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Stereoelectronic effects in the reactivity of electrogenerated cation radicals of arylselenides

V.V. Jouikov *, D.S. Fattakhova

Physical Chemistry Department, Kazan State University, 420008 Kazan, Russia

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Abstract

The role of stereoelectronic effects in the electrochemical oxidation of arylselenides Se-substituted by a trimethylsilylmethyl group and those with substituents bearing a carbonyl group have been considered. Although the HOMO of these compounds is formed of p_z-type electrons of the ArSe moiety, the predominant contribution from the lone pair of Se makes the heteroatom more susceptible to direct electronic effects than to effects transmitted through the aromatic ring. The σ-p hyperconjugation and the interaction through space were shown to lower the charge localization on the reaction center and to stabilize cation radicals of these compounds, thus changing the control of the potential-determining reaction and promoting second order reactions.

Keywords: Electrooxidation; Cation radicals; Arylselenides; Silicon organic compounds; Reactivity; Stereoelectronic effects

1. Introduction

Electrochemical oxidation of a large number of organic selenides has been studied to date [1–7]. When the reversibility of electron transfer was proved electrochemically, electrogenerated cation radicals were shown to react in first (rupture either of Se–C_{sp3} or C_{sp3}–H bond [8–11]) or second (disproportionation, dimerization [1,12–14]) kinetic order ensuing bulk reactions. A necessary and sufficient condition for the second order reactions to occur is the presence in the molecule of diorganylselenide of two aromatic groups which are immediately bound to the selenium atom [5,12,13,15]. If only one or no aromatic fragment is linked to selenium, first order reactions of cation radicals (if not dissociative electron transfer at all) take place [8–10,16]. The feature which accounts for this discrimination is a specific combination of two factors: the electronic structure of the frontier orbitals of these compounds and the energy of the weakest bond adjacent to selenium. The ability of arylselenides to give electrons in oxidation reactions is determined by the nature of their HOMO formed with the lone pair of selenium and π-electrons of one aromatic ring [17–19]. In other words, the ArSe moiety is the fragment which is mainly responsible for the primary redox properties of arylselenides in oxidation processes. Obviously, it is not the electronic structure of the second aryl which determines the occurrence of second order reactions of diarylselenides because there is not any significant conjugation between the orbitals of selenium and the π-system of the second aromatic ring [20]. The reason why the second order potential-determining reactions are inherent to diarylselenides is higher dissociation energy of the Se–C_{sp2} bond compared to the Se–C_{sp3} bond strength [21] and the fact that the deprotonation of an aromatic ring is very unfavorable.

The possibility for cation radicals of arylselenides other than Ar_2Se to react in second order reactions was only shown for arylethynylselenides ArSeC≡CAr [14] having no acid α-protons, and for arylmethylselenides ArSeMe, whose methyl group is not stable enough as a leaving group [22] to enable direct cleavage of the cation radical. In the last case, the rupture of the Se–C_{sp3} bond in the cation radicals is very unfavorable, and the only possible potential-determining reaction is

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* Corresponding author. Present address: UMR 6510 Synthèse et Electrosynthèse Organiques, Université de Rennes I, Campus de Beaulieu, 35042 Rennes, France.

E-mail address: jouikov@ksu.ru (V.V. Jouikov).

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the elimination of an acid methyl proton. Suppression of this reaction by introducing a strong proton donor enables the cation radicals to develop their second order reactions [9,16,22].

The role of steric and inductive effects of alkyls attached to selenium [8,23], as well as the effect of substituents in the aromatic ring [24] with respect to the behavior of alkylarylselenides upon oxidation were studied in terms of multiparameter correlation of their E_{ox} with $-E_S$, R_S, σ^* and σ^+ constants of substituents. However, the potential-determining reaction in all these cases was always of first kinetic order.

Due to the larger size of selenium and relatively low conjugation of its lone pair with the aromatic system compared to analogous sulfur compounds, the electronic effects transmitted through the aromatic ring (mesomeric and direct polar conjugation) do not change the electrochemical behavior of arylselenides dramatically. Since the selenium atom is seemingly more affected by direct electronic interactions, the role of stereoelectronic effects in the electrochemical reactivity of arylselenides and of their cation radicals has been considered in this paper.

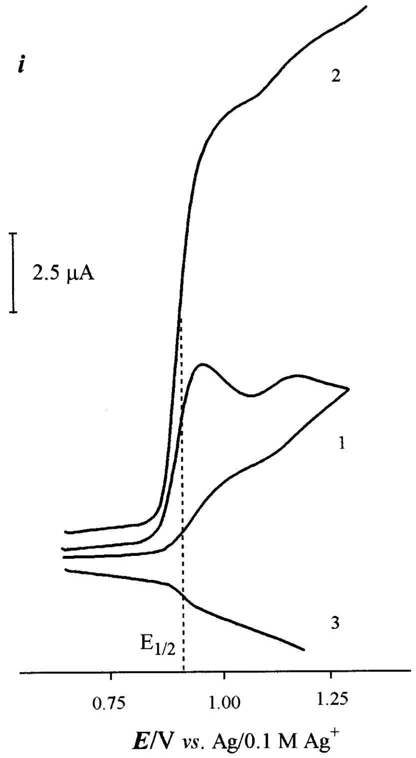

Fig. 1. Oxidation of arylselenide **1c** ($C = 10^{-3}$ mol l^{-1}, $T = 20$°C) in CH_3CN–0.01 M Et_4NClO_4. (1) Cyclic voltammogram, $v = 0.5$ V s^{-1}; (2) and (3) are curves registered at a Pt rotating disk electrode, $\omega = 20$ s^{-1}, (2) classical curve, (3) commutated curve with the connection according to the second scheme; switch frequency $f = 100$ Hz, capacitive current reduced.

