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Electrochemical Synthesis of Organochalcogenides in Aqueous Medium

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Pedro B. Ribeiro Neto,[a] Sonydelane O. Santana,[a] Guillaume Levitre,[b] Danilo Galdino,[a] Jadson L. Oliveira,[a] Rogério T. Ribeiro,[a] Maria E. S. B. Barros,[a] Lothar W. Bieber,[a] Paulo H. Menezes[a] and Marcelo Navarro[a]*

The electrochemical preparation of telluride, selenide and sulfide ions was carried out in NaOH aqueous solution, using a two compartment cell. Organochalcogenides were prepared from halogenated compounds in a two steps procedure. The monochalcogenides were obtained as major products in good yields.

The synthesis of organochalcogenides is a subject of great interest, not only due to their application in the synthesis of complex molecules[1-4] but also to their application in materials science[5-7] and biochemistry.[8]

Two main approaches can be used to prepare this class of compounds: the use of electrophilic chalcogenides and the appropriate organometallic reagent[9,10] or the use of nucleophilic chalcogenides and electrophilic species such as aryl halides or diazonium salts.[11] However, the preparation of lithium or magnesium organometallic reagents or the use of toxic solvents or organochalcogenols - compounds with a stench smell - is still a drawback in these reactions. To circumvent this problem, some methods based on transition metal-catalyzed reactions[12-16] or ionic liquids[17] were also described. Nonetheless, the majority of them are restricted for the synthesis of diaryl chalcogenides.

Electrochemistry provides a feasible alternative for organochalcogenide synthesis, since the use of electrochemical techniques is gaining more space as an efficient method of synthesis, in special due to the high yield of products, current efficiency and control of the process; therefore, cleaner, faster and cheaper processes can become economically and environmentally viable by using electrochemical procedures.[18] The electrochemical synthesis of diaryldichalcogenides (Se and Te) was described by a SNR1 reaction mechanism of aryl halides using sacrificial cathodes (Se and Te) in aprotic medium (acetonitrile, DMSO and DMF). The procedure involves the simultaneous reduction of the selenium or tellurium electrode and aryl halide furnishing good to moderate product yields.[19-21]

In this work, we describe the electrochemical preparation of organochalcogenides based on the selective generation of Se^{2-}, Te^{2-}, and S^{2-} anions in aqueous medium aiming to develop a procedure that meets the standards of the green chemistry.

The electrochemical preparation of selenide (Se^{2-}) telluride (Te^{2-}) and sulfide (S^{2-}) anions was chemoselectively carried out in aqueous medium using an electrochemical cell of two compartments separated by a Nafion® membrane (Fig. 1).

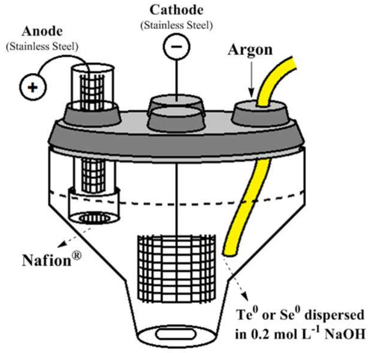

Figure 1. Two compartments electrochemical cell.

The appropriate chalcogenide (Y^0, 0.5 mmol) was electro-reduced into their corresponding anions in 25 mL of 0.2 mol L^{-1} NaOH solution (pH 13) at constant current (I = -70 mA) according to Scheme 1. All reactions were carried out under argon atmosphere to avoid the oxidation of the formed anions by O_2 in solution.

$$Y^0_{(s)} + 2e^- \rightarrow Y^{2-}_{(aq)} \qquad (Y = Te, Se \text{ or } S)$$

Scheme 1. Electroreduction of chalcogenides.

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[a] *Universidade Federal de Pernambuco, CCEN, Departamento de Química Fundamental, Recife–PE, Brazil.*
[b] *Université Paris-Est Créteil Val de Marne, IUT Créteil-Vitry, Vitry sur Seine, France.*

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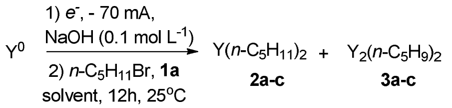
In the course of developing the best reaction conditions, the electrochemical synthesis of dipentylchalcogenides [$Y(C_5H_9)_2$, where Y = Te, Se or S) were first investigated in the presence of different co-solvents (acetonitrile, N,N-dimethylformamide (DMF), ethanol and tetrahydrofuran (THF)). Thus, after the elemental chalcogenide (Y^0) reduction in 0.2 mol L^{-1} NaOH solution, 20 mL of co-solvent was added. The electrolysis was maintained at constant current (I = -70 mA) and under argon[22,23] till the solution remains colorless. The current was stopped, and 1-bromo pentane (**1a**, 1.0 mmol, solvated in 5 mL of the appropriate co-solvent, previously deoxygenated with argon) was added to the electrochemical cell. The mixture was stirred for 12 hours at room temperature and under argon. The results are depicted on Table 1.

