

Spontaneous and Photoinduced Formation of Radical Anions in the Reaction of Borohydrides with Unsaturated Compounds

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The spontaneous and photoinduced reactions of tetrabutylammonium borohydride, Bu_4NBH_4 , with a number of quinones, ketones, cyano derivatives and nitrogen-containing heteroaromatic bases have been studied by means of EPR spectroscopy in benzene and in ethereal solvents. In the absence of UV irradiation, formation of radical anions resulting from electron transfer from the borohydride negative ion, BH_4^- , to the organic substrate has been detected with compounds having reduction potentials less negative than -1.5 V vs. SCE. With the less easily reducible compounds, UV irradiation leads in some cases to radical anions produced by photoinduced ET and in other cases to radical adducts of the borane radical anion, $\text{BH}_3^{\cdot-}$.

Borohydrides are among the most popular laboratory reducing agents, being extensively used in the reduction of a wide variety of compounds such as aldehydes, ketones, nitriles, α,β -enones, etc. These reactions are usually considered to proceed through a heterolytic pathway involving a formal hydride-ion transfer as one of the key steps.¹

Several examples of homolytic reactions of boranes have also been reported in the last few years by Roberts and coworkers and recently some synthetically useful procedures have been proposed.² In these reactions the radical species are either the borane radical anion, $\text{BH}_3^{\cdot-}$, or ligated boryl radicals, $\text{L}\rightarrow\text{BH}_2^{\cdot}$, where L can be a nitrogen, phosphorus, or sulfur ligand.^{3,4}

On the other hand it has also been shown that electron deficient compounds may react with borohydrides by a single electron transfer (SET) mechanism to give radical complexes easily detectable by EPR spectroscopy.⁵ In the course of our current studies on the radical reactivity of boranes we have found that some aromatic nitro compounds react spontaneously with tetrabutylammonium borohydride Bu_4NBH_4 , to afford the corresponding radical anions. Nitroalkanes, in contrast, do not afford paramagnetic species under the same conditions, while upon photolysis they are transformed into boroxo aminoxy radicals, $\text{RN}(\text{O}^{\cdot})\text{OBH}_3^-$. These species result from the attack on RNO_2 of the $\text{BH}_3^{\cdot-}$ radical produced from the borohydride via hydrogen abstraction by the excited nitro compound.⁶

In order to gain better insight of the processes involving borohydrides and leading to the formation of radical anions, we have undertaken an EPR study of the spontaneous and photoinduced reaction of Bu_4NBH_4 , which is soluble in organic solvents even of low polarity, such as benzene, with a variety of easily reducible compounds with reduction potentials (see Table 1) spanning the range from -2.0 to 0.3 V vs. SCE.

Results and Discussion

In the present study we have examined compounds belonging to four different chemical families, i.e., aromatic cyano derivatives, quinones, aryl- and diaryl-ketones and nitrogen-containing heteroaromatic bases. For the sake of simplicity each class of compound will be discussed separately.

Cyano Derivatives.—Mixing of Bu_4NBH_4 and 9,10-dicyanoanthracene (1), 1,2,4,5-tetracyanobenzene (2) and tetracy-

Table 1 Reduction potential measured in ACN or other polar solvents vs. SCE

Compounds	E_1/V^a	Ref.
Cyano derivatives		
9,10-Dicyanoanthracene	1 -0.89	7
1,2,4,5-Tetracyanobenzene	2 -0.71	8
Tetracyanoethylene	3 +0.24	9
1,4-Dicyanobenzene	4 -1.64	9
Quinones		
<i>p</i> -Benzoquinone	5 -0.51	10
2,6-Di- <i>tert</i> -butyl- <i>p</i> -benzoquinone	6 -0.71	11
Duroquinone	7 -0.84	12
1,4-Naphthoquinone	8 -0.56	13
9,10-Anthraquinone	9 -0.82	14
Phthalic anhydride	10 -1.31	8
Ketones		
Diphenyl ketone	11 -1.68	15
2,2'-Dithienyl ketone	12 -1.55	This work
2,2'-Dipyridyl ketone	13 -1.47	This work
Fluoren-9-one	14 -1.29	16
Xanthen-9-one	15 -1.73	This work
Thioxanthen-9-one	16 -1.67	This work
Methyl phenyl ketone	17 -1.85	17
Dibenzoyl	18 -0.85	18
Heteroaromatic bases		
Phenazine	19 -1.20	19
1,4,5,8-Tetraazaphthalene	20 -1.06	This work
Benzo[2,1,3]thiadiazole	21 -1.49	This work
Benzo[<i>c</i>]cinnoline	22 -1.50	This work
Pyrazine	23 -2.12	20

^a E_1 for the first reduction process, which is a one-electron diffusion-controlled reversible process. E_1 were obtained from cyclic voltammetry averaging the cathodic and anodic peak potentials.

