ELECTROCHEMICAL STUDIES ON NEW TRIPHENYL ARSONIUM DERIVATIVES

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Iodine and bromine salts of benzyl triphenyl arsonium derivatives were characterized by cyclic voltammetry, differential pulse voltammetry and rotating disk electrode voltammetry, and the effect of -NO_2, -OCH_3 and -CH_3 substituents on their electrochemical behaviour has been analysed.

Keywords: organic arsonium salts, electrochemistry in organic solvents, benzyltriphenylarsonium bromide, (3-methoxybenzyl)triphenylarsonium iodide, (3-nitrobenzyl) triphenyl-arsonium iodide, (3-methylbenzyl)triphenylarsonium iodide

1. Introduction

Organoarsenium compounds are less studied due to both arsonium relatively low abundance and their toxicity. However, in the last years it was proved that the organic arsonium compounds are much less toxic than their inorganic correspondents [1]. Therefore, new research efforts were made to measure the arsonium ions properties (especially those containing fluorine) to find new industrial and medical applications [2]. Therefore, their electrochemical properties must lead to the understanding of their chemistry and toxicity.

Quaternary organic derivatives of As, Sb and Bi, as well as corresponding derivatives of P, are strong electrolytes in polar solvents. The nature of anions, normally halogens, has no influence on the electrochemistry of cations. No systematic studies of bismonium salt electrochemistry have been reported. Electrochemical studies of quaternary arsonium and stibonium salts were mostly performed in an aqueous or buffered aqueous solution using polarographic methods, for example reduction on a dropping mercury electrode [6].

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All quaternary arsonium salts are reduced in a chemically irreversible two-electron process on mercury electrodes in aqueous solution and thus resemble analogue phosphonium salts [7 - 9]. Arsonium salts in aqueous solution are reduced to potentials which are displaced by about 0.3 V in the positive direction compared to those of the corresponding phosphonium salts, while the first electron transfer for the stibonium salts is displaced by more than 0.5 - 1.0 V in the positive direction.

The half-wave potentials depend on the concentration of the substrate, as well as the lifetime of the mercury electrode drop and the height of the mercury column, and often the current (i) versus potential (E) curves show high polarographic maximums due to adsorption processes.

The effect of structure on the polarographic half-wave potential was studied in an aqueous solution for organic substituents of arsonium ions [7-9]. The two-electron reduction process is chemically irreversible and, consequently, the effect of a change of substituents on the value of the half-wave potential ($E_{1/2}$) reflects the combined effects of the substituent on the electron-accepting properties of the ion and kinetics of the subsequent reaction. Taking the tetraphenyl arsonium ion as a reference, it appears that the substitution on one of the phenyl groups has a minor influence on the $E_{1/2}$ value, while the replacement of one of the phenyl groups with an alkyl group shifts the potential in the negative direction with about 0.12 V per alkyl group [9].

Until now, no systematic studies on the reduction of R_4M^+ in aprotic solvents have been performed. The reduction of Ph_4As^+ in DMF [12] on mercury has been reported to occur in a two-electron process, while the reduction of Ph_4Bi^+ in MeCN has been reported to occur in two single-electron steps [1]. The number of electrons involved in DME reduction processes has not been mentioned [11].

There are indications, however, that the reduction mechanism in aprotic solvents may be different for cations in which one of the substituents possesses α-hydrogen. The reduction of a series of 10-methyl-10-arylphenoxarsinium salts has been studied in DMF by polarography in the absence and presence of added proton donors [13].

In the present paper 4 trphenylarsonium salts (Fig. 1) were investigated in aprotic solvent (dimethylformamide) in presence of tetrabutilamonium perchlorate as supporting electrolyte: benzyltriphenylarsonium bromide (**L1**), (3-methoxybenzyl)triphenylarsonium iodide (**L2**), (3-nitrobenzyl) triphenyl-arsonium iodide (**L3**), (3-methylbenzyl)triphenylarsonium iodide (**L4**). The study was done by cycling voltammetry, differential voltammetry and rotating disk electrode voltammetry, and the main electrochemical processes were assessed.