Table 1. Reaction of 1-bromopentane with electrochemically generated chalcogenide ions in aqueous solution[a].



$$Y^0 \xrightarrow[\substack{2)\ n\text{-}C_5H_{11}Br,\ \mathbf{1a} \\ \text{solvent, 12h, 25}^{o}\text{C}}]{\substack{1)\ e^-,\ -\ 70\ \text{mA}, \\ \text{NaOH (0.1 mol L}^{-1})}} \underset{\mathbf{2a\text{-}c}}{Y(n\text{-}C_5H_{11})_2} + \underset{\mathbf{3a\text{-}c}}{Y_2(n\text{-}C_5H_9)_2}$$

entry	**Y^0**	**co-solvent**	**Yield(%)[b]**			
			$Y(n\text{-}C_5H_{11})_2$		**$Y_2(n\text{-}C_5H_{11})_2$**	
1	Te	MeCN		97		2
2	Te	DMF	$Te(n\text{-}C_5H_{11})_2$	92	$Te_2(n\text{-}C_5H_{11})_2$	4
3	Te	EtOH	**2a**	41	**3a**	8
4	Te	THF		92		0
5	Se	MeCN		80		20
6	Se	DMF	$Se(n\text{-}C_5H_{11})_2$	91	$Se_2(n\text{-}C_5H_{11})_2$	9
7	Se	EtOH	**2b**	87	**3b**	13
8	Se	THF		83		8
9	S	MeCN	$S(n\text{-}C_5H_{11})_2$	22	$S_2(n\text{-}C_5H_{11})_2$	48
10	S	THF	**2c**	59	**3c**	16

[a] *Reaction conditions:* Elemental chalcogenide (Y^0) dispersed in 0.2 mol L^{-1} NaOH (25 mL), was electro-reduced at -70 mA under argon atmosphere. 20 mL of THF was added and the electrolysis (-70 mA) was maintained till colorless solution. **1a** (1.0 mmol) in the appropriate solvent (5 mL) was added and the mixture was stirred at 25°C for 12h. [b] Determined by GC with respect to **1a**.

When elemental tellurium (Te^0) was used as chalcogenide source, it was observed that the use of polar non-protic co-solvents such as acetonitrile and DMF gave the corresponding telluride **2a** in good yields together with a small amount of 1,2-dipentylditellane **3a** (Table 1, entries 1 and 2). The use of a protic co-solvent in the reaction gave the desired product **2a** in low yield, together with a small amount of **3a** (Table 1, entry 3). The best condition was found when THF was used as co-solvent, where **2a** was obtained in 92% yield as a sole product (Table 1, entry 4). The same conditions were applied to the reactions using elemental selenium (Table 1, entries 5 to 8), and comparable yields to those obtained with tellurium were observed. However, a lower selectivity was observed for the reaction involving selenium, where higher amounts of the corresponding diselenide were observed in all cases. When acetonitrile was used as co-solvent, the desired product **2b** was obtained in 80% yield together with 20% of the corresponding diselenide **3b** (Table 1, entry 5). When DMF was used as co-solvent, higher conversions to **2b** were observed together with a small amount of **3b** (Table 1, entry 6). The best result was observed when THF was used as the co-solvent where the selenide **2b** was obtained in 83% yield together with the diselenide **3b** in 8% (Table 1, entry 8). Due to the lower reactivity of sulfide ions, the reactions were carried out only using acetonitrile or THF as co-solvent (Table 1, entries 9 and 10). The desired sulfide **2c** was obtained only in 22% in acetonitrile and 59% in THF. **3c** was obtained in major amounts (48% and 16%, respectively), demonstrating that the reaction selectivity decreases according to the nucleophilicity of chalcogenide ion. Despite the good results observed when acetonitrile was used as the reaction co-solvent, it was discarded due to environmental concerns and toxicity.[24] It is also interesting to note that the reaction conditions could be adapted to run using other solvents with similar polarity and Lewis base strength such as 2-Me-THF, a solvent produced from renewable resources and commercially available.[25]