2. Results and discussion

2.1. *β-Effect*

It is known that substituents containing silicon atom at the β-position to a heteroatom (N, O, S) lower the oxidation potential of a molecule by 0.05–0.7 V depending on the energy difference between the interacting orbitals [25–30]. This effect does not need the assistance of any group conducting electronic effects and affects the heteroatom immediately. Since the magnitude of the β-effect is not affected by the nature of the substitution at the aromatic ring[1] but only by a relative level of thus modified HOMO of the ArSe moiety, the oxidation of the following β-silylated arylselenides with different *para*-substituents was studied:

p-R–C_6H_4–$SeCH_2SiMe_3$

1a R = MeO

1b R = Me

1c R = H

1d R = Cl

1e R = Br

Upon oxidation at an oxidized platinum rotating disk electrode in CH_3CN–0.01 M Et_4NClO_4, aryl(trimethylsilylmethyl)selenides **1a**–**1e** behave like aryl(trimethylsilylmethyl)sulfides [30]. Their voltammograms (Fig. 1) show two oxidation steps (for non-silylated ArSeAlk, there is a single two-electron wave). The limiting current of the first wave is controlled by diffusion ($i_l/C = \text{const}$; $i_l/\omega^{1/2} = \text{const}$; $n \cong 1$; $R\Delta\lg(i_l)/\Delta(1/T) = 6.2$ kJ mol^{-1} which corresponds to the temperature coefficient of the viscosity of the solvent; $\Delta E/\Delta\lg((i_d - i)/i_d) = 60$ mV). Using cyclic voltammetry, no signals of reduction of cation radicals were detected up to the sweep rate $v = 50$ V s^{-1}. However, using commutative voltammetry at the rotating disk electrode [31] at the switch frequency $f = 100$ Hz, the signals of reduction of cation radicals have been recorded. These reduction currents disappear at about 1.5 V indicating further oxidation of the cation radicals at these potentials. Characteristic dependences of $E_{1/2}$ on $\lg(\omega)$ and on $\lg(C)$ ($\Delta E_{1/2}/\Delta\lg(\omega) \cong 20$ mV and $\Delta E_{1/2}/\Delta\lg(C) \cong 20$ mV (Table 1)) indicate that the potential-determining reaction (PDR) of cation radicals of aryl(trimethylsilylmethyl)selenides **1a**–**1e** is of second kinetic order, in contrast to first order reactions of cation radicals of non-silylated alkylarylselenides.

The second oxidation wave is not as well shaped as the first one and tends do disappear when increasing

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[1] Only if the substituent does not bring any sterical hindrance which can affect this stereoelectronic effect.

Table 1
Characteristics of the first wave of oxidation of silylated arylselenides $RC_6H_4SeCH_2SiMe_3$ at a Pt oxidized RDE in CH_3CN–0.01 M Et_4NClO_4; $C = 10^{-3}$ mol l^{-1}, $T = 20°C$, $\omega = 20$ s^{-1}

R	$E_{1/2}$ (mV) [a]	n	$\Delta E/\Delta \lg((i_d - i)/i_d)$ (mV)	$\Delta E/\Delta \lg(\omega)$ (mV) [b]	$\Delta E/\Delta \lg C$ (mV) [c]	σ_R^+
1a	690	1.2	60	18	22	−0.778
1b	790	0.9	60	20	20	−0.311
1c	890	1.0	60	20	24	0
1d	920	0.9	70	20	19	+0.114
1e	910	1.1	75	22	20	+0.15

[a] Versus Ag/0.01 M $AgNO_3$.
[b] ±3 mV.
[c] ±5 mV.

either the rate of rotation of the disk electrode or the potential sweep rate. The process responsible for this wave was shown to be mainly the oxidation of a diaryldiselenide resulting from the process at the potentials of the first wave.

So the whole feature of the oxidation of β-silylated compounds (E + C2 + C1 scheme, Eqs. (1–3)) is quite different from the oxidation of simple alkylarylselenides which occurs according to a E + C1 + E scheme and involves two electrons in the overall process [16].

Since electron transfer in the course of electrooxidation of β-silylated arylselenides follows a stepwise mechanism, two points related to the peculiarities of the electronic structure of these compounds arise here: first, with respect to the oxidation potentials, and second, with respect to the role of these factors in the stability of the cation radicals. At the level of the effective oxidation potential $E_{1/2}$, these two factors partially compensate each other. Indeed, an additional splitting of the HOMO of the ArSe moiety due to the conjugation of the lone pair of selenium with the σ C–Si bond raises the level of the HOMO of $ArSeCH_2SiMe_3$ and lowers the ionization potential of the molecule. This effect is to be reflected in a decrease of the oxidation potential. On the other side, reduced reactivity of the cation radicals, caused by their stabilization by the β-effect, will diminish a negative kinetic shift of the effective potential $E_{1/2}$ with respect to E_0. Thus the total effect of these intramolecular electronic interactions on $E_{1/2}$ will not be very large.

Some quantitative estimations can be made from the consideration of oxidation of a non-silylated analog of phenyl(trimethylsilylmethyl)selenide, *iso*-amylphenylselenide. The electrochemical behavior of this compound (one wave, $n = 2$; $E_p = 1.089$ V; $\Delta E_{1/2}/\Delta \lg((i_l - i)/i_l) = 120$ mV; $\Delta E_{1/2}/\Delta \lg(\omega) = 33$ mV) is quite different from the behavior of its silylated counterpart. The difference in effective oxidation potentials of **1c** and of *iso*-amylphenylselenide ($\Delta E_p = 0.20$ V) is consistent with the difference in the HOMO levels of these compounds which is 0.23 eV, especially taking into account that E_p of *iso*-amylphenylselenide was subjected to a larger negative kinetic shift with respect to E_0 [23] than that of **1c**[2].

A much more spectacular effect of these specific interactions is seen through the alteration of the nature of ensuing reactions of electrogenerated cation radicals. The behavior of these species can be considered from the following standpoint.

Applying the principle of microscopic reversibility to the potential-determining cleavage of a cation radical $AB^{\bullet +}$, and considering this cation radical as the transition state of the back reaction (formation of the cation radical from the radical and the cationic fragments, $B^{\bullet}$ and A^+, Fig. 2), one can apply the general expression of perturbation theory for a two-center interaction (admitting that kinetic shifts do not affect remarkably the relative energy profiles of the components on the reaction coordinate). The energy of interaction in this case includes contributions from two terms, covalent (orbital) and coulombic (charge), and their ratio deter-

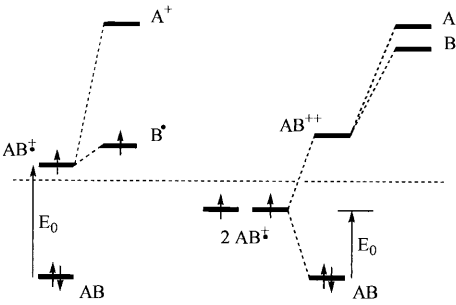

Fig. 2. Correlation of frontier orbitals in first and second order potential-determining reactions of cation radicals $AB^{\bullet +}$. Left: charge-controlled cleavage of the cation radical; right: fragmentation of a dication AB^{2+} preceded by an orbital-controlled disproportionation of cation radicals. The orbital energy corresponds to the direction of ordinate axes so the presentation of orbitals is turned upside down. Horizontal dotted line designates the energy level which delimits charge- and orbital-controlled interactions of cation radicals.