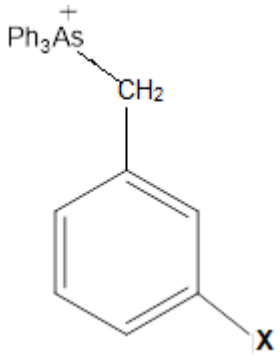


Fig. 1 General formula of the investigated compounds
X: H, OCH_3, NO_2, CH_3

2. Experimental Section

The derivatives **L1 - L4** were synthesized in the Institute of Organic Chemistry "C.D. Nenitzescu" [14]. Acetonitrile (CH_3CN), dimethylformamide (DMF), and tetrabutylammonium perchlorate (TBAP) from Fluka were used as received for solvents and supporting electrolyte.

The electrochemical experiments were carried out by cyclic voltammetry (CV), differential pulse voltammetry (DPV), and rotating disk electrode voltammetry (RDE) using a PGSTAT12 AUTOLAB potentiostat coupled to a three-compartment cell. The CV curves were recorded at 0.1 – 1 V/s scan rates. DPV curves were recorded at 0.01V/s with a pulse height of 0.025V and a step time of 0.2 s. RDE experiments were recorded at 0.01 V/s with rotation rates between 500 and 2000 rpm. A glassy carbon disk (3 mm in diameter) was used as working electrode. Before each experiment the working electrode active surface was polished with diamond paste (0.25 μm). Ag/10 mM $AgNO_3$ in 0.1 M TBAP, CH_3CN was used as reference electrode. The potentials were referred to the ferrocene/ferricinium redox couple (Fc/Fc^+) potential (in our experimental conditions +0.07 V). As auxiliary electrode a platinum wire was used. The experiments were performed at 25 ºC under argon atmosphere.

3. Results and discussion

The electrochemical behaviour of these new derivatives was studied on glassy carbon electrode by electrochemical methods: CV, DPV, and RDE voltammetry. The redox processes evidenced by CV and DPV in solutions of 0.1M TBAP in DMF were established, analysed, and partially assessed to a process occurring at a certain functional group at which they take place, according to the active structures in the investigated salts. The curves CV and DPV and respectively DPV and RDE for each arsonium salt solution in 0.1 M TBAP, DMF

on glassy carbon were usually placed on the same graph, to notice the correspondences between them. The DPV and RDE currents were shown in absolute values (see further) to allow an easy comparison of anodic and cathodic peak currents.

All curves were recorded individually, starting from the potential of 0 V. Anodic (a1, a2, …) and cathodic (c1, c2, …) processes were denoted in the order in which they appear in the voltammograms.

3.1. Study of benzyltriphenylarsonium bromide (L1)

The electrochemical experiments carried out by CV and DPV obtained for two concentrations (2.5 and 5 mM) of the compound **L1** in the supporting electrolyte (0.1 M TBAP in DMF) are shown in Fig. 2. Two anodic (a1 and a2) and three cathodic (c1, c2, and c3) processes, irreversible (i) or quasireversible (q), are clearly evidenced from CV and DPV curves (see further discussion). The DPV peak potentials are given in Table 1. The DPV and RDE curves obtained in a solution of **L1** (2.5 mM) in 0.1 M TBAP, DMF on glassy carbon at different rotation rates are given in Fig. 3. They were put on the same graph to evidence their correspondence.

