, %: C 46.18; H 3.21; Found ($C_{12}H_{10}Se_2$) %: C 46.23; H 3.24.

3. Results and discussion

Upon oxidation in AN/0.1 M Bu_4NBF_4, selenides **1**–**5** show a well-defined peak at $E_p \approx 1$ V, followed by a less developed second oxidation step (Fig. 1). Because of adsorption of seleno ethers at the Pt interface, voltammograms of **1**–**5** at a glassy carbon (GC) electrode are better shaped, in spite of its higher internal capacity compared to that of a Pt electrode. The activation energy of the limiting current of **1**–**5** ($R\Delta\log(i_p)/\Delta(1/T) = 6.2 \pm 0.5$ kJ mol^{-1}) is practically the same as the temperature coefficient of viscosity of acetonitrile [35]. The oxidation currents i_p vary linearly with the square root of the scan rate $v^{1/2}$ and with the concentration (for $C \leq 5 \times 10^{-3}$ mol L^{-1}), which attests to a diffusion-controlled process [36]. The electron stoichiometry of the first oxidation step was determined from comparison of the oxidation currents i_p of **1**–**5** with the one-electron current of ferrocene. Although at slow scan rates, only the anodic peak is present, at $v \geq 100$ V s^{-1} some reversibility starts to appear, corresponding to the reduction of electrogenerated cation radicals (Fig. 2).

Characteristic slopes $\Delta E_p/\Delta\log(v)$, determined from cyclic voltammetry at various scan rates (Table 1), are consistent with those obtained earlier using a rotating disk electrode, $\Delta E_p/\Delta\log(\omega)$ [21], both indicating the bimolecular character of the reaction of electrogenerated cation radicals **1**$^{+\bullet}$–**5**$^{+\bullet}$. The process at E_p[1] thus corresponds to an EC scheme with electrochemically reversible electron transfer followed by fast second-order bulk reaction of the primary products [36]. Such reactivity is typical for thioethers [37] or diarylselenides [26,28,38,39], but is quite unusual for selenides, for which monomolecular cleavages usually occur. This reveals radical side of reactivity of the cation radicals **1**$^{+\bullet}$–**5**$^{+\bullet}$, which became possible because the charge localization on Se in these species is insufficient for inducing Se–C or (Se)C–H bond cleavage directly, as in dialkyl and alkyl arylselenides [25]. Remarkably, the cation radicals of **6** and **7** both react in a monomolecular process (Table 1), in accordance with the general trend for selenoethers [38].

The chemical nature and the size of Se atom [40] imply that the positive charge in the cation radicals of selenoethers, even those of diarylselenides [39], is mostly localized on Se, so that this dichotomy directly stems from transannular stabilization of the charge on Se by the oxygen of internal carboxy or acetamide groups in **1**$^{+\bullet}$–**5**$^{+\bullet}$.

Supposing equation (1) to hold for cation radicals **1**$^{+\bullet}$–**5**$^{+\bullet}$, we considered their reactivity in media of different polarities, using binary mixtures of acetonitrile ($\varepsilon = 36$) with THF ($\varepsilon = 7.4$) and ethylene carbonate (EC, $\varepsilon = 90$ at 313 K [35]). The available polarities in this medium cover the $8 < \varepsilon < 90$ range. The complete account of all solute–solvent

Table 1
Parameters of the electrochemical oxidation of aryl alkyl selenides ArSeAlk at a GC electrode in AN and is mixtures with THF and EC (0.1 M Et_4NBF_4).

Cpd	E_p, V[a]	$E_p - E_{p/2}$, mV	n	$\Delta E_p/\Delta\log(v)$, mV			$\Delta E_{1/2}/\Delta\log(\omega)$
				THF-AN[b]	AN	EC-AN[b]	
1	0.965	62	1.3	21	21	30	19[c]
2	0.972	60	1.2	22	20	30	20[c]
3	1.125	64	1.1	23	20	32	20[c]
4	1.090	67	1.2	20	22	30	20[c]
5	1.065	62	1.2	22	21	31	
6	1.235	105	2.0	20	29	31	30[c]
7	1.110	95	2.0	32	31	32	31[d]

[a] vs. Ag/0.1 M $AgNO_3$ in CN_3CN.
[b] $x_{AN} = 0.1$.
[c] In AN, at a 0.5-mm oxidized Pt rotating disk electrode [21].
[d] [25].