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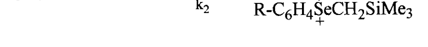
[2] Apparently, at the concentration $C = 1$ mmol l^{-1} the rate of the second order potential determining reaction is lower than that of the first order reaction, as was shown for the oxidation of arylmethylselenides [11]; so the total kinetic shift of the effective potential E_p is less for the second order reaction.

Table 2
Vertical ionization potentials (IP) of β-trimethylsilylsubstituted arylselenides p-R–$C_6H_4SeCH_2SiMe_3$ (eV)

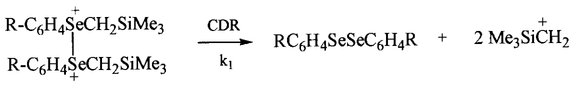
Compound	IP_1	IP_2	IP_3
1a	7.58	9.12	10.00
1b	7.68	9.02	10.62
1c	7.77	9.03	
1e	7.81	9.04	10.06

mines the type of control of the potential-determining reaction. The harder the reaction center, the larger the charge term and more likely the charge-controlled reactions are. Usually, these reactions are of first or pseudo-first order (cleavage or the reaction with macro components of the solution). When the separation of the orbital energy levels is too large to control the process efficiently (Fig. 2), another pathway becomes preferable. Now, it first involves an orbital-controlled disproportionation of two cation radicals resulting in the starting molecule AB and a dication AB^{2+} (the covalent term of the energy of interaction is maximal since the SOMOs of cation radicals are degenerated). A large gain in energy in the ensuing reaction of the dication is a driving force of the entire process. Therefore, one can imagine an arbitrary energy barrier separating charge and orbital-controlled interactions. The cation radicals with the energy below this barrier disproportionate whereas those species, whose energy is higher undergo direct cleavage. So for the direct cleavage, electrogenerated cationic species must have enough energy to assure the separation of orbitals of the species resulting from the cleavage to be not too large to be ineffective. The cleavage of the cation radicals of the reaction series **1a**–**1e** and of alkylarylselenides gives $ArSe^+$ fragments (A^+), which are similar for both reaction series, and alkyl radicals ($B^\bullet$) which have approximately similar energy. Obviously, the stabilization of the cation radicals of **1a**–**1e** by the β-effect, due to an additional conjugation of the reaction center with electrons of the bonding C–Si σ-orbital, lowers the energy of these species thus making their direct cleavage unfavorable. The process now follows an $E + C2 + C1$ scheme. Although the main products of an exhaustive electrooxidation ($Q \cong 1.1$ F mol^{-1}) of selenides **1a**–**1e** are corresponding diaryldiselenides, i.e. formally products of the $Se–C_{sp3}$ bond cleavage, the mechanism is more complex and includes orbital-controlled dimerization of electrogenerated cation radicals giving a dimeric dication which then cleaves to give diaryldiselenide and two α-silylcarbocations, $Me_3SiCH_2^+$:

$$R\text{-}C_6H_4SeCH_2SiMe_3 \xrightleftharpoons{-e} [R\text{-}C_6H_4SeCH_2SiMe_3]^{+\bullet} \qquad (1)$$



$$2\,[R\text{-}C_6H_4SeCH_2SiMe_3]^{+\bullet} \xrightarrow[k_2]{PDR} \begin{array}{c} R\text{-}C_6H_4\overset{+}{Se}CH_2SiMe_3 \\ | \\ R\text{-}C_6H_4\underset{+}{Se}CH_2SiMe_3 \end{array} \qquad (2)$$



$$\begin{array}{c} R\text{-}C_6H_4\overset{+}{Se}CH_2SiMe_3 \\ | \\ R\text{-}C_6H_4\underset{+}{Se}CH_2SiMe_3 \end{array} \xrightarrow[k_1]{CDR} RC_6H_4SeSeC_6H_4R + 2\,Me_3Si\overset{+}{C}H_2 \qquad (3)$$

The reaction with the rate constant k_1 is current-determining (CDR) for the second wave of the oxidation of selenides **1a**–**1e**.

The oxidation potentials of aryl(trimethylsilylmethyl)selenides are generally lower than those of selenides without a β-trimethylsilyl substituent, but the difference is not so remarkable as in the case of homologous sulfides and ethers [26]. The reason for this is a less effective overlapping of diffuse π-type lone pair of selenium with the C–Si σ-bond.

Half wave oxidation potentials $E_{1/2}$ of **1a**–**1e** were found to correlate well with the σ_R^+ constants of substituents in the aromatic ring (see Eq. (3) in ref. [30]). The positive sign of the polarographic reaction constant ($\rho = 0.253$ V) is in agreement with the nature of the effects of substituents: donor substituents raise the level of the HOMO thus facilitating the removal of an electron upon oxidation. The absolute value of the constant ρ is close to values of the constants of reaction series of compounds with similar types of HOMO [32]. Since the effective reaction constant ρ has a complex nature and besides a thermodynamic term (ρ_π) might contain a contribution from the potential-determining chemical reaction [33], it is necessary to elucidate corresponding thermodynamic and kinetic terms separately by some independent physicochemical method. In order to obtain characteristics of frontier orbitals determining redox properties of selenides **1a**–**1e** and to characterize intramolecular electronic effects in these compounds, their photoelectron spectra were studied. The experimental data are collected in Table 2.

