

Electrochemical Determination of Absolute and Relative Reactivities of Phenyl Chalcogenide Anions toward Aryl Radicals

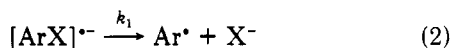
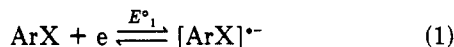
Chantal Degrand*[†] and Rita Prest

Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS (URA 33), Faculté des Sciences, 6 bd Gabriel 21000 Dijon, France

Received July 24, 1989

Absolute and/or relative reactivities of PhE^- anions ($\text{E} = \text{Se}, \text{Te}$) toward the radicals resulting from the reductive cleavage of 9-bromoanthracene and 2- and 4-bromobenzophenone were determined by electrochemically stimulated $\text{S}_{\text{RN}}1$ substitution in MeCN and Me_2SO . Cyclic voltammetry and preparative-scale electrolyses were carried out under experimental conditions where the nucleophilic attack (rate constant k_2) was competing only with H atom abstraction (rate constant k_{H}) and so k_2/k_{H} ratios could be measured. Taking into account results previously published by Savéant et al. concerning k_{H} and the reactivity of PhS^- nucleophile toward aryl radicals, the following conclusions were drawn out. The absolute reactivity of PhSeNBu_4 toward 9-anthryl radical is 12 times higher in MeCN ($k_2 = 8.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) than in Me_2SO ($k_2 = 6.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). In Me_2SO , the relative reactivities of PhSLi , PhSeLi , and PhTeLi are 1, 1.4, and 3.2. In MeCN the rate k_2 is close to the diffusion limit in the nucleophilic attack of PhSeNBu_4 and PhSNBu_4 upon radicals corresponding to reduction of bromobenzophenone.

Phenyl chalcogenide anions PhE^- ($\text{E} = \text{S}, \text{Se}, \text{Te}$) play an important role as nucleophiles in $\text{S}_{\text{RN}}1$ substitution (reactions 1-4).¹ Substitution occurs catalytically because the standard potential E°_2 of the redox couple $(\text{ArEPh})/(\text{ArEPh})^{*-}$ is negative to E°_1 .^{1d}



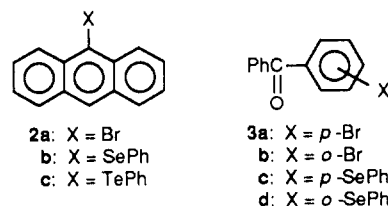
Photochemical stimulation in liquid ammonia has been mainly developed by Bunnett and Rossi.¹ On the other hand, Saveant, Amatore, and Thiébaud groups have thoroughly studied the electrochemically stimulated process.² With a few other,³⁻⁵ they have examined the reactivity of PhS^- anions toward aryl radicals and have carried out the electrochemical synthesis of thio derivatives 1 in liquid ammonia or solvents such as Me_2SO and MeCN .⁶⁻¹⁰ Our group has been involved in the electrochemical synthesis of seleno and telluro derivatives 1 in acetonitrile ($\text{Ar} = \text{NCC}_6\text{H}_4, \text{PhCOC}_6\text{H}_4$).¹¹⁻¹⁵

Although it is established that the reactivity of the benzene chalcogenate anions PhE^- decreases in the order $\text{PhTe}^- > \text{PhSe}^- > \text{PhS}^-$,¹ there is very little quantitative data on the reactivities of the seleno and telluro anions toward aryl radicals. To our knowledge the only quantitative study was derived from competition experiments carried out in liquid ammonia by Rossi et al. who have shown that the relative reactivities of the nucleophiles PhS^- , PhSe^- , and PhTe^- toward 2-quinolyl radicals are 1, 5.8, and 28, respectively.¹⁶

As shown by Saveant et al.,^{8d} quantitative data on k_2 can be derived in H-donating solvents SH, from voltammetric measurements at a stationary electrode, and/or from preparative electrolysis.

From voltammetric experiments and preparative electrolyses carried out in Me_2SO and CH_3CN , we have determined the reactivities of PhSe^- and PhTe^- anions toward the aryl radicals generated by electrochemical reduction of the aryl halides **2a** and **3a,b**. We have compared

our results with those obtained by Saveant et al. and which correspond to PhS^- anions.