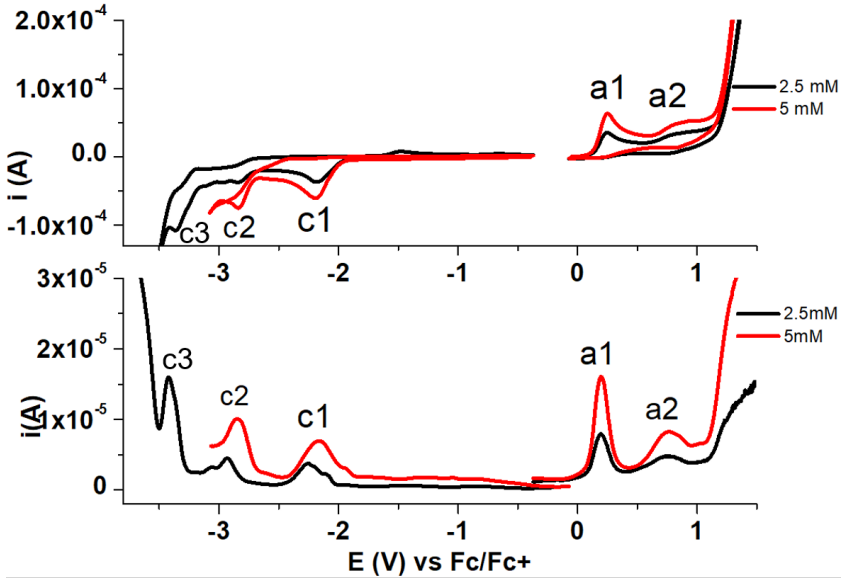


Fig. 2. CV (0.1 V/s, up) and DPV (down) curves obtained for different concentrations of **L1** on glassy carbon in 0.1 M TBAP, DMF; the DPV cathodic currents are in absolute values

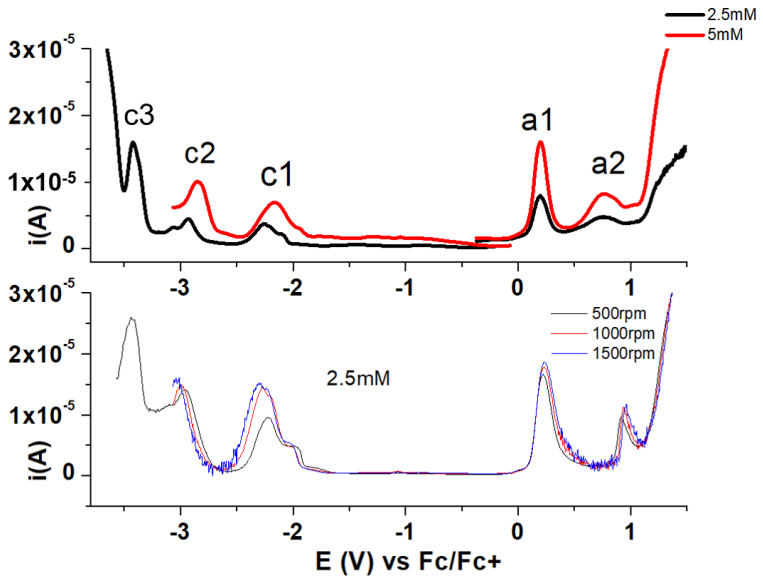


Fig. 3. DPV (up) and RDE (down) curves obtained in a solution of **L1** (2.5 mM) in 0.1 M TBAP, DMF on glassy carbon at different rotation rates of RDE; the RDE cathodic currents are in absolute values

Table1

Potentials (V) of the DPV peaks and their assessment for L1 (2.5mM) vs Fc/Fc^+

Peak	E_{DPV} (V)	Assessed process
c1	-2.258 (i)	$Ph_3As\text{-}CH_2\text{-}C_6H_5^+ + e^- = Ph_3As + Ph\text{-}CH_2\blacksquare$
c2	-2.936 (i)	$Ph_3As + e^- = Ph_2As^- + Ph\blacksquare$
c3	-3.452 (q)	$Ph\text{-}CH_2\blacksquare$ + e- = Ph CH_2^-
a1	0.193 (i)	$Br^- - e^- = 1/2Br_2$
a2	0.760 (i)	$Br^- - 2e^- + H_2O = BrO^- + 2H^+$

3.2. Study of (3-methoxybenzyl)triphenylarsonium iodide (L2)

The CV and DPV curves for compound **L2** are given in Fig. 4 for two concentrations (2.5 and 5 mM) of the studied compound. From the DPV curves three anodic (a1 – a3) and three cathodic (c1 – c3) processes, irreversible (i) or quasireversible (q), are noticed. Their DPV peak potentials are given in Table 2. Anodic and cathodic RDE curves obtained in a solution of **L2** (2.5 mM) in 0.1 M TBAP, DMF on glassy carbon at 1000 rpm rotation rate are given in Fig. 5 in parallel with the DPV curves.