With the optimized reaction conditions, the generality of the method was explored by extending the method to different halides. The results are depicted on Table 2. Good conversions were observed when 1-bromopentane reacted with telluride and selenide anions, giving the corresponding chalcogenides in good yields (Table 2, entries 1-3). 1-Iodohexane showed lower reactivity face to the chalcogenide ions tested, with yields ranging from 79% to 24% (Table 2, entries 4-6). Again, the reaction with Te^{2-} anion was more selective yielding only the corresponding telluride **2d** in 64% (Table 2, entry 4). Similar results were observed for Se^{2-} anion, where selenide **2e** was obtained in 74% yield together with 5% of diselenide **3e** (Table 1, entry 5). Much lower yields and selectivities were observed when S^{2-} anion was used (Table 1, entry 6). The application of the developed set of conditions to the less expensive and more commercially available alkyl chlorides proved to be unsuccessful while the desired diorganochalcogenides **2g**-**i** were not observed when 1-chlorobutane was used (Table 2, entries 7-9).

Despite the results obtained for the synthesis of sulfides and the use of alkyl chlorides, the methodology is very promising while it was already described in the literature that poorer chalcogenide/dichalcogenide ratios were observed when longer straight chains are used for the synthesis of these classes of compounds.[26]

The reaction of chalcogenide anions with bromocyclopentane, a secondary halide, gave the desired chalcogenides in moderate to lower yields (Table 2, entries 10-12). The reaction with Te^{2-} showed an excellent selectivity giving the telluride **2j** in 72% yield as a sole reaction product (Table 2, entry 4). Surprisingly, in the reaction of cyclopentyl bromide with Se^{2-}, a reversal composition of the main product was observed where diselenide **3k** was obtained in 75% yield together with selenide **2k** in only 5% yield (Table 2, entry 5). This result is probably due to the low reactivity of cyclopentyl bromide face

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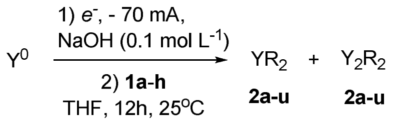
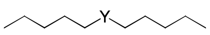
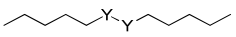
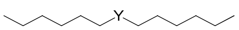
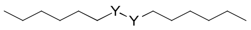
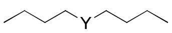
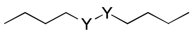
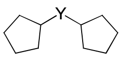
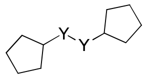
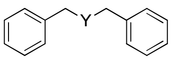
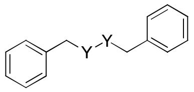
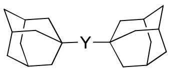
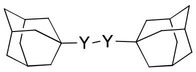
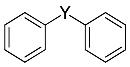
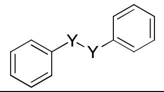
Table 2. Reaction of R-X with electrochemically generated chalcogenide ions in aqueous solution[a].



entry	R-X	Yield (%)[b]					
		YR₂			Y₂R₂		
1	n-C_5H_{11}-Br **1a**	Y = Te	**2a**, 92		Y = Te	**3a**, 0	
2		Y= Se	**2b**, 83		Y= Se	**3b**, 8	
3		Y = S	**2c**, 59		Y = S	**3c**, 16	
4	n-C_6H_{12}-I **1b**	Y = Te	**2d**, 64		Y = Te	**3d**, 0	
5		Y= Se	**2e**, 74		Y= Se	**3e**, 5	
6		Y = S	**2f**, 17		Y = S	**3f**, 7	
7	n-C_4H_9-Cl **1c**	Y = Te	**2g**, 0		Y = Te	**3g**, 0	
8		Y= Se	**2h**, 0		Y= Se	**3g**, 0	
9		Y = S	**2i**, 0		Y = S	**3i**, 0	
10	c-C_5H_9-Br **1d**	Y = Te	**2j**, 72		Y = Te	**3j**, 0	
11		Y= Se	**2k**, 5		Y= Se	**3k**, 75	
12		Y = S	**2l**, 5		Y = S	**3l**, 2	
13	Bn-Br **1e**	Y = Te	**2m**, 95		Y = Te	**3m**, 0	
14		Y= Se	**2n**, 96		Y= Se	**3n**, 0	
15		Y = S	**2o**, 56		Y = S	**3o**, 9	
16	Adamantyl-Br **1f**	Y = Te	**2p**, 0		Y = Te	**3p**, 0	
17		Y= Se	**2q**, 0		Y= Se	**3q**, 0	
18		Y = S	**2r**, 0		Y = S	**3r**, 0	
19	Ph-X **1g**, X = Br **1h**, X = I	Y = Te	**2s**, 0		Y = Te	**2s**, 0	
20		Y= Se	**2t**, 0		Y= Se	**2t**, 0	
21		Y = S	**2u**, 0		Y = S	**2u**, 0	