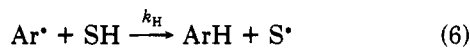
Results and Discussion

In H-donating solvents, the key step (3) is in competition with the side reactions 5 and 6, and so the determination of k_2 implies that k_1 and k_{H} are known. In the limit situation where k_1 is moderate ($k_1 < 10^5 \text{ s}^{-1}$), the voltammetric and coulometric determination of the ratio k_2/k_{H} can be easily carried out. The results presented below correspond to this limit case (vide infra). In voltammetry, the ratio k_2/k_{H} can thus be derived from eq 7 where i_p° is the peak current of ArX at a stationary cathode, in the absence of PhE^- , and i_p the peak current in the presence of PhE^- .^{8d} In preparative electrolysis k_2/k_{H} is derived from eq 8 where

- (1) For reviews, see: (a) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413. (b) Rossi, R. A. *Acc. Chem. Res.* **1982**, *15*, 164. (c) Rossi, R. A.; De Rossi, R. H. *Aromatic Substitution by the $\text{S}_{\text{RN}}1$ Mechanism*, ACS Monograph 178; American Chemical Society: Washington, DC, 1983. (d) Degrand, C.; Prest, R.; Compagnon, P. L. *J. Org. Chem.* **1987**, *52*, 5229.
- (2) Savéant, J. M. *Acc. Chem. Res.* **1980**, *13*, 323.
- (3) Swartz, J. E.; Stenzel, T. T. *J. Am. Chem. Soc.* **1984**, *106*, 2520.
- (4) Simonet, J.; Djeghidjeh, N. *J. Electroanal. Chem.* **1987**, *218*, 367.
- (5) Roffia, S.; Concialini, V.; Bubani, B.; Spinelli, D. *Seventh Euchem Conference on Electrochemistry*, Assisi, Italy, April 18, 1989; Poster 7A.
- (6) (a) Pinson, J.; Savéant, J. M. *J. Chem. Soc., Chem. Commun.* **1974**, 934. (b) *J. Am. Chem.* **1978**, *100*, 1506.
- (7) Amatore, C.; Chaussard, J.; Pinson, J.; Savéant, J. M.; Thiébaud, A. *J. Am. Chem. Soc.* **1979**, *101*, 6012.
- (8) (a) Amatore, C.; Pinson, J.; Savéant, J. M.; Thiébaud, A. *J. Electroanal. Chem.* **1980**, *107*, 75. (b) *Ibid.* **1981**, *123*, 231. (c) *J. Am. Chem. Soc.* **1981**, *103*, 6930. (d) *Ibid.* **1982**, *104*, 817.
- (9) (a) Amatore, C.; Oturan, M. A.; Pinson, J.; Savéant, J. M.; Thiébaud, A. *J. Am. Chem. Soc.* **1984**, *106*, 6318. (b) *Ibid.* **1985**, *107*, 3451.
- (10) Amatore, C.; Combellas, C.; Pinson, J.; Oturan, M. A.; Robveille, S.; Savéant, J. M.; Thiébaud, A. *J. Am. Chem. Soc.* **1985**, *107*, 4846.
- (11) Degrand, C. *J. Chem. Soc., Chem. Commun.* **1986**, 1113.
- (12) Degrand, C. *J. Org. Chem.* **1987**, *53*, 1421.
- (13) Degrand, C. *J. Electroanal. Chem.* **1987**, *238*, 239.
- (14) Degrand, C.; Prest, R.; Compagnon, P. L. *J. Org. Chem.* **1987**, *52*, 5229.
- (15) Pierini, A. B.; Penenory, A. B.; Rossi, R. A. *J. Org. Chem.* **1984**, *49*, 486.
- (16) M'Halla, F.; Pinson, J.; Savéant, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 4120.

[†] Present address: Université de Clermont-Ferrand, Laboratoire d'Electrochimie (URA 434), 24 avenue des Landais, 63177 Aubière Cédex, France.

R is the yield of substitution product 1, assuming that the electrophile concentration $[\text{PhE}^-]$ is constant during electrolysis and that (5) is negligible. Such conditions are filled when k_1 is moderate or when a redox mediator is added when k_1 is high, and so Ar^* is generated in the bulk of the solution.



$$i_p^\circ / i_p = 1 + (k_2/k_H)[\text{PhE}^-] \quad (7)$$

$$R(\%) = \frac{100}{1 + k_H/(k_2[\text{PhE}^-])} \quad (8)$$

Under our experimental conditions, we avoid the use of large amounts of toxic PhEPh , which is the precursor of PhE^- , and so only 1 equiv of nucleophile PhE^- is present at the beginning of each electrolysis (the initial concentration C° of PhE^- and ArX is usually 4×10^{-2} M). Thus the concentration of PhE^- is decreasing as the electrolysis proceeds, and the yield of 1 cannot be derived directly from eq 8. Therefore the expected yield \bar{R} of ArEPh is lower than the yield R derived from eq 8. It is given by eq 10 where C° and C_f are the concentrations of PhE^- at the beginning and at the end of the electrolysis.