First ionization potentials IP_1 of these compounds show a fairly good correlation (even with such a small number of points) with the same type of constants of substituents as the oxidation potentials E_p:

$$\begin{array}{l} IP_1 = (0.249 \pm 0.013)\sigma_R^+ + 7.768 \pm 0.005 \\ n = 4,\ r = 0.997,\ s_d = 0.009,\ P = 0.0027 \end{array} \qquad (4)$$

The obtained reaction constant of electron transfer ($\rho_{IP} = 0.249$ eV) reflects the susceptibility of the energy of HOMO of the reaction series **1a**–**1e** to electronic effects of *para*-substituents in the aromatic ring. The value of this constant is practically the same as that of the polarographic reaction constant. It means that the latter does not contain any kinetic contribution and characterizes only the electron transfer step or, more likely, that the kinetic shift of the effective potential ($\Delta E_k = E_{1/2} - E_0$) is practically constant and independent of the electronic effects transmitted through the aromatic ring from *para*-substituents. It is to be noted that the complex polarographic reaction constant of the oxidation of methylarylselenides ArSeMe ($\rho = 0.282$ V) does contain some kinetic term (the reaction constant of the potential-determining reaction $\rho_k = 1.1$ [11]). This fact is in agreement with the charge controlled deprotonation of the cation radicals being more sensitive to the electronic effects of *para*-substituents than the orbital controlled dimerization of the cation radicals of the reaction series **1a**–**1e**.

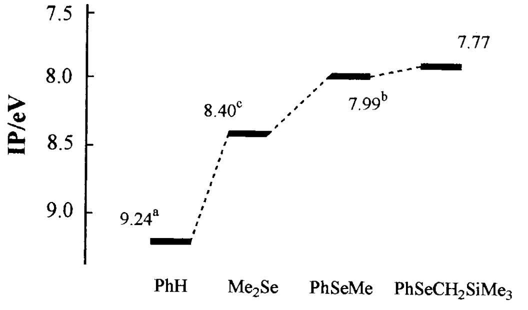


Fig. 3. Diagram of the correlation of HOMOs of molecular fragments contributing to the HOMO of $PhSeCH_2SiMe_3$. (a) [38], (b) [39], (c) [40,41].

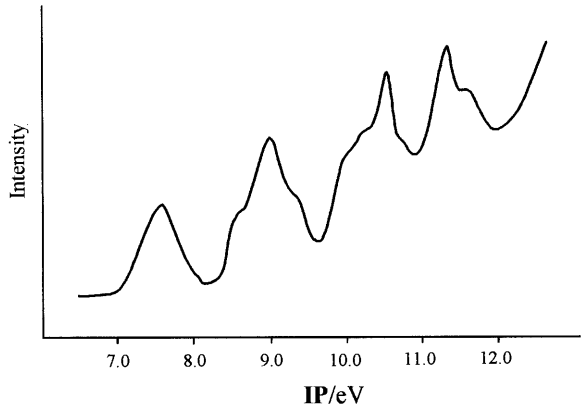


Fig. 4. Photoelectron spectrum of p-$MeC_6H_4SeCH_2SiMe_3$. Clearly seen is the complex nature of the second ionization band.

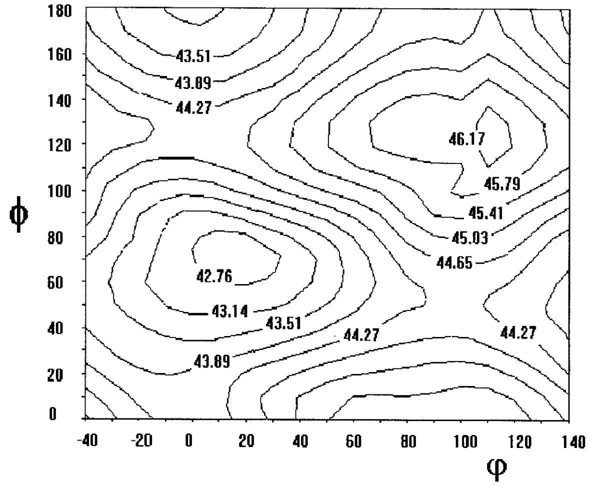


Fig. 5. Diagram of MMX energy of the molecule **1b** as a function of two torsion angles: (φ) $\angle C_{sp2}(2)$–$C_{sp2}(1)$–Se–C_{sp3} and (ϕ) $\angle C_{sp2}(1)$–Se–C_{sp3}–Si.

Analysis of the electronic structure of these compounds reveals several types of intramolecular interactions which can affect the HOMO responsible for the first ionization potential IP_1 (Fig. 3). The main factor is a conjugation of one of two lone pairs of selenium (evidently, that of p_z-type) with the π-system of the aromatic ring. This interaction raises the level of the HOMO compared to the HOMO level of benzene, like in the molecules of alkylaryl and diaryl selenides [20]. On the other side, the lone pair of selenium can interact with the filled orbital of the Si–C σ-bond of the CH_2SiMe_3 group according to a α-p conjugation mechanism. This interaction also results in an increase in the HOMO level.

Considering the PE spectrum of **1b**, one can see that the second ionization band is not simple (Fig. 4) which might be caused by some intramolecular electronic interactions involving the second lone pair of selenium. In order to clarify this point, the electronic structure of this compound has been modeled using both semi-empirical PM3 calculations [34,35] and ab initio calculations with a 6-31G* basis set [36,37]. These calculations showed that the minimum of potential energy of the system corresponds to a conformation with the torsion angle $\angle C_{sp2}(2)$–$C_{sp2}(1)$–Se–C_{sp3} (φ) equal to 20°, which provides the optimal overlapping of the p_z orbital of Se (n^{π}) with the π-electrons of the benzene ring. Plotting a 2D diagram of potential energy as a function of two torsion angles of rotation about the C_{sp2}–Se and the Se–C_{sp3} bonds (Fig. 5) revealed a steady minimum with the orthogonal arrangement of the HOMO-forming components (n^{π} electrons of Se and p_z-orbitals of the aromatic ring) and the $\angle C_{sp2}(1)$–Se–C_{sp3}–Si angle (ϕ) equal to 67°. Obviously, these parameters are most favorable for the effective σ-p conjugation of the secondary HOMO-forming fragment (CH_2SiMe_3 group) with the orbitals of the ArSe moiety. Unfavorable configuration is characterized by the values $\varphi \cong 90°$ and $\phi \cong 127°$ and corresponds to the overlap of the σ-type lower-lying lone pair of selenium with the π-system of the aromatic ring (Fig. 5).