[a] *Reaction conditions:* Elemental chalcogenide (Y^0) dispersed in 0.2 mol L^{-1} NaOH (25 mL), was electro-reduced at -70 mA under argon atmosphere. 20 mL of THF was added and the electrolysis (-70 mA) was maintained till colorless solution. The appropriate organic halide (R-X) (1.0 mmol) in THF (5 mL) was added and the mixture was stirred at 25°C for 12h. [b] Determined by GC with respect to the organic halide (**1a**-**h**).

to the Se^{2-} anion, allowing the formation of Se_2^{2-} ion in solution, which is a more nucleophilic reagent. In the case of the sulfide ion, lower conversions were observed again (Table 2, entry 12). Excellent results were observed when benzyl bromide was used as the electrophile. In this case, better yields for the three chalcogenide ions were observed (Table 2, entries 13-15). The reaction with Te^{2-} ion again proved to be very selective leading to the corresponding telluride **2m** in 95% yield as the only reaction product (Table 2, entry 13). The same behavior was observed for Se^{2-} ion, where the corresponding selenide **2n** was obtained in 96% yield (Table 2, entry 14). The reaction with S^{2-} ion gave the corresponding sulfide in moderate yield and selectivity, where dibenzylsulfide **2o** was obtained in 56% yield together with 9% of dibenzyldisulfide (Table 2, entry 15). When the sterically hindered 1-bromo-adamantane was used as the substrate the reaction was not effective to promote the synthesis of chalcogenides (Table 2, entries 16-18). The same behavior was also observed when the aryl halides bromobenzene and iodobenzene were used as the reaction electrophiles (Table 2, entries 19-21).

The developed method is interesting not only due to its simplicity, but also because it allows to monitoring the formation of the desired anions. Indeed, the electrochemical reduction of chalcogenes (Y^0) into the corresponding chalcogenide anions (Y^{2-}) furnished a colorless solution in the electrochemical cell (Scheme 2). However, in some cases, during the electrochemical reduction of Te^0 into Te^{2-} it could be observed a purple color, indicative of the formation of ditelluride ion (Te_2^{2-}). In the same way, during the electrochemical reduction of Se^0 to Se^{2-} it could be observed the development of a yellow color in the cathodic compartment, indicative of the formation of diselenide anion (Se_2^{2-})(Scheme 2a).[22,23]

$$Y^{2-}{}_{(aq)} + Y^0{}_{(s)} \rightarrow Y_2{}^{-2}{}_{(aq)} \qquad (a)$$

$$Y_2{}^{-2}{}_{(aq)} + 2e^- \rightarrow Y^{2-}{}_{(aq)} \qquad (b)$$

Scheme 2. Electroreduction of dichalcogenides (Y_2^{-2}) into the corresponding chalcogenide anion (Y^{2-}).

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Conversely, these species can be easily reduced during the electrolysis course, till the cathodic solution becomes colorless again (Scheme 2b). When halogenated compounds are not very reactive, the molecular oxygen slowly reacts with Y^{2-} giving Y^0 (Scheme 3), which remains in the medium or can react according to Scheme 2.

$$Y^{-2}{}_{(aq)} + O_{2(aq)} + 2\ H_2O_{(l)} \rightarrow Y^0{}_{(s)} + 4\ HO^-{}_{(aq)}$$

Scheme 3. Oxidation of chalcogenide anion (Y^{2-}) into the corresponding chalcogenide (Y^0).

This behavior explains the increase of dichalcogenide product in the sequence: Te > Se > S.

Conclusions

The electrochemical reduction of elemental chalcogens in aqueous medium showed to be a simple, efficient and clean procedure for obtaining chalcogenide ions. From the results shown in Tables 1 and 2, high yields were observed when benzyl and primary alkyl halides were used as substrate in the reaction, conversely, secondary halides gave lower yields and no reaction were observed when adamantyl and aryl halides were used suggesting a S_N2 type reaction. The reactivity and nucleophilic character of telluride ion is responsible for selectivity and high yields were observed in organochalcogenide reactions. The selenide ion is less reactive and in most cases the reaction presented a mixture of selenide and diselenide products. The sulfide ion is even less reactive and only presented good results when reactive halogenated compounds were used to give the corresponding mono and disulfide products in lower selectivity for all cases.

Acknowledgements

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