$$\bar{R}(\%) = \frac{100}{C^\circ - C_f} \int_{C_f}^{C^\circ} \frac{d[\text{PhE}^-]}{1 + k_H/(k_2[\text{PhE}^-])} \quad (9)$$

$$\bar{R}(\%) = 100 \left[1 - \frac{k_H/k_2}{C^\circ - C_f} \ln \frac{k_H/k_2 + C^\circ}{k_H/k_2 + C_f} \right] \quad (10)$$

When the electrolysis is stopped after total consumption of ArX , C_f is related to the final concentration $(\text{ArEPh})_f$ of 1 by eq 11 since, under our experimental conditions, C_f and the final concentration $[\text{ArH}]_f$ of ArH are equal if the products formed are the substitution and the reduction products.

$$C_f = [\text{ArH}]_f = C^\circ - [\text{ArEPh}]_f \quad (11)$$

An acceptable value of C_f is obtained by considering that $[\text{ArEPh}]_f \leq C^\circ / (1 + k_H/(k_2 C^\circ))$ (cf. eq 8 where $(\text{PhE}^-) \leq C^\circ$) and therefore the lowest value of C_f corresponds to eq 12.

$$C_f = C^\circ - \frac{C^\circ}{1 + k_H/(k_2 C^\circ)} = \frac{k_H/k_2}{1 + k_H/(k_2 C^\circ)} \quad (12)$$

The variations of R (eq 8) and \bar{R} (eq 10) with the ratio k_2/k_H are compared in Figure 1 when $C^\circ = 4 \times 10^{-2}$ M. The highest difference between R and \bar{R} is observed when $k_2/k_H = 50 \text{ M}^{-1}$ ($\bar{R}/R = 0.83$).

The expected yield \bar{R} can be also obtained by coulometry from eq 13 in which n is the number of electrons involved per mole of ArX in the side reaction (6), assuming that S^* is further reduced to S^- and that S^- is unreactive. Therefore, combining eqs 10, 12, and 13 allows the determination of k_H/k_2 from C° and n values.

$$\bar{R}(\%) = 100(1 - n/2) \quad (13)$$

The determination of k_2/k_H from the ratio i_p°/i_p in voltammetry (eq 7) or from the yield \bar{R} in coulometry (eq 13) implies that no side reaction but (6) is involved in the $\text{S}_{\text{RN}}1$ substitution process. However there is another competing reaction (eq 14) which has to be considered, because it might interfere with the homogeneous electron exchange (4). This side reaction occurs more readily in the case of telluro derivatives than for the seleno homo-

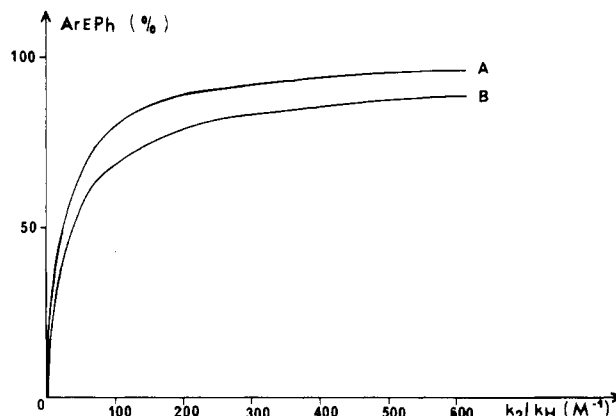
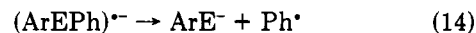


Figure 1. Variation of the yield of ArEPh with the ratio k_2/k_H from eq 8 (curve A) and eqs 10 and 12 (curve B) when the initial concentration of PhE^- is 4×10^{-2} M.

logues.^{1c,13-15} It results from the fragility of C-Se and C-Te bonds and may lead to a scrambling of the aromatic rings according to the global reaction (15). For the ArX/PhE^- systems which are examined below, the side reaction (14) does not take place or is negligible (vide infra).



Substitution of 9-Bromoanthracene (2a). The reduction of 2a in Me_2SO and MeCN has been thoroughly studied.¹⁶ The rate constants k_1 are moderate ($k_1 = 9 \times 10^4 \text{ s}^{-1}$ in DMSO and $1.5 \times 10^5 \text{ s}^{-1}$ in MeCN), and so the further cathodic reduction (5) of the intermediate Ar^* radicals is negligible since these radicals are not generated close to the electrode. Therefore eq 7 can be applied in voltammetry, from which the ratio k_2/k_H can be derived. In the case of PhSLi , its value is 56 M^{-1} at a hanging mercury drop electrode (HMDE), in Me_2SO containing 10% H_2O and 0.1 M LiClO_4 as supporting electrolyte.^{8d} Thus $k_2 = 4.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ since k_H is known from deuteration experiments ($k_H = 8.5 \times 10^6 \text{ s}^{-1}$).¹⁶