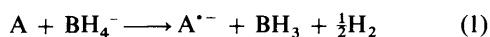
anoethylene (3), all having reduction potentials more positive than -1.0 V vs. SCE, in deoxygenated 1,2-dimethoxyethane (DME) or benzene solution resulted in the formation of the corresponding radical anions which were detected and identified by EPR spectroscopy. The lines of the spectra recorded in benzene are broader and show more pronounced asymmetric linewidth effects than in DME. We attribute this to

Table 2 EPR spectral parameters of the radical anions of compounds 1–3, 5–16, 18–20 and 22 measured in benzene solution

Compound	Coupling constants/G ^a	g-factor
1	$a(\text{H}^{1,4,5,8}) = a(\text{H}^{2,3,6,7})$ 1.27, $a(2\text{ N})$ 1.07	2.0028
2	$a(2\text{ H})$ 1.07, $a(4\text{ N})$ 1.14	2.0029
3	$a(4\text{ N})$ 1.57	2.0028
5	$a(4\text{ H})$ 2.43	2.0051
6	$a(2\text{ H})$ 1.65	2.0048
7	$a(12\text{ H})$ 1.93	2.0048
8	$a(\text{H}^{5,8})$ 0.30, $a(\text{H}^{6,7})$ 0.63, $a(\text{H}^{2,3})$ 3.30	2.0048
9	$a(\text{H}^{2,3,6,7})$ 0.30, $a(\text{H}^{1,4,5,8})$ 0.98	2.0045
10	$a(\text{H}^{4,7})$ 0.21, $a(\text{H}^{5,6})$ 2.56	2.0036
11	$a(4\text{ H}^m)$ 0.88, $a(4\text{ H}^o)$ 2.63, $a(2\text{ H}^p)$ 3.52	2.0037
12	$a(\text{H}^{4,4'})$ 0.97, $a(\text{H}^{5,5'})$ 3.80, $a(\text{H}^{3,3'})$ 4.29	2.0040
13	$a(\text{H}^{3,3'})$ 0.30 or 0.60, $a(\text{H}^{5,5'})$ 0.60 or 0.30, $a(\text{H}^{6,6'})$ 1.94, $a(\text{H}^{4,4'})$ 3.13, $a(2\text{ N})$ 1.80	2.0043
14	$a(\text{H}^{2,7})$ 0.15, $a(\text{H}^{4,5})$ 0.67, $a(\text{H}^{1,8})$ 2.12, $a(\text{H}^{3,6})$ 3.15	2.0037
15	$a(\text{H}^{4,5}) < 0.1$, $a(\text{H}^{2,7})$ 0.91, $a(\text{H}^{1,3,6,8})$ 3.87	2.0035
16	$a(\text{H}^{4,5})$ 0.38, $a(\text{H}^{2,7})$ 0.97, $a(\text{H}^{3,6})$ 3.37, $a(\text{H}^{1,8})$ 3.75	2.0038
18	$a(4\text{ H}^m)$ 0.35, $a(4\text{ H}^o)$ 1.01, $a(2\text{ H}^p)$ 1.11	2.0050
19	$a(8\text{ H})$ 1.67, $a(2\text{ N})$ 5.11	2.0034
20	$a(4\text{ H})$ 3.12, $a(4\text{ N})$ 3.38	2.0037
22	$a(\text{H}^{3,8})$ 0.28, $a(\text{H}^{1,10})$ 0.75, $a(\text{H}^{2,9})$ 2.82, $a(\text{H}^{4,7})$ 3.52, $a(2\text{ N})$ 5.37	2.0033

^a 1 G = 10⁻⁴ T.

the presence in solution of ion pairs made by the radical anion and the tetrabutylammonium counterion, since the polarity of benzene is not sufficient to cause the dissociation of the charged species. These very bulky ion pairs are expected not to tumble fast enough completely to average the anisotropy of the hyperfine and *g*-tensors, giving rise to the observed line-broadening effects. The EPR parameters measured in benzene are reported in Table 2. It is worth noting that these values are somewhat different from those reported in the literature and obtained in more polar solvents.²¹ The formation of the radical anions was accompanied by evolution of a gas which is believed to be hydrogen. These findings can be explained by an electron-transfer reaction [eqn. (1)] analogous to that already proposed for the reduction of nitroarenes with Bu₄NBH₄.⁶



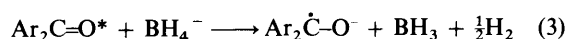
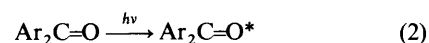
When reacting 1,4-dicyanobenzene (4, $E_{\frac{1}{2}} = -1.64$ V) with borohydride no EPR signals could be detected either in benzene or in ethereal solvents. Therefore, consistent with findings reported in our previous paper,⁶ electron transfer seems to take place spontaneously only when the reduction potential of the reducible substrate is more positive than *ca.* -1.0 V in benzene and *ca.* -1.5 V in ethers such as THF or DME.

Even photolysis did not lead to the appearance of a spectrum of the radical anion of 4. In this context it should be mentioned that the electron transfer can take place more easily under UV irradiation, since the electron affinity of the acceptor is increased or the ionization potential of the donor is decreased proportionally to the excitation energy.^{22,23} In the present case where the BH₄⁻ ion does not show absorption above 200 nm, photolysis should only affect the electron affinity of the organic substrate. It should, however, be noted that the photoexcited species are often characterized by lifetimes too short to allow their bimolecular reactions with other compounds.

Quinones and Quinonoid Compounds.—*para*-Benzoquinone (5), 2,6-di-*tert*-butyl-*p*-benzoquinone (6), duroquinone (7), 1,4-naphthoquinone (8), 9,10-anthraquinone (9), all having reduction potentials between -1.0 and -0.5 V, when reacted with Bu₄NBH₄ in deoxygenated benzene solutions immediately developed strong colours due to the formation of the corresponding radical anions which were detected and identified by EPR spectroscopy (see Table 2). Phthalic anhydride

(10), on the other hand, under similar conditions reacted with evolution of gas without spontaneously affording any EPR signals. The spectrum of the radical anion was instead obtained upon UV irradiation of the sample; this species was, however, short-lived and disappeared on removal of the light.

Ketones.—The behaviour of diaryl ketones when reacted with Bu₄NBH₄ was more complex than that exhibited by the