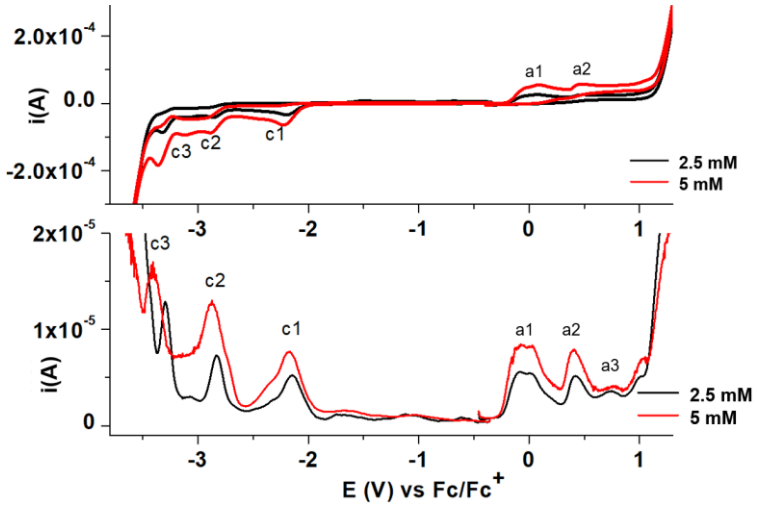


Fig. 4. CV (0.1 V/s, up) and DPV (down) curves obtained for different concentrations of **L2** on glassy carbon in 0.1 M TBAP, DMF; the DPV cathodic currents are in absolute values

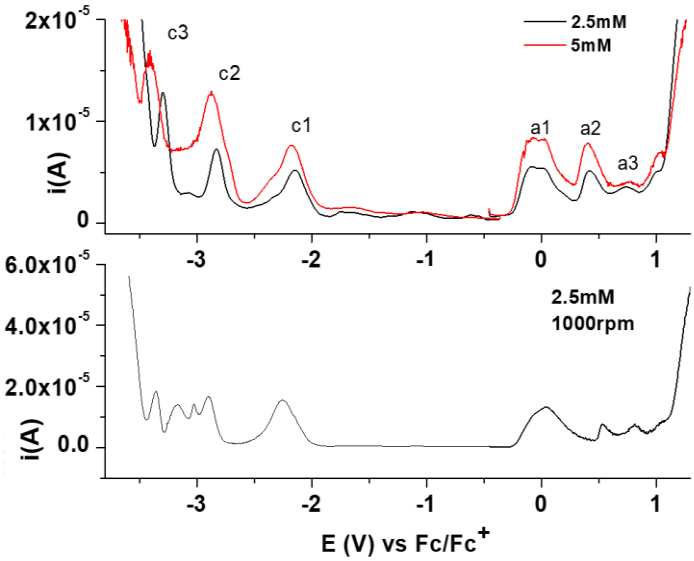


Fig. 5. DPV (up) and RDE (down) curves obtained in solutions of **L2** in 0.1M TBAP, DMF on glassy carbon at 1000 rpm of RDE; the RDE cathodic currents are in absolute values

Table 2

Potentials (V) of the DPV peaks for L2 *vs.* Fc/Fc$^+$

Peak	E_{DPV} (V)	Assessed process
c1	-2.153 (i)	Ph_3As^+-CH_2-$C_6H_4OCH_3$ + e^- = Ph_3As + ▪CH_2-$C_6H_4OCH_3$
c2	-2.830 (i)	Ph_3As + e^- = Ph_2As^- + Ph▪
c3	-3.297 (q)	▪CH_2-$C_6H_4OCH_3$ + e^- = $^-CH_2$-$C_6H_4OCH_3$
a1	-0.091 – 0.014 (i)	I^- - e^- = 1/2I_2
a2	0.425 (i)	I^- - 2e^- + H_2O = IO^- + 2H^+
a3	0.750 (i)	I^- - 6e^- + 3H_2O = IO_3^- + 6H^+