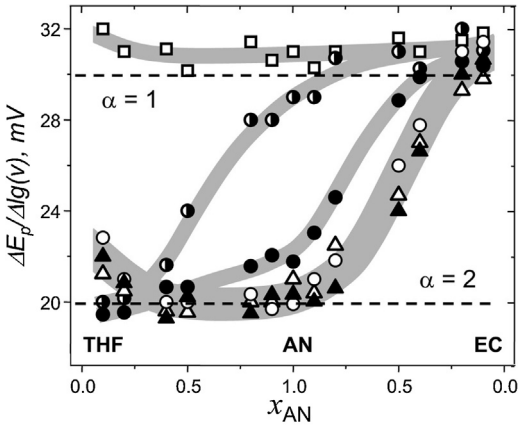


Fig. 3. Dependence of the $\Delta E_p/\Delta\log(\nu)$ value on the molar fraction of acetonitrile in binary solvents THF-AN and AN-EC. (8) **1**; (7) **2**; (–) **3**; (,) **4**; (4) 6; (∀) 7. GC electrode, T = 298 K.

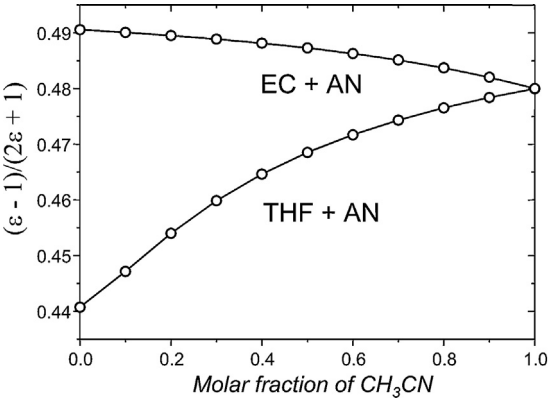


Fig. 4. Dielectric function $(\varepsilon–1)/(2\varepsilon+1)$ for the binary mixtures THF-AN and EC-AN with different compositions.

interactions is quite complex [3] and the "polarity" of a solvent can be described through a number of parameters [41,42]. In this context, certainly not the most selective [43], though having a simple physical sense, the solvent dielectric permittivity ε is a convenient characteristic of the polarity of the used medium.

The evolution of the slope of the characteristic function E_p–log(ν) for the oxidation of selenides **1**–**5** with the dielectric permittivity of the binary mixture is shown in Fig. 3. All selenides, for which transannular Se···O interaction is important, exhibit a change of this parameter from 20 mV to 30 mV upon increasing the medium's polarity, attesting to a progressive evolution of the potential-determining reaction of the cations radicals **1**$^{+\bullet}$–**5**$^{+\bullet}$ from disproportionation (kinetic order α = 2) to a first-order reaction (α = 1). The test compound **7**, in which such interactions are absent, shows no dependence of the nature of the follow-up reaction on solvent polarity. Selenide **6**, whose cation radicals exhibit monomolecular reaction in AN (Table 1), also shows the dichotomy of reactivity (Fig. 3), as observed for **1**–**5**; however, this change occurs in the media less polar than AN, at $\varepsilon \cong 16$.

The solvatochromism of electronic (UV/Vis) or molecular (IR) modes is often considered for studying specific interactions of substrates with the solvent [44]; obviously, intramolecular interactions show similar trends of optical properties. However, UV/Vis spectroscopy is precluded for the case of selenides **1**–**5** because of strong aromatic absorption of the PhSe moiety. In place, solution IR spectroscopy was used [42], because THF, AN, and EC are all optically transparent in the window of characteristic amide I and II vibrations [45]. Since it is difficult to separate specific solute–solvent interactions from purely dielectric effects [46], a simple model was adopted. In binary solvents, given a large excess of solvent compared to the selenide (at a substrate concentration of 1 mmol L^{-1}, for each molecule of the selenide there are approximately 10^4–10^2 molecules of solvent, depending on whether it is pure or added as a co-solvent at ≥ 1%), solvent–solute interactions (solvation of C=O and N–H groups and Se) in the whole range of co-solvent concentrations are supposed to be constant, since only few solvent molecules can coordinate at once with the substrate. With this assumption (corroborated by the continuity of the E_p vs. log(ν) graph upon switching THF-AN to EC-AN mixture), any change of vibrational modes can be considered as arising from dielectric-sensitive intramolecular interactions. At 1 mmol L^{-1}, solubility changes and aggregation phenomena are neglected. For this model of solvent polarity, the dielectric function $(\varepsilon–1)/(2\varepsilon+1)$, developed for a diatomic oscillator in a dielectric continuum with macroscopic dielectric constant ε, was used (Fig. 4) [47]. Dielectric permittivities of solvents in binary mixtures being additive, the resulting ε has been calculated using the simplified Shakhparonov equation [48]:

$$\varepsilon = x\varepsilon_{AN} + (1-x)\varepsilon_{solv} + 0.043\frac{(\varepsilon_{AN} - \varepsilon_{solv})^2}{x\varepsilon_{AN} + (1-x)\varepsilon_{solv}} \qquad (2)$$

(where x is molar fraction of acetonitrile in the binary mixture, ε_{AN} and ε_{solv} are low-frequency dielectric permittivities of acetonitrile and of the co-solvent, respectively).

Corresponding shifts of C=O and N–H vibrations with solvent polarity are shown in Fig. 5. In IR spectra of neat compounds, the amide I band of the stretching vibrations of C=O group in *N*-(2-(phenylselenyl)hexyl)acetamide **2** is shifted to 1625 cm^{-1} compared to *N*-hexyl acetamide **7** in which Se···O interactions are absent, $\nu_{C=O}$ = 1645 cm^{-1}. In dilute acetonitrile solutions, this vibration is freed from solid-state associations and appears at higher frequency (1670 cm^{-1}), and is progressively shifted to higher frequencies with a change of polarity of the solvent (Fig. 5). For amide II band vibration $\nu_{N–H}$, an analogous trend was found, which was even more pronounced. The influence of Se on amide II absorption (1530 cm^{-1} in acetonitrile) is complex, resulting from the complex nature of this vibration due to the interaction between C–N stretching and N–H bending modes of the C–N–H fragment. The fact that $\nu_{N–H}$ vibration mode is more sensitive to solvent polarity than $\nu_{C=O}$ attests to the fact that Se···O interaction prevails over Se···H(N) in solution for neutral selenides. This feature reflects the fact that Se···O interaction in a non-oxidized molecule **2** has a repulsive and destabilizing character, contrary to stabilizing Se$^{(+)}$···O interaction between positively charged Se and electron-rich carbonyl oxygen in the cation radical

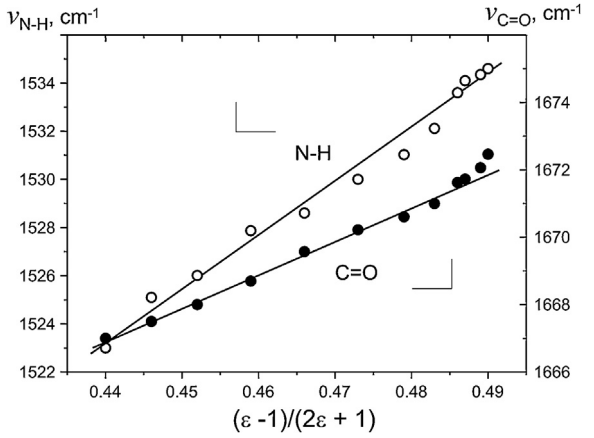
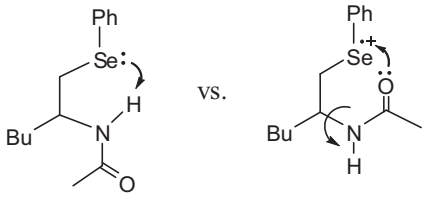


Fig. 5. Solvatochromic shifts of $\nu_{C=O}$ and ν_{N-H} vibration frequencies in **2** with solvent dielectric parameter $(\varepsilon-1)/(2\varepsilon+1)$.



Scheme 1. Through-space interactions in **2** and **2**$^{+\bullet}$.

(Scheme 1). Induced by electron withdrawal, the geometry change in **2**$^{+\bullet}$ occurs due to free rotation about C_{sp3}-N σ-bond, driven by the formation of a 2c–3e system similar to what was realized in di- and tri-seleno-substituted derivatives upon one-electron oxidation [17,18].