We have carried out a voltammetric study of 2a at HMDE in MeCN in the presence of PhSeNBu_4 . Stock solution of this nucleophile was prepared by cathodic reduction of PhSeSePh in MeCN containing 0.1 M Bu_4NPF_6 . As seen in Figure 2, addition of PhSeNBu_4 decreases the peak current of 2a, which drops from 5.2 to $0.70 \mu\text{A}$ (curves a and b) whereas the reversible reduction peak of 2b to 2b⁻ takes place at more negative potentials. The stability of 2b⁻ is moderate since the corresponding oxidation peak presents a small amplitude (curve a of Figure 3). However, it does not lead to a scrambling of aromatic rings resulting from eq 14 since a large-scale electrolysis of 2a in MeCN , in the presence of 1 equiv of PhSeNBu_4 , gives a mixture of anthracene (18%) and 2c (74%). The isolated yield of anthracene is close to the yield (15%) calculated from (13) since $n = 0.30$ (entry 1 of Table II). Therefore, as expected from eq 7 ($i_p^\circ/i_p - 1$ is proportional to the concentration of PhSeNBu_4 (Figure 4C). The slope of Figure 4C gives the ratio k_2/k_H and hence k_2 since k_H is known (Table I). A series of voltammetric measurements carried out in mixtures $\text{MeCN}/\text{Me}_2\text{SO}$ containing 0.1 M Bu_4NPF_6 indicates that the substitution process is more favorable in MeCN than in Me_2SO . That is shown in Figure 2 which compares the influence of PhSeNBu_4 in pure MeCN and in a 3/7 $\text{MeCN}/\text{Me}_2\text{SO}$ mixture. A stronger decrease of the peak current is observed in MeCN ($i_p^\circ/i_p = 7.5$) than in the solvent mixture ($i_p^\circ/i_p = 3.8$). The ratios k_2/k_H derived

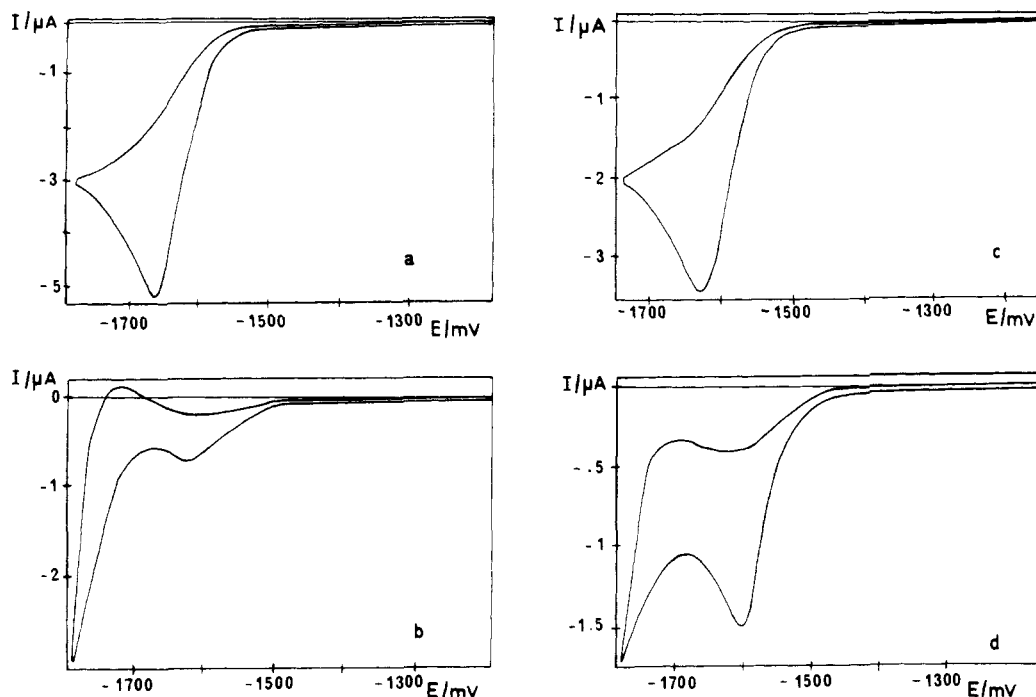
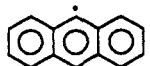
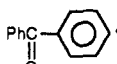
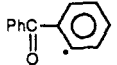


Figure 2. Cyclic voltammograms of **2a** (2×10^{-3} M) at a HMDE in the absence (curves a and c) and in the presence (curves b and d) of PhSeNBu₄ (1.6×10^{-2} M). Curves a and b: MeCN + Bu₄NPF₆ 0.1 M. Curves c and d: 3/7 MeCN/Me₂SO mixture + Bu₄NPF₆ 0.1 M. Sweep rate: 0.1 V s⁻¹.