The complex character of the second band in the PE spectrum of **1b** might result from the superposition of two bands. A PM3 modeling of inner occupied orbitals of this molecule allows us to shed some light on the nature of this band (Fig. 6). The theoretical value of the IP_1 of **1b** (Table 3) is shifted with respect to the experimental value by $\Delta = 8.38 - 7.68 = 0.7$ eV. Taking this value into account, an experimental value of IP_2 in the first approach must be

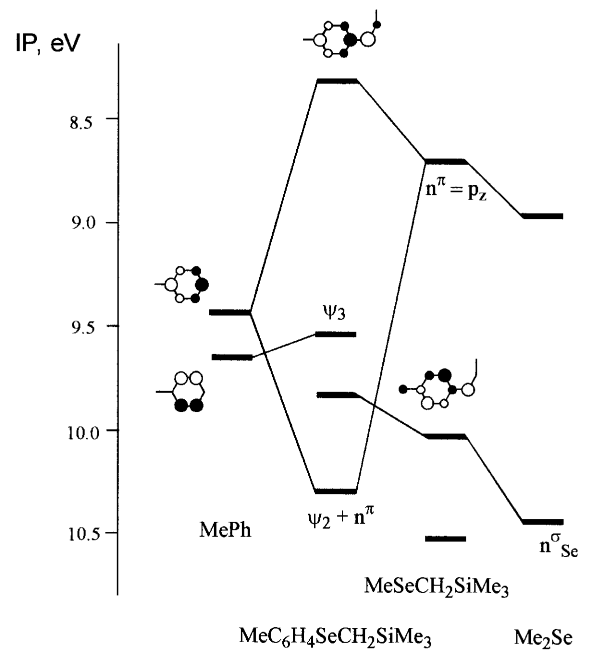


Fig. 6. Orbital correlation of the molecular fragments upon the formation of **1b** and its lower-lying occupied MOs according to PM3 calculation. To fit all energies to the same scale, orbital levels of toluene have been calculated too. For the $MeSeCH_2SiMe_3$ molecule, the same geometry has been taken as in the corresponding fragment in $Me–C_6H_4SeCH_2SiMe_3$.

Table 3
Energies of filled orbitals (IP, eV) for the molecules $R–C_6H_4SeCH_2SiMe_3$ according to the PM3 calculations

Compound	IP_1	IP_2	IP_3	IP_4
1b	8.378	9.534	9.830	10.320
1c	8.541	9.566	9.958	
1d	8.540	9.779	9.832	10.346
1e	8.597	9.803	10.018	

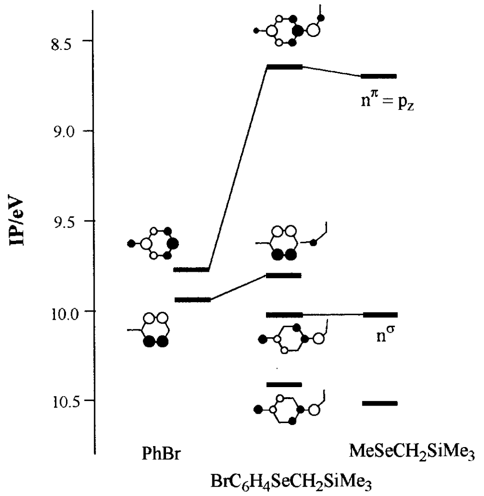


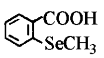
Fig. 7. Correlation of molecular orbitals upon the formation of $BrC_6H_4SeCH_2SiMe_3$.

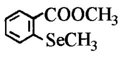
$9.53 - 0.7 = 8.83$ eV, which is in good agreement with the energy of the left shoulder of a complex second band in the PE spectrum (Fig. 4). The ionization of the n^{σ} orbital of Se in this case should occur at $9.83 - 0.7 = 9.13$ eV, which actually corresponds to the right shoulder of this absorbance band. Thus the IP_1 of **1b** corresponds to the ionization of the HOMO which is built up with the π-electrons of the unsymmetric ψ_2 orbital of the aromatic ring, n^{π}-electrons of Se and the electrons of the bonding $C_{sp3}–Si$ σ-orbital, whereas the ionization of the unsymmetric ψ_3 orbital and the n^{σ} orbital of selenium occurs with the overlapping of the absorbance bands giving a complex signal with an average value of $IP_2 = 9.02$ eV.

It is noteworthy that according to the PM3 calculations, the next after the HOMO bonding orbital of methyl and bromo (Fig. 7) derivatives practically corresponds to the unsymmetrical ψ_3 orbital of the aromatic ring whereas in the chloro compound there are two close lying mixed orbitals (Fig. 8). Obviously, larger conjugation of the lone pair of chlorine with the π-system of the aromatic ring causes a redistribution of contributions from corresponding fragments forming this orbital.

2.2. Field effect (interaction through space)

Among different neighboring groups which can affect the electrochemical behavior of organo-element compounds (e.g. amino [25], methylthio [42,43], sulfur, selenium [44] or tellurium [45]), the carbonyl group presents particular interest because it does not undergo oxidation within the range of electroactivity of arylseleno compounds. So the oxidation of some alkylarylselenides containing a carbonyl group attached either to the aromatic ring (**2a**, **2b**) or to the alkyl group (**3a**–**3e**) have been considered.


2a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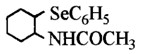
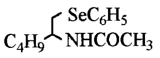

3a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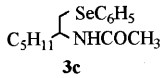
3c

$C_6H_5Se(CH_2)_2COOH$
3d

$C_6H_5SeCH_2COOC_2H_5$
3e

Being oxidized under the conditions described above, these alkylarylselenides show two oxidation waves (see Fig. 2 in ref. [22]), the first is controlled by diffusion ($i_l/\omega^{1/2} = \text{const}$, $i_l/C = \text{const}$; $n \cong 1$; $R\Delta \lg(i_l)/\Delta(1/T) = 6.2$ kJ mol^{-1}; $\Delta E/\Delta \lg((i_d - i)/i_d) = 60$ mV). Their half wave potentials $E_{1/2}$ shift towards more positive potentials by 20 mV upon an increase in the rotation speed by a factor of 10, except for the compound **3e**, for which this value is 30 mV. Thus the primary oxidation steps of **2a**, **2b** and **3a**–**3d** follow an E + C2 mechanism:

a reversible electron transfer with a second order PDR of cation radicals formed. By experiments with the addition of pyridine this reaction was shown to be disproportionation, as in the case of the oxidation of diphenylselenide [46].