The low stability of cation radicals **1**$^{+\bullet}$–**5**$^{+\bullet}$ does not allow direct measurement of the $\nu_{C=O}$ shift caused by the $Se^{(+)}\cdots O(C)$ interaction. In order to support the above model, the geometries of selenides **1**–**5** and of their cation radicals were optimized at the DFT B3LYP/6-311+G* level for media with different dielectric permittivities, using the isodensity polarized continuum model (IPCM) implemented in Gaussian 03 [49]. Thus obtained atomic charges at Se and carbonyl oxygen in these species in AN are collected in Table 2.

Partitioning of charges in the Mulliken scheme is not distance selective, so it only shows their evolution upon electron withdrawal. Distance-dependent CHelpG

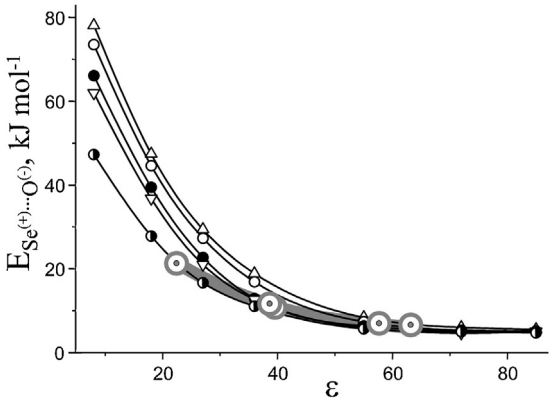


Fig. 6. Correlation of Se···O interaction energy with solvent polarity for cation radicals: (8) **1**$^{+\bullet}$; (–) **3**$^{+\bullet}$; (,) **4**$^{+\bullet}$; (X) **5**$^{+\bullet}$; (4) **6**$^{+\bullet}$. From DFT B3LYP/6-311+G*. Dichotomy points from Fig. 2 (ε at α = 1.5) are marked with grey circles.

calculations [50] would supposedly provide a better account of charge distribution in these species, but proper open-shell treatment involving Se atom is still a very delicate task. As a compromise, NBO charges can be used for estimating Se···O interaction energy in a first approach (Fig. 6).

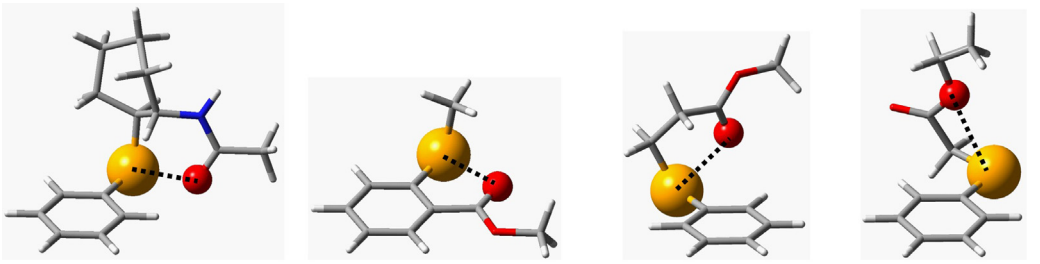
Depending on the structure of the selenide, Se and O atoms can form six- to four-membered spatial rings (Fig. 7) providing their maximal approach. Only cation radical **4**$^{+\bullet}$ is planar and rigid, while in **1**$^{+\bullet}$, **2**$^{+\bullet}$, **5**$^{+\bullet}$ and **6**$^{+\bullet}$, a free rotation about Se–C and C–C bonds is possible, which enables minimizing the Se···O distance. While these atoms approach, dative interaction from n-electrons of the carbonyl oxygen to positively charged Se provokes the concomitant elongation of the C=O bond in **1**$^{+\bullet}$–**5**$^{+\bullet}$ (Table 2). Interestingly, C=O bond becomes longer in **6**$^{+\bullet}$ compared to **6**, but this is due to a different orientation of the carboxyethyl group: contrary to **1**$^{+\bullet}$–**5**$^{+\bullet}$, the Se···O coordination in **6**$^{+\bullet}$ occurs at the ester oxygen (Fig. 7).

From this consideration, it is clear that taking into account solely the electrostatic interaction between two point charges, one neglects ring strain energy and orbital overlap contribution [51], since interatomic distance Se···O (2.44–2.80 Å) becomes comparable to that of a stretched Se–O chemical bond (gas phase Se–O length is 1.779 Å [52]). In addition, polarization of non-valent core electrons of bulky interacting atoms is totally omitted in this model.