Table I. Reactivity of PhE⁻ Nucleophiles on Aryl Radicals from Voltammetric Measurements

Ar [•]	solvent	k_H , s ⁻¹	supporting electrolyte	stationary electrode	nucleophile	k_2/k_H , M ⁻¹	k_2 , M ⁻¹ s ⁻¹
	Me ₂ SO + 10% H ₂ O	8.5×10^6 ^a	LiClO ₄	Hg	PhSLi	56 ^a	4.5×10^8 ^a
	Me ₂ SO + 10% H ₂ O	8.5×10^6 ^a	LiClO ₄	glassy C	PhSeLi	77	6.5×10^8
					PhTeLi	180	1.5×10^9
	Me ₂ SO	8.5×10^6 ^a	Bu ₄ NPF ₆	Hg	PhSeNBu ₄	80	6.8×10^8
	MeCN	2×10^7 ^a	Bu ₄ NPF ₆	Hg	PhSNBu ₄	330	6.6×10^9
					PhSeNBu ₄	406	8.1×10^9
	MeCN	5.5×10^7	Et ₄ NClO ₄	glassy C	PhSNEt ₄	360 (290 ^b)	2×10^{10}
					PhSeNEt ₄	360	2×10^{10}
	MeCN	4.5×10^7	Et ₄ NClO ₄	glassy C	PhSeNEt ₄	445	2×10^{10}

^a From ref 1b. ^b From ref 8d.

Table II. Comparative Yields of Substitution Compounds Predicted by Voltammetry and Coulometry

entry	ArX	nucleophile	solvent	k_2/k_H , M ⁻¹	\bar{R} (eq 10 ^a), %	n	\bar{R} (eq 13), %	isolated yield, %
1	2a	PhSeNBu ₄	MeCN	406	86	0.30	85	74
2	2a	PhTeLi	Me ₂ SO	180	66	0.64	68	49
3	3a	PhSeNEt ₄	MeCN	360	85	0.19	90	86 ^b
4	3b	PhSeNEt ₄	MeCN	445	87	0.13	93.5	75 ^c

^a C[•]: 4×10^{-2} M. ^b See ref 14. ^c See ref 19.

from eq 7 and corresponding to different mixtures appear in Figure 5. Extrapolation of the observed straight line indicates that $k_2/k_H = 80$ M⁻¹ in pure DMSO containing 0.1 M Bu₄NPF₆. A similar ratio ($k_2/k_H = 77$ M⁻¹) is obtained with PhSeLi as nucleophile (Table I and Figure 4A) under the conditions chosen by Saveant et al. for the study of PhSLi (Me₂SO + 10% H₂O + LiClO₄ 0.1 M).^{8d} Taking into account the values of k_2/k_H in pure MeCN and Me₂SO and the fact that $k_H(\text{MeCN}) = 2.3k_H(\text{Me}_2\text{SO})$,¹⁷ one finds $k_2(\text{MeCN}) = 12k_2(\text{Me}_2\text{SO})$. A similar effect is observed with PhSNBu₄. In pure acetonitrile, $k_2/k_H = 330$ M⁻¹, that

is to say about 6 times higher than the value observed for PhSLi in Me₂SO.^{8d}

A preparative-scale electrolysis of **2a** in the presence of PhTeLi in Me₂SO + 10% H₂O + 0.1 M LiClO₄ leads to a mixture of **2c** (49%), anthracene (42%),¹⁷ and an unidentified minor compound (3% in weight) (entry 2 of Table II). Hence the side reaction (14) does not take place or is negligible although the radical anion **2c^{-•}** is very unstable, as observed in Figure 3b where no anodic peak is seen. Thus k_2/k_H can be derived from eq 7, and one finds $k_2/k_H = 180$ M⁻¹ (Figure 4B and Table I).

Taking into account the reactivity of PhSLi in Me₂SO which is chosen as reference, it is concluded from the values of Table I that the relative reactivities of PhSLi, PhSeLi, and PhTeLi are 1, 1.4, and 3.2, respectively.

(17) The yield of anthracene is higher than the coulometric yield (32%). As suggested by a reviewer, this would indicate that only a fraction of S^{•-} would be reduced to S⁻ in the mixture Me₂SO/H₂O.