The potentials of the second wave of alkylarylselenides in the presence of CF_3COOH (i.e. when electrogenerated cation radicals follow a second order reaction and the oxidation of secondary radicals does not interfere with the current of their oxidation) have practically the same values as the potentials of disappearance of the reduction signals on commutated voltammograms. Therefore, the second wave of **2a**, **2b** and **3a**–**3e** can be attributed to the oxidation of cation radicals generated at the first wave potentials.

Second kinetic order potential-determining reactions are not typical for alkylarylselenides bearing no carbonyl group and even for selenide **3e** which has a carbonyl group. For these compounds, the cation radicals undergo a first order reaction. Evidently, the main feature which distinguishes selenides **2a**, **2b** and **3a**–**3d** from all the rest and determines the second order of PDR is that Se and O atoms in these compounds are separated by a chain comprising three or four other atoms, allowing free rotation about included bonds. This chain assures a maximal approach of the carbonyl oxygen to selenium. In the cation radical, the latter becomes positively charged and its attractive interaction through space with the oxygen carrying partial negative charge can provide an additional stabilization to this species. Molecules **2a** and **2b** are planar and rigid, whereas **3a**–**3e** (Fig. 9) allow a free rotation enabling cation radicals to arrange the distance $Se^{(\delta+)}\cdots O^{(\delta-)}$ at a minimum.

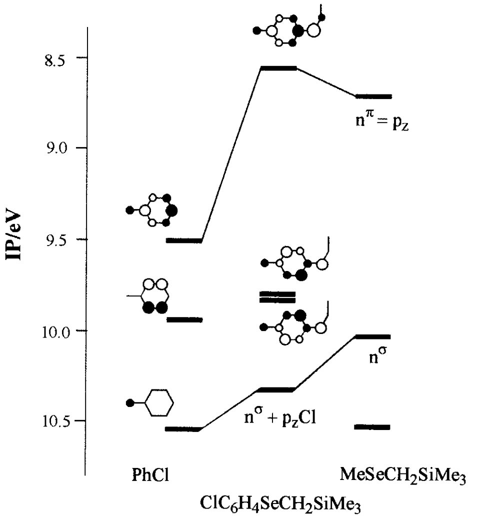

Fig. 8. Correlation of molecular orbitals upon the formation of $ClC_6H_4SeCH_2SiMe_3$.

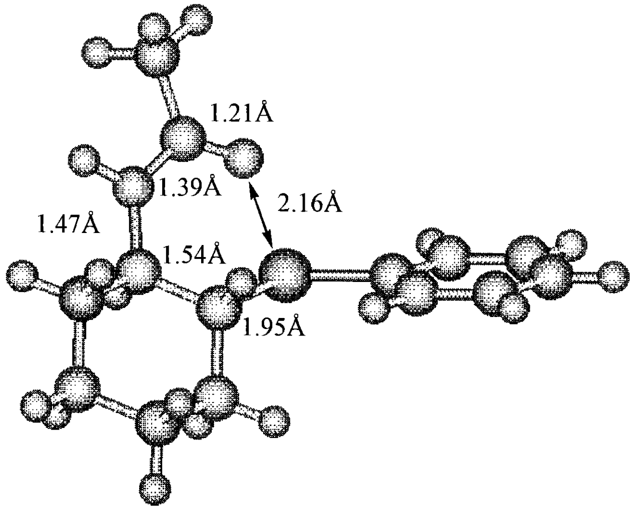

Fig. 9. Cation radical of **3a** according to a PM3 calculation. A *trans*-isomer has been studied.

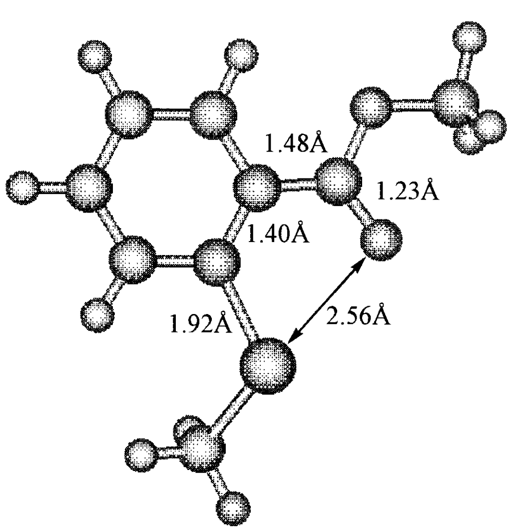

Fig. 10. Cation radical *o*-$MeSeC_6H_4COOMe^{+\bullet}$ according to 6-31G* ab initio calculations.

In a first approach, the energy of the interaction through space stabilizing cation radicals **2a**, **2b** and **3a**–**3e** can be estimated in terms of a purely electrostatic model. For this estimation, charge density distribution and geometry of the molecule of *o*-methylselenobenzene acid **2a** and its cation radical have been calculated ab initio using the SCF/3-21G* basis set [37].

Charge distribution on the SeMe fragment is practically the same in the neutral molecule and in the molecule of selenoanisole: $Se^{(+0.37)}–C^{(-0.12)}$ and $Se^{(+0.35)}–C^{(-0.14)}$ respectively. More than three quarters of the total positive charge in the cation radical was shown to be localized on the Se atom. In the cation radical, the Se and O atoms are closer to each other with respect to the neutral molecule (Fig. 10) and the Se···O distance is comparable with the length of a stretched chemical bond ($l = 2.56$ Å). The participation

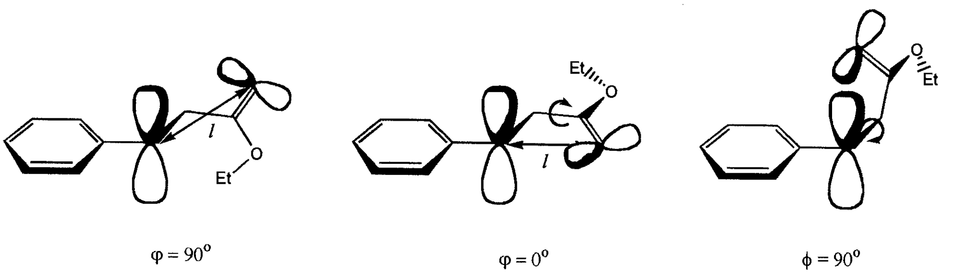

Fig. 11. Rotation about C_{sp3}–C(O) and the Se–C_{sp3} bonds favoring shortest Se···O interatomic distance l (torsion angle φ) and frontal orientation of interacting orbitals (torsion angle ϕ).

of the n-electrons of oxygen in the interaction with positively charged Se atom results in the change of the C=O bond multiplicity index and elongation of this bond (1.207 and 1.231 Å in neutral molecule and in the cation radical, respectively). Besides, the torsion $\angle C_{sp2}$–C_{sp2}–Se–C_{sp3} and the diedral $\angle C_{sp2}$–C_{sp2}–C=O angles change (by +4.2° and −13.6°, respectively) towards the flatening of the Se–C_{sp2}–C_{sp2}–C=O fragment.