Table 2
Distances Se···O and C=O, Mulliken ($_M$) and NBO ($_{NBO}$) charges in selenides **1**–**7** and their cation radicals (CR) in CH_3CN[a].

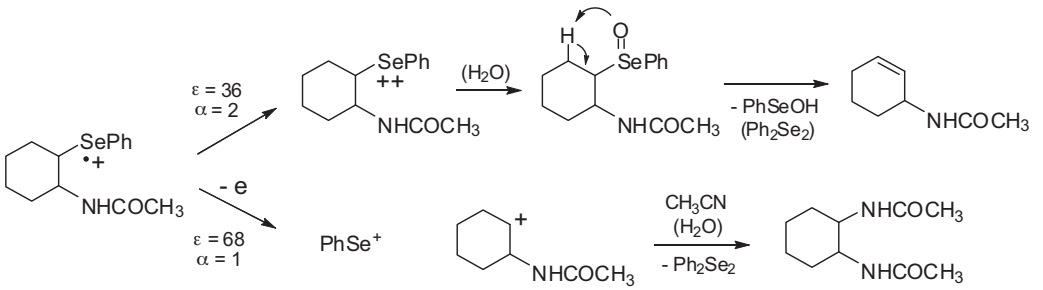
Cpd	l_{Se-O}, Å		$l_{C=O}$, Å		q_{Se}			q_O		
	Neutr.	CR	Neutr.	CR	Neutr.	CR_M	CR_{NBO}	Neutr.	CR_M	CR_{NBO}
1	3.892	2.441	1.230	1.251	0.123	0.740	1.108	−0.690	−0.697	−0.745
2	3.891	2.449	1.230	1.251	0.123	0.739	1.108	−0.690	−0.697	−0.744
3	3.882	2.482	1.230	1.251	0.135	0.758	1.118	−0.690	−0.699	−0.747
4	3.071	2.526	1.210	1.226	0.144	0.773	1.137	−0.654	−0.678	−0.693
5	3.377	2.555	1.208	1.224	0.130	0.765	1.132	−0.656	−0.658	−0.697
6	3.353	2.808	1.211	1.205[b]	0.204	0.805	1.162	−0.709	−0.711	−0.615
7					0.111	0.742				

[a] From DFT B3LYP/6–311+G* using IPCM solvation model [44].
[b] Se···O(C_{sp}^3) coordination instead of Se···O = C.



$3^{+\cdot}$ $4^{+\cdot}$ $5^{+\cdot}$ $6^{+\cdot}$

Fig. 7. Optimized geometries of cation radicals $\mathbf{3^{+\bullet}}$–$\mathbf{6^{+\bullet}}$ and transannular distances Se···O. Van der Waals radii for Se and O atoms are used.



Scheme 2. Electrooxidation of **3** in media of different polarities.

In order to check the synthetic consequences of solvent-induced dichotomy, large-scale electrooxidation of **2** was carried out in binary solvents corresponding to the zones of first- ($\varepsilon = 36$) and second-order ($\varepsilon = 68$) reactivity of its cation radicals. The oxidation was carried out at a GC anode at the potential set at 0.9 V (at ca. 80% of the i_p). The electrolyses were stopped when the current dropped to ca. 5% of the initial value, which was checked to correspond to 2.3 and 1.2 F/mol in polar and non-polar media, respectively, in good agreement with the results of cyclic voltammetry. In acetonitrile, *N*-cyclohexenyl acetamide was found to be the main oxidation product. Its formation involves β-elimination of the intermediate selenoxyde [53] resulting from the reaction of a selenium-centered dication with traces of water. The eliminated phenylselenenic acid was transformed into diphenyldiselenide during the work-up of the reaction mixture. In a more polar AN-EC (1:8) mixture, bifunctional 1,2-bis(acetamido)cyclohexane was formed as the main product. A direct cleavage of Se-C_{sp3} bond and second electron transfer gave $PhSe^+$ and a carbocation, whose reaction with acetonitrile finally led to the di-acetamido product. Similarly, Ph_2Se_2 was the final product carrying eliminated PhSe moiety (Scheme 2).