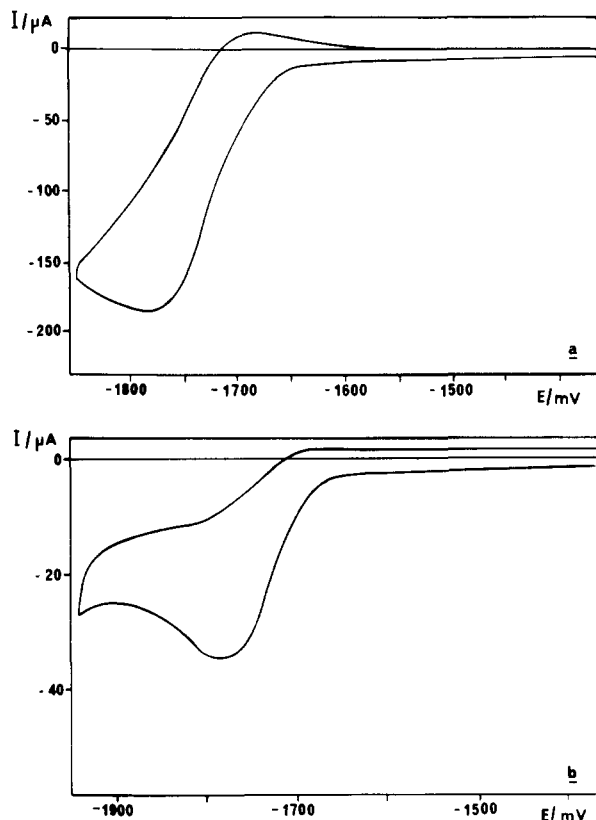


Figure 3. Cyclic voltammograms of **2b** (2×10^{-3} M) in MeCN + Bu₄NPF₆ 0.1 M (above curve) and **2c** (2.7×10^{-3} M) in Me₂SO + H₂O (10%) + LiClO₄ 0.1 M. Sweep rate: 0.1 V s⁻¹.

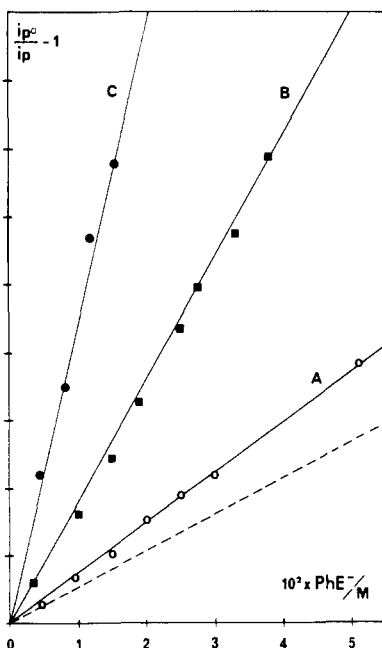


Figure 4. Variations of the peak height (i_p) of **2a** (2×10^{-3} M) with the concentration of PhE⁻ in DMSO + 10% H₂O + 0.1 M LiClO₄ (curves A (E = Se) and B (E = Te)) or in MeCN + Bu₄NPF₆ (curve C (E = Se)). Glassy carbon SDE, sweep rate 0.2 V s⁻¹. i_p^0 is the peak height in the absence of PhE⁻. Dotted curve: PhSLi in DMSO + 10% H₂O + 0.1 M LiClO₄; Hg electrode (from ref 8d).

Substitution of Bromobenzophenones 3a and 3b. In MeCN, the cathodic reduction of *p*-bromobenzene (**3a**) gives a radical anion which does not decompose rapidly ($k_1 = 2.4 \times 10^3$ s⁻¹).¹⁸ The radical anion **3c⁻** is stable.¹⁹

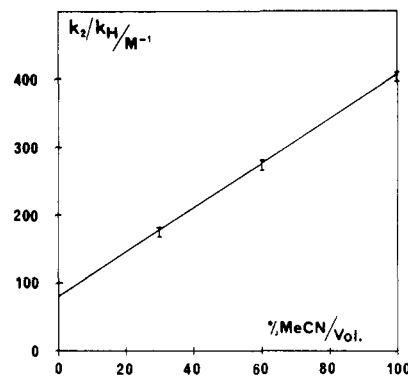


Figure 5. Variation of the ratio k_2/k_H with the MeCN content (vol) in a Me₂SO/MeCN mixture, under the conditions of Figure 2.