3.3. Study of (3-nitrobenzyl)triphenylarsonium iodide (L3)

The CV and DPV curves for compound **L3** are given in Fig. 5 for two concentrations (2.3 and 4.6 mM) of the studied compound. From the DPV curves 3 anodic (a1 – a3) and 5 cathodic (c1 – c5) processes, reversible (r), irreversible (i) or quasireversible (q), are noticed. Their DPV peak potentials are given in Table 3. Anodic and cathodic RDE curves obtained in a solution of **L3** (2.3 mM) in 0.1 M TBAP, DMF on glassy carbon at 1000 rpm rotation rate are given in Fig. 7 in parallel with the DPV curves.

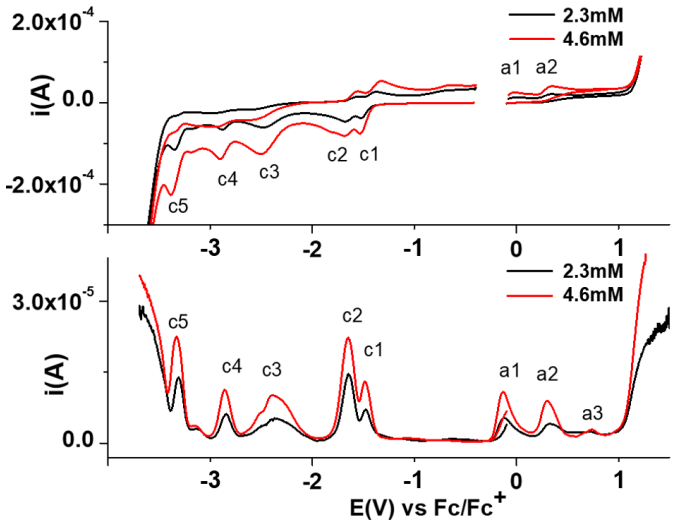


Fig. 6. CV (0.1 V/ s, up) and DPV (down) curves obtained for different concentrations of **L3** on glassy carbon in 0.1 M TBAP, DMF; the DPV cathodic currents are in absolute values

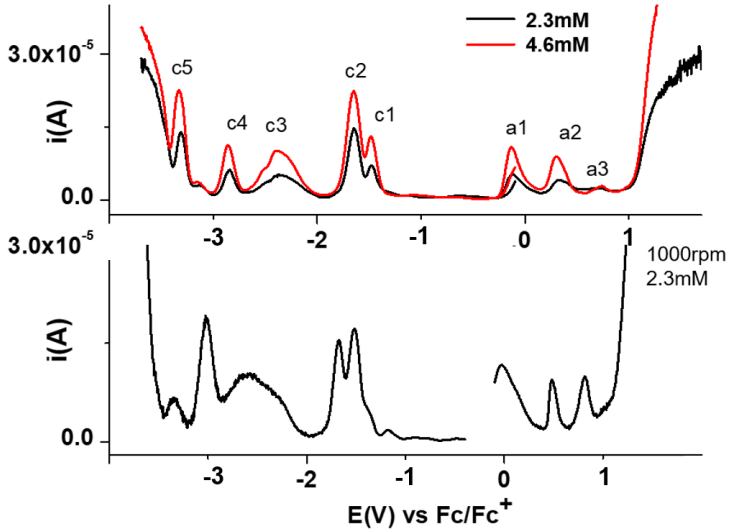


Fig. 7. DPV (up) and RDE (down) curves obtained in solutions of **L3** in 0.1M TBAP, DMF on glassy carbon at 1000 rpm rotation rate of RDE; the RDE cathodic currents are in absolute values