For the purely coulombic model of interaction, the interaction energy stabilizing the cation radical of **2a** in acetonitrile and related to 1 mol is

$$\begin{aligned} E &= -\frac{q_{Se}q_{O}e^{2}}{36\varepsilon_0 l} \\ &= -\frac{1.03(-0.67)(1.6\times10^{-19})^{2}6.022\times10^{23}}{36\times8.85\times10^{-12}\times2.56\times10^{-10}\times4.184} \\ &= 31.17\ \text{kcal mol}^{-1} \end{aligned} \qquad (5)$$

The decrease of the cation radical total energy by this value brings the system below the barrier delimiting orbital and charge controlled potential-determining reactions of such species (Fig. 2). Of course, one has to be careful when using this value because its derivation presumes some assumptions (besides the very use of data obtained by quantum chemical calculations for the estimation of the interaction energy):

1. The covalent term of the total energy of the two-center interaction [47] has not been taken into account though the interatomic distance l (Se···O) is of the order of a stretched σ-bond. In addition, even in spite of becoming positively charged in the cation radical, the Se atom still has a large volume, hence a point charge assumption is not quite correct.
2. The polarization of electron shells of the interacting atoms has not been taken into account.
3. Interactions with the supporting salt ions were not considered.

In principle, the last factor must decrease the energy of coulomb interactions, although this effect is partially compensated by neglecting the contribution from the covalent interactions.

The ethyl ester of 2-phenylselenoacetic acid **3e** also has a carbonyl group which can approach selenium but its voltammetric behavior is fairly different. The voltammogram of this compound shows a single wave, the current of which is controlled by diffusion and corresponds to the transfer of two electrons. At low concentrations, the wave slope is close to 60 mV, and the value of $\Delta E_{1/2}/\Delta \lg(\omega)$ is 30 ± 3 mV. These data allow us to conclude that a reversible electron transfer takes place followed by a charge-controlled reaction of first order (E + C1 + E mechanism), as for the oxidation of the majority of alkylarylselenides. Seemingly, the interaction through space in **3e** is not strong enough to stabilize the cation radical and to change its reactivity. In addition, the α-proton in the cation radical of **3e** is more acid, than the corresponding proton in PhSeMe, because of the proximity of an acceptor COOEt group, so the deprotonation of the cation radical is favored kinetically. The last reason seems to be the major one because fixed orientation of the oxygen lone pair along with the possibility of free rotation about the C_{sp3}–C(O) and the Se–C_{sp3} bonds enable almost frontal and hence the most efficient overlapping of interacting orbitals (Fig. 11) so the through space stabilization of this species must be very efficient.

An attempt to increase the energy of the interaction through space and thus to stabilize the cation radical has been made by decreasing the polarity of the media. A 25:75 mixture of toluene and acetonitrile has a static dielectric permittivity $\varepsilon = 16$ so in such a solvent, the energy of interaction of two charges must be two times higher than in acetonitrile alone ($\varepsilon = 36$). Indeed, being oxidized in this binary solvent, **3e** shows a different slope of the dependence $\Delta E_{1/2} - \Delta \lg(\omega)$ which becomes 22 ± 5 mV indicating second order of the potential-determining reaction. Apparently, the stabilization energy is now large enough to bring the cation radical of **3e** below the range of charge-controlled cleavage (see Fig. 2).

It is interesting that oxidative behavior of selenochromanone, also carrying a carbonyl group at the *ortho*-position to selenium but oriented in the opposite direction so as it cannot interact with the selenium atom, is typical for alkylarylselenides ($n = 2$, $\Delta E/\Delta \lg((i_l - i)/i_l) = 100$ mV, $\Delta E_{1/2}/\Delta \lg(\omega) = 31$ mV). It is also seen that its oxidation potential ($E_{1/2} = 1.155$ V [48]) is more positive than the potentials of **2a** and **2b**, affected by field effect[3].

3. Conclusions

The electrochemical behavior of arylselenides can be summarized as follows. Upon oxidation, primary redox properties of these compounds are determined by a frontier orbital, HOMO, which is built up with π-electrons of the unsymmetric ψ_2 orbital of the aromatic ring and of n-electrons of the p_z-orbital of the heteroatom (Fig. 3). For this reason the redox properties of Ar_2Se and ArSeAlk are very similar because it is the same fragment ArSe which is responsible for them[4]. In a cation radical, the localization of the positive charge on Se is very high and this fact along with the $Se{-}C_{sp3}$ and (Se)C–H bonds being weaker compared to the $Se{-}C_{sp2}$ bond make the cation radicals of Ar_2Se and ArSeAlk behave differently: those of Ar_2Se undergo orbital-controlled second order reactions whereas those of ArSeAlk cleave in first order charge-controlled reactions. For arylselenides, the match between π and n levels is less favorable for an effective conjugation than in corresponding sulfides so the HOMO of seleno derivatives is less sensitive to electronic effects acting through the aromatic ring. The decrease of the conjugation of the heteroatom with the aromatic ring and an increased role of its lone pair in the formation of the HOMO is clearly seen through the decrease in the polarographic reaction constants ρ. As the transmission of the electronic effects via the ring decreases along with the increasing contribution from n-electrons of the heteroatom, ρ decreases ($\rho = 0.346$ [49] and 0.275 [50] for ArSMe and $ArSCH_2SiMe_3$ and $\rho = 0.282$ and 0.253 for ArSeMe and $ArSeCH_2SiMe_3$, respectively). So in spite of the β-effect being the weakest for arylselenides, the selenium atom is more sensitive to direct electronic effects namely because of this weakened π-n conjugation.