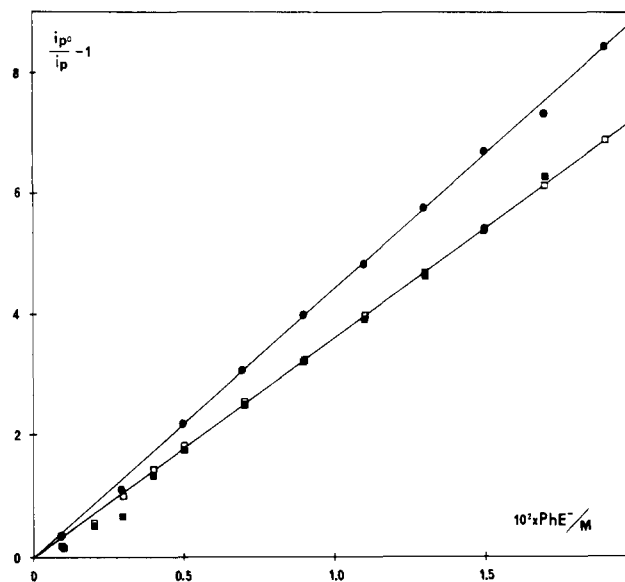


Figure 6. Variations of the peak height (i_p) of **3a** (2×10^{-3} M) with the concentration of PhSNET₄ (■) and PhSeNET₄ (□) and **3b** (2×10^{-3} M) with the concentration of PhSeNET₄ (●) in MeCN + 0.1 M Et₄NClO₄. Glassy carbon SDE. The sweep rate was 0.2 V s⁻¹.

Therefore the peak current i_p is anticipated to vary with the chalcogenate concentration according to eq 7. That is indeed what is observed in Figure 6 with PhSeNET₄. Furthermore, the thio nucleophile behaves identically (Figure 6), and the ratio k_2/k_H is 360 M⁻¹ (stationary glassy carbon electrode). As expected this value is close to the value previously determined by Saveant et al. in the case of PhSNET₄ ($k_2/k_H = 290$ M⁻¹ at a Hg electrode).^{8d} The identical effect observed in the presence of thio and seleno nucleophiles indicates that k_2 reaches the diffusion limit²⁰ in each case, hence $k_2 \cong 2 \times 10^{10}$ M⁻¹ s⁻¹ and $k_H = 5.5 \times 10^7$ s⁻¹ for the para radical of benzophenone. When *o*-bromobenzophenone (**3b**) is reduced in the presence of PhSeNET₄, the ratio k_2/k_H is again high (Figure 6 and Table I) since $k_2/k_H = 445$ M⁻¹. It suggests that the key step (3) is again diffusion controlled, and so $k_H = 4.5 \times 10^7$ s⁻¹.

Results of large-scale electrolyses^{14,19} are consistent with the above results (Table II). A comparison of the yields of seleno derivatives predicted by eq 10 and corresponding

(18) Nadjó, L.; Savéant, J. M. *J. Electroanal. Chem.* 1971, 30, 41.

(19) Prest, R.; Degrand, C. *J. Chem. Soc., Perkin Trans. 2* 1989, 607.

(20) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; M'Halla, F.; Savéant, J. M. *J. Am. Chem. Soc.* 1980, 102, 3806.

to the k_2/k_H values given in Table I are very similar to the yields given by eq 13 (coulometric yields). The seleno ketones **3c** and **3d** were isolated in high yields (86% and 72%) together with benzophenone as a minor compound.^{14,19}

Conclusion

Differences of reactivities between the thio, seleno, and telluro nucleophiles are expected to be observed as long as k_2 is below the diffusion limit. Due to the high electrophilic abilities of the radical derivatives of benzophenone, k_2 is close to the diffusion limit whatever the chalcogeno nucleophile, and so no difference of reactivity can be observed. When 9-anthryl radical is involved in the $S_{RN}1$ substitution, the reactivities of PhS^- , PhSe^- , and PhTe^- anions are different in Me_2SO because k_2 is below the diffusion limit. Thus our structure-reactivity observations are limited to this series. However several other results have to be pointed out which promote the use of MeCN as solvent in large-scale electrolyses. First the substituted compounds **2b**, **3c**, and **3d** are obtained in high yields in MeCN (Table II, $R \geq 85\%$) although the hydrogenation process (6) is rapid (Table I, $k_H \geq 2.10^7 \text{ s}^{-1}$). Then, it is worth noting that the reactivity of the PhSNBu_4 and PhSeNBu_4 nucleophiles toward the 9-anthryl radical are higher in MeCN than in Me_2SO whereas an opposite effect was claimed for PhSLi toward 2-naphthyl radical.^{6b,8d} The study of other radicals is currently underway in our laboratory.

Experimental Section

The solvents, supporting electrolyte, and compounds **2a** and **3a** were from commercial origin. The ketone **3b** was prepared according to ref 21. Analytical-grade MeCN (spectrosol SDS) was carefully dried on neutral alumina.

Elemental analyses were performed by Service Central d'Analyses, CNRS, Lyon.