4. Conclusion

The electrooxidation of the family of alkyl arylselenides, whose cation radicals show Se···O transannular interactions, was studied by cyclic voltammetry and the related methods and supported by DFT calculations. Using binary mixtures of acetonitrile with aprotic solvents of lower and higher polarity allowed one to demonstrate the alteration of the reaction of electrogenerated cation radicals from bimolecular (orbital-controlled) to monomolecular (charge-controlled); this dichotomy has distinct synthetic consequences, as was shown by large-scale electrolysis. Whatever the exact mechanism of this phenomenon, a simple parameter linked to solvent polarity, dielectric permittivity, provides a rather good account for the observed behavior.

The only variable parameter in the present study was solvent polarity. It is clear that such an approach takes into account only intramolecular phenomena, leaving aside intermolecular interactions (e.g., with an external nucleophile or with the anions of supporting electrolyte), which also must play an important role in the electrochemical reactivity of cation radicals of alkyl arylselenides.

Disclosure of interest

The authors declare that they have no conflicts of interest concerning this article.

References

[1] G. Bekker, Introduction to Electronic Theory of Organic Reactions (Russian translation by V.M. Potapov), Mir, Moscow, 1977, p. 658.
[2] L. Salem, in: L.S. Efros (Ed.), Electrons in Chemical Reactions (Russian translation by Y.L. Kaminsky), Mir, Moscow, 1985, p. 285.
[3] R.W. Fawcett, Liquids, Solutions, and Interfaces, Oxford University Press, Oxford, 2004, p. 102.
[4] K. Taras-Goslinska, M. Jonsson, J. Phys. Chem. A 110 (2006) 9513.
[5] S. Manda, I. Nakanishi, K. Ohkubo, T. Kawashima, K. Matsumoto, T. Ozawa, S.I. Fukuzumi, N. Ikota, K. Anzai, Chem. Lett. 36 (2007) 914.
[6] S. Sasaki, K. Sasaki, M. Watanabe, K. Ogawa, N. Morita, M. Yoshifuji, Phosphorus Sulfur Silicon Relat. Elem. 188 (2013) 256.