Table 3

Potentials (V) of the DPV peaks for L3 *vs.* Fc/Fc^+

Peak	E_{DPV} (V)	Assessed process
c1	-1.477 (r)	Ph_3As^+-CH_2-$C_6H_4NO_2$ + $4e^-$ + 4H+= Ph_3As^+-CH_2-C_6H_4NHOH + H_2O
c2	-1.624 (r)	Ph_3As^+-CH_2-C_6H_4NHOH +$2e^-$ + 2H+= Ph_3As^+-CH_2-$C_6H_4NH_2$ + H_2O
c3	-2.354 (i)	Ph_3As^+-CH_2-$C_6H_4NH_2$ + e^- = Ph_3As + ▪CH_2-$C_6H_4NH_2$
c4	-2.849 (i)	Ph_3As + e^- = Ph_2As^- + Ph▪
c5	-3.412 (q)	▪CH_2-$C_6H_4NH_2$ + e- = $^-CH_2$-$C_6H_4NH_2$
a1	-0.113 (i)	I^- - e^- = $1/2I_2$
a2	0.321 (i)	I^- - $2e^-$ + H_2O = IO^- + $2H^+$
a3	0.350 (i)	I^- - $6e^-$ + $3H_2O$ = IO_3^- + $6H^+$

3.4. Study of (3-methylbenzyl)triphenylarsonium iodide (L4)

The CV and DPV curves for compound **L4** are given in Fig. 8 for two concentrations (2.5 and 5 mM) of the studied compound. From the DPV curves 3 anodic (a1 – a3) and 3 cathodic (c1 – c3) processes, irreversible (i) or quasireversible (q), are noticed. Their DPV peak potentials are given in Table 4. Anodic and cathodic RDE curves obtained in a solution of **L4** (2.5 mM) in 0.1 M TBAP, DMF on glassy carbon at 1000 rpm rotation rate are given in Fig. 9 in parallel with the DPV curves.

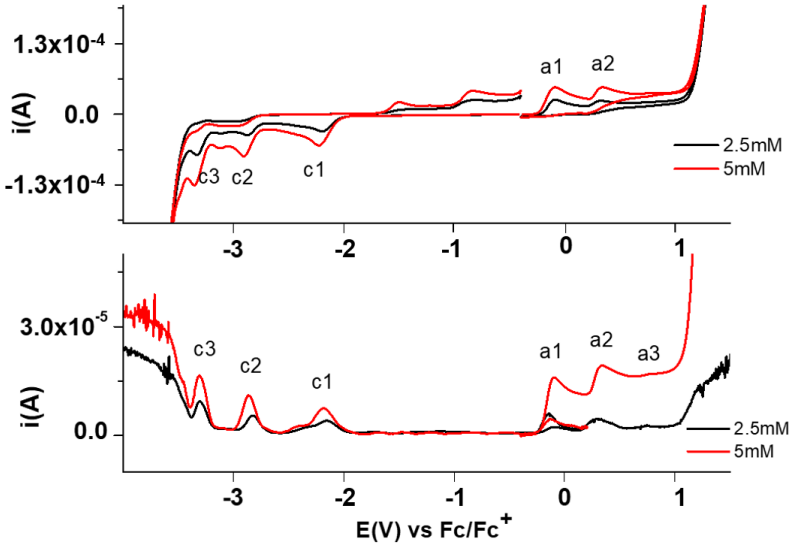


Fig. 8. CV (0.1 V/s, up) and DPV (down) curves obtained for different concentrations of **L4** on glassy carbon in 0.1 M TBAP, DMF; the DPV cathodic currents are in absolute values