When first order ensuing reactions of electrogenerated cation radicals are unfavorable for some reason, dimerization or disproportionation takes place. These two reactions are not kinetically competitive since they have a common transition state [47]. In some cases (β-silylated arylselenides) this transition state resolves through the dimerization pathway, in others (arylselenides bearing a substituent with the carbonyl group interacting through space with the reaction center) it is disproportionation which takes place. The charge term of the orbital controlled formation of such a transition state is negligibly small. Thus the action of both of these stereoelectronic effects leads to similar results and consists in stabilization of primary cation radicals, lowering electrostatic repulsion of these species and thus favoring their latent second order reactions. Of course, these effects, being not very strong, can intervene only in the cases when the energy profiles of the two reaction pathways are close on the reaction coordinate.

Here, only intramolecular interactions were considered, but intermolecular interactions (with an external nucleophile or with supporting electrolyte anions) must also be an important factor in the electrochemical reactivity of alkylarylselenides.

4. Experimental

Voltammetric measurements were carried out using a polarographic complex including a PU-1 polarograph with a microcomputer BK-0010 connected via a 1113-PV1A analog-to-digital converter. Rotation velocity in the rotating disk experiments was controlled by a FP-37 numeric counter. A Pt oxidized working electrode in a three-electrode configuration was used. The auxiliary electrode was a Pt wire and the reference electrode was Ag/0.1 M $AgNO_3$ in CH_3CN. The working electrode was carefully washed in acetonitrile and rinsed in diethyl ether before each run.

Photoelectron spectra were registered using a spectrometer ES-3201 with a hemispherical analyzer. The photon source was a resonance line of He(I). The precision of measurements of ionization potentials was as good as 0.02–0.04 eV, depending on the overlapping of absorbance bands.

β-Silylated arylselenides **1a**–**1e** were synthesized according to described procedures [55,56,50]. **2a** was prepared according to [57,58], its methyl ether **2b** was obtained by methylation of **2a** by MeI in a methanol solution of NaOH [50]. Selenides **3a**–**3c** were prepared by electrochemical oxidation of Ph_2Se_2 in acetonitrile in the presence of cyclohexene, hexene-1 and heptene-1, respectively, according to [59].

1-Phenylseleno-2-acetamidocyclohexane, **3a**. M.p. 148°C. $C_{14}H_{19}NOSe$. Anal. Calc.: C 56.77, H 6.42. Found: C 56.85; H 6.4%. IR: ν(N–H) s 3300 cm^{-1};

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[3] In principle, the presence of an electron withdrawing substituent at the *ortho*-position to Se in **2a** and **2b** must increase their oxidation potentials in two ways: by acceptor mesomeric effect and by disturbing the conjugation of the heteroatom with the π-system due to the *ortho*-repulsion of two neighboring groups.

[4] This is proven by IP, dipole moments and NMR chemical shifts [14,51,52], oxidation potentials $E_{1/2}$ [1,9–14,17,24] and the correlation of $E_{1/2}$ of large numbers of alkylarylselenides and $h\nu$ of their charge transfer complexes with electrophilic σ^+ constants [8,11,14,17,24]. In addition, nucleophilic reactions of cationic intermediates electrogenerated from arylselenides occur at the heteroatom [1–5,16,18,53] or at the α-carbon [9,54] to selenium.

ν(C=O) s 1625 cm^{-1}, ν(C–H) m 715 cm^{-1}. NMR (100 MHz, $CDCl_3$, TMS), δ ppm: 7.6 (d 2H), 7.22 (m 3H), 5.95 (broad s 1H), 3.32 (m 1H, $J = 4.06$ Hz), 2.8 (m 1H, $J = 3.99$ Hz), 2.2 (m 2H), 1.96–1.85 (m 2H), 1.76 (s 3H), 1.6–1.3 (m 4H). Mass, m/e (%): 297 (M^+, 3), 238 (30), 236 (16), 157 (20), 140 (22), 129 (4), 98 (90), 81 (100), 60 (48).

1-Phenylseleno-2-acetamidohexane, **3b**. M.p. 73°C. $C_{14}H_{21}NOSe$. Anal. Calc.: C 56.19, H 7.02. Found: C 56.21; H 6.95%. IR: ν(N–H) s 3300 cm^{-1}; ν(C=O) s 1625 cm^{-1}, ν(C–H) s 725 cm^{-1}. NMR (100 MHz, $CDCl_3$, TMS), δ ppm: 7.6 (d 2H), 7.2 (m 3H), 6.6 (d 1H), 3.98 (m 1H, $J = 4.01$ Hz), 2.98 (d 2H, $J = 4.0$ Hz), 1.75 (s 3H), 1.6–1.3 (m 6H), 1.12 (t 3H). Mass, m/e (%): 299 (M^+, 4), 240 (18), 238 (9), 197 (4), 157 (12), 142 (70), 100 (20), 86 (100).

1-Phenylseleno-2-acetamidoheptane, **3c**. M.p. 81°C. $C_{15}H_{23}NOSe$. Anal. Calc.: C 57.51; H 7.35. Found: C 57.56; H 7.28%. IR: ν(N–H) s 3300 cm^{-1}; ν(C=O) s 1625 cm^{-1}, ν(C–H) s 725 cm^{-1}. NMR (100 MHz, $CDCl_3$, TMS), δ ppm: 7.6 (d 2H), 7.22 (m 3H), 6.1 (d 1H), 3.93 (m 1H, $J = 4.0$ Hz), 2.8 (d 2H, $J = 3.98$ Hz), 1.9 (s 3H), 1.72–1.56 (m 8H), 1.2 (t 3H). Mass, m/e (%): 313 (M^+, 4), 254 (14), 189 (4), 172 (6), 156 (64), 142 (10), 114 (16), 100 (100), 91 (22).

3d and **3e** were prepared by reaction of PhSeH with 3-chloropropionic acid and ethyl ether of 2-chloroacetic acid, respectively, according to Ref. [60].

Analytical grade acetonitrile was additionally purified according to [61] and kept over molecular sieves 4A. Et_4NBF_4 was obtained by neutralization of 40% aqueous solution of Et_4NOH with 7.8 M HBF_4 then recrystallized from EtOH, dried and kept over P_2O_5.

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