[7] E.G. Bakalbassis, A.T. Lithoxoidou, P.A. Vafiadis, J. Phys. Chem. A 110 (2006) 11151–11159.
[8] B.E. Cooper, W.J. Owen, J. Organomet. Chem. 29 (1971) 33.
[9] M.D. Ryan, D.D. Swanson, R.S. Glass, G.S. Wilson, J. Phys. Chem. 85 (1981) 1069.
[10] H. Fujihara, N. Furukawa, Phosphorus Sulfur Silicon Relat. Elem. 67 (1992) 131.
[11] F. Hisashi, N. Takeshi, A. Ryonichi, E. Tomoki, F. Naomichi, Tetrahedron Lett. 32/35 (1991) 4537.
[12] H. Fujihara, R. Akaishi, N. Furukawa, Chem. Lett. (1990) 549.
[13] H. Fujihara, T. Ninoi, R. Akaishi, T. Erata, N. Furukawa, Tetrahedron Lett. 32 (1991) 4537.
[14] N. Nakayama, O. Takahashi, O. Kikuchi, N. Furukawa, Heteroatom Chem. 11 (2000) 31.
[15] R.S. Glass, E. Block, E. Lorance, U.I. Zakai, N.E. Gruhn, J. Jin, S.Z. Zhang, J. Am. Chem. Soc. 128 (2006) 12685.
[16] E. Block, E.V. Dikarev, R.S. Glass, J. Jin, B. Li, X. Li, S.-Z. Zhang, J. Am. Chem. Soc. 128 (2006) 14949.
[17] H. Fujihara, R. Akaishi, N. Furukawa, Chem. Lett. 4 (1990) 549.
[18] H. Fujihara, Y. Higuchi, H. Mima, N. Furukawa, Chem. Lett. 3 (1994) 619.
[19] H. Fujihara, M. Yabe, N. Furukawa, J. Chem. Soc., Perkin Trans. 1 (1996) 1783.
[20] M. Watanabe, S. Suga, J.I. Yoshida, Bull. Chem. Soc. Jpn. 73 (2000) 243.
[21] V.V. Jouikov, V. Ivkov, Electrochim. Acta 40 (1995) 1617.
[22] V.V. Jouikov, D.S. Fattakhova, J. Organometal. Chem. 613 (2000) 220.
[23] V.Z. Latypova, V.V. Zhouikov, Y.M. Kargin, M.Y. Postnikova, E.G. Kataev, Zh. Obsch. Khim. 56 (1986) 822.
[24] V.V. Jouikov, V. Ivkov, D. Fattahova, Tetrahedron Lett. 34 (1993) 6045.
[25] V.V. Jouikov, J. Electroanal. Chem. 398 (1995) 159.
[26] R. Seeber, A. Cinquantini, P. Zanello, G. Mazzocchin, J. Electroanal. Chem. 88 (1978) 137.
[27] V.Z. Latypova, Y.M. Kargin, N.M. Khusaenov, Y.V. Rydvanskii, O.G. Yakovleva, L.M. Kataev, E.G. Kataev, Zh. Obsch. Khim. 49 (1979) 1801.
[28] R. Muller, L. Lamberts, M. Evers, J. Electroanal. Chem. 417 (1996) 35.
[29] V.V. Jouikov, J. Simonet, Electrochemical reactions of sulfur organic compounds, in: A. Bard, M. Stratman, H. Shaefer (Eds.), Encyclopedia of Electrochemistry, Vol. 8, Ch. 9, Wiley-VCH, New York, 2004, p. 235.
[30] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision B. 01, Gaussian, Inc., Pittsburgh, PA, 2003.
[31] R. Lesser, G. Weiss, Chem. Ber. Bd 46 (1913) S2641.
[32] D. Thompson, P. Boudjouk, J. Org. Chem. 53 (1988) 2109.
[33] V.V. Jouikov, V. Latypova, V. Berestovitskaia, Y. Kargin, Zh. Org. Khim. 23 (1987) 1696.
[34] M. Detty, G. Wood, J. Org. Chem. 45 (1980) 80.
[35] Y.A. Karapetyan, V.N. Eychis, Khimia, Moscow (1989) 252.
[36] H. Lund, O. Hammerich (Eds.), Organic Electrochemistry, fourth ed., Marcel Dekker Inc., New York, 2001.
[37] H. Wendt, H. Hoffelner, Electrochim. Acta 28 (1983) 1465.
[38] V.V. Jouikov, Curr. Top. Electrochem. 4 (1997) 1.
[39] V.V. Jouikov, D.S. Fattakhova, A.Y. Kozhevnikov, Electrochim. Acta 46 (2001) 807.
[40] N.N. Vturina, G.A. Tchmutova, Zh. Obsch. Khim. 48 (1978) 2564.
[41] T.M. Krygowski, W.R. Fawcett, J. Am. Chem. Soc. 97 (1975) 2143.
[42] C. Reinchards, Solvents and Solvent Effects in Organic Chemistry, second ed., VCH Publishers, Weinheim, Germany, 1988, p. 285.
[43] C.J. Cramer, D.G. Truhlar, Acc. Chem. Res. 41 (2008) 760.
[44] F.M. Nicol, Appl. Spectrosc. Rev. 8 (1974) 183.
[45] R.M. Silverstein, G.C. Bassler, T.C. Morrill, Spectrometric Identification of Organic Compounds, John Wiley and Sons, New York, 1991, p. 101.
[46] M.C.R. Symons, Chem. Soc. Rev. 12 (1983) 1.
[47] A.E. Lutskii, V.V. Prezhdo, L.I. Degtareva, V.G. Gordienko, Russ. Chem. Rev. 51 (1982) 802.
[48] Y.A. Fialkov, Y.Y. Borovikov, Zh. Phys. Khim. 40 (1966) 371.
[49] J. Tomasi, B. Mennucci, R. Cammi, Chem. Rev. 105 (2005) 2999.
[50] C.M. Breneman, K.B. Wiberg, J. Comput. Chem. 11 (1990) 361.
[51] G. Klopman (Ed.), The Reactivity and Reaction Pathways (Russian translation: N.S. Zefirov), Mir, Moscow, 1977, p. 383.
[52] G. Gundersen, D.W. Rankin, Gas-Phase Molecular Structures Determined by Electron Diffraction. In: Spectroscopic Properties of Inorganic and Organometallic Compounds, Specialist Periodical Reports, vol. 14, Royal Society of Chemistry, London, 1981, p. 410.
[53] H.J. Reich, J.M. Renga, I.I. Reich, J. Am. Chem. Soc. 97 (1975) 5434.