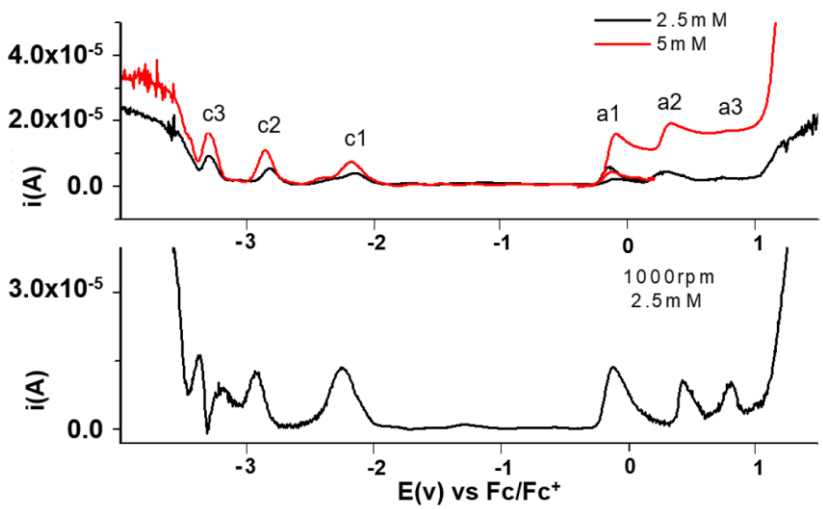


Fig. 9. DPV (up) and RDE (down) curves obtained in solutions of **L4** in 0.1M TBAP, DMF on glassy carbon at 1000 rpm rotation rate of RDE; the RDE cathodic currents are in absolute values

Table 4

Potentials (V) of the peaks and their assessment for L4 *vs.* Fc/Fc$^+$

Peak	E_{DPV} (V)	Assessed process
c1	-2.154 (i)	Ph_3As^+-CH_2-$C_6H_4CH_3$ + e^- = Ph_3As + ▪CH_2- $C_6H_4CH_3$
c2	-2.824 (i)	$Ph_3As + e^- = Ph_2As^- + Ph$▪
c3	-3.310 (q)	▪CH_2- $C_6H_4CH_3$ + e- = $^-CH_2$-$C_6H_4CH_3$
a1	-0.148 (i)	$I^- - e^- = 1/2I_2$
a2	0.296 (i)	$I^- - 2e^- + H_2O = IO^- + 2H^+$
a3	0.750 (i)	$I^- - 6e^- + 3H_2O = IO_3^- + 6H^+$

4. Discussions

The study of arsonium salts **L1 - L4** focused on electrochemical characterization by CV, DPV, and RDE voltammetry of new triphenylarsonium derivatives, containing a benzyl (X = H) or substituted (in position 3) benzyl ring (X = OCH_3, NO_2 and CH_3). The synthesis resulted in bromides and iodides; therefore, the comparison of the data was more difficult because of different anions of these arsonium salts.

From the examination of the curves obtained in Fig. 2 and Fig. 3 for **L1** it can be seen the irreversible (i) character of the processes c1 and c2, and the quasi-reversible (q) character of the process c3. The areas of peaks a1 and c1 are approximately equal, which is consistent with the number of electrons involved in the mechanism steps for these processes, described in the equations given in Table 1. The ratios of the other areas are consistent with the number of electrons in all mechanism stages described in Table 1. All RDE curves show maxima that

indicate that the reduction reactions take place with the decomposition of the molecules. The anodic curves are consistent with the bromine anion oxidation.

From the examination of the curves obtained in Fig. 4 and Fig. 5 for **L2** , and Fig. 8 and Fig 9 for **L4**, respectively, it can be seen similar character of the processes as those described for **L1**, and a similar mechanism was assumed and is given in Table 2 and Table 4, respectively. The anodic curves are consistent with the iodine anion oxidation.

From the examination of the curves obtained in Fig. 6 and Fig. 7 for **L3** it can be seen the reversible (r), irreversible (i) and the quasi-reversible (q) character of the processes c1 and c2, c3 and c4, and c5, respectively, as seen in Table 3. The anodic curves are consistent with the bromine anion oxidation. The peaks c1 and c2 were attributed to the 4 electrons nitro group reversible reduction which occurs before the arsonium salt discharge, while c3, c4 and c5 correspond to the arsonium reduction of the reduced **L3**, which occur at potentials in agreement with the potentials of the other substituted arsonium salts **L1**, **L2**, and **L4**. For all curves, the same pattern of the reduction curves can be seen.

The comparison of the studied arsonium derivatives in terms of reduction (c1) and oxidation (a1) potentials is given in Table 5.