Cyclic voltammograms at a hanging mercury drop electrode (HMDE) and glassy carbon stationary disc electrode (SDE) (V25 Carbone Lorraine; diameter = 3 mm) were obtained using an IR-compensated potentiostat driven by a Dacfamov 05 programmer and a Apple IIC computer. The glassy carbon electrode was polished on 400, 800, and 1200 grit sand papers ESCIL, on a polishing wheel, then on damp polishing cloth Escil-Pal, finally dried with acetone. An Amel 552 potentiostat (output voltage 200V at full load) and a Tacussel IG5-N integrator were used in coulometry and preparative electrolysis. All the potentials referred

to the aqueous saturated calomel electrode (SCE).

The electrochemical synthesis of **3c,d** by large-scale electrolysis of **3a,b** in the presence of PhSe^- are described in refs 14 and 19. The electrochemical synthesis of **2b** and **2c** was carried out in an H-type cell, the three compartments of which were separated by ion-exchange membranes Ionax MA 3475 (anodic side) and MC 3470 (cathodic side). The cathode was a graphite cloth of cylindrical shape and the anode a Pt grid. The cathodic solution (100 mL) was stirred mechanically and deaerated with argon prior to and during electrolysis.

Electrochemical Synthesis of 2c (Entry 1 of Table II). Diphenyl diselenide (2 mmol) was introduced and reduced to PhSe^- in MeCN containing Bu_4NPF_6 0.1 M. The potential had to be changed from -1.1 to -2.1 V, whereas the faradaic current dropped from 100 mA (initial value) to a negligible value, after consumption of 386 C (4 mmol of electrons). The electrolysis was interrupted, **2a** (4 mmol) was added, and the potential was reduced at $-1.40 \pm 0.05 \text{ V}$. The faradaic current dropped from 20 mA (initial value) to 4 mA, after consumption of 116 C (1.2 mmol of electrons). The cathodic solution was diluted with water, and electrolysis products were extracted with diethyl ether. After the solution was dried, the ether was removed. The crude product (1.23 g) was separated by column chromatography with 1/9 $\text{CH}_2\text{Cl}_2/\text{hexane}$, and the compounds were isolated in the order: a mixture of anthracene (128 mg, 0.72 mmol, 18%) and PhSeSePh (88 mg, 0.28 mmol, 14%), and then **2c** (987 mg, 2.96 mmol, 74%).

9-(Phenylseleno)anthracene (2c): yellow powder; mp 117 °C (CH_2Cl_2 -hexane). Anal. Calcd for $\text{C}_{20}\text{H}_{14}\text{Se}$: C, 72.07; H, 4.23; Se, 23.69. Found: C, 72.01; H, 4.21; Se, 24.05.

Electrochemical Synthesis of 2d (Entry 2 of Table II). Diphenyl ditelluride (1 mmol) was introduced and reduced to PhTe^- in $\text{Me}_2\text{SO} + 10\% \text{ H}_2\text{O} + \text{LiClO}_4$ 0.1 M. The potential had to be changed from -0.94 to -2.0 V whereas the faradaic current dropped from 40 to 5 mA after consumption of 234 C (2.4 mmol of electrons) (N.B. PhTe^- anions are very sensitive to traces of oxygen and so PhTeTePh is regenerated). The electrolysis was interrupted, **2a** (2 mmol) was added, and the potential was reduced at $-1.40 \pm 0.1 \text{ V}$. The faradaic current dropped from 20 mA (initial value) to 8 mA after consumption of 94.5 C (0.98 mmol of electrons). The crude product (684 mg) was obtained and separated as above. The compounds were isolated in the order: **2a** (118 mg, 0.46 mmol, 23%), a mixture of PhTeTePh (53 mg, 0.13 mmol, 13%) and anthracene (117 mg, 0.65 mmol, 32.5%), **2d** (286 mg, 0.75 mmol, 37.5%), and several minor compounds (23 mg). Taking into account **2a** left, the yields of anthracene and **2d** are 42.5% and 49% whereas 0.64 electron equiv was consumed.

9-(Phenyltelluro)anthracene (2d): bright yellow powder; mp 127 °C (CH_2Cl_2 -hexane). Anal. Calcd for $\text{C}_{20}\text{H}_{14}\text{Te}$: C, 62.90; H, 3.69; Te, 33.41. Found: C, 62.70; H, 3.58; Te, 33.44.

Acknowledgment. Work was supported by CNRS (Pirseme Grant). We are grateful to Mrs. Raveau-Fouquet for technical assistance.

(21) Koopal, S. A. *Recl. Trav. Chim. Pays-Bas* 1915, 34, 152.