Table 5

Potential (V) vs Fc/Fc+ for the first reduction (c1) and oxidation (a1) peaks of the benzyl triphenyl arsonium derivatives L1 - L4

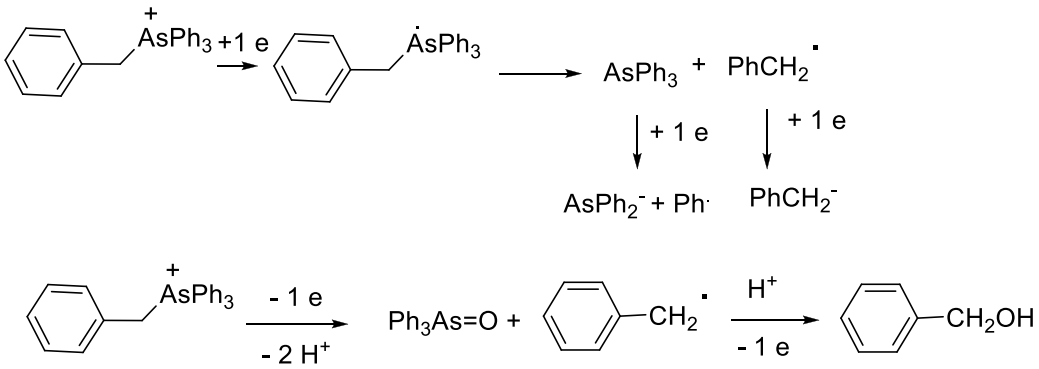
No.	**Derivative**	**L1**	**L2**	**L3**	**L4**
1	**Anion**	**Br^-**	**I^-**	**I^-**	**I^-**
2	**X**	H	OCH_3	NO_2 (NHOH)	CH_3
3	c1	-2.258	-2.153	-1.477(-2.343)	-2.154
4	a1	0.193	-0.091	-0.113	-0.148

The interest for the studied arsonium salts is especially connected to their reduction, as As is in the higher oxidation state. From this point of view the presence of the different anions does not bother, so the data from line 3 of Table 5 are relevant (with the potential values for peak c1 from Tables 1 - 4). It can be noticed that for NO_2-substituted derivative is most easily reduced, but the reduction leads to a hydroxyamino or amino groups (with a high repellent effect) which shifts the arsonium reduction to more negative potentials than for OCH_3 and CH_3 substituted arsonium salts. The reduction potential of the unsubstituted derivative **L1** (X = H) is not surprising either, because the correlations of the reduction potentials are conditioned not only by the effects of the substituents, but also, by the symmetry of the molecule, which is higher for **L1** than for **L2** and **L4**.

To evaluate their oxidation the potential values for the peak a1 should be seen (line 4, Table 5). The following comparisons can be done:

1. **L1** and **L4** should have the closest potentials. because the CH_3 group has only a weak inductive effect, so the order found is correct, because the Br^- anion is discharged at a more positive potential (0.193 V) than I^- (-0.148 V).
2. **L2**, **L3**, and **L4** should have closed potentials, because in all cases the same anion (I^-) is oxidized; indeed, it is observed that the values of the oxidation potentials do not differ much for the 3 compounds. Also, the DPV and RDE curves of the 3 compounds are very similar in the anodic domain.

All compounds follow reduction and oxidation schemes (Scheme 2) with decomposition of their molecules, which involves parallel reactions which complicate the analysis of the peaks making difficult to interpret and assign each peak. However, the presence of halide anions leading to the anodic processes shown in Tables 1 – 4 for a1- a3 peaks, agree with the redox potential of iodine and bromine at various valence states [15]. These peaks are not much influenced by the substituents on the benzyl ring. This result of their study in organic solvent (DMF) confirms other data obtained in aqueous solvents [9].



Scheme 2. Electrochemical reduction and oxidation processes of arsonium derivatives

4. Conclusions

Our study relates the electrochemical characterization by CV, DPV, and RDE voltammetry of new triphenylbenzylarsonium compounds. The study of arsonium salts containing a benzyl (X = H) or substituted (in position 3) benzyl ring (X = OCH_3, NO_2 and CH_3) allows the comparison of arsonium derivatives in terms of their reduction, leading to the see the small influence of the substituents on the arsonium discharge. Their electrochemical study is valuable for subsequent applications of arsonium salts.

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R E F E R E N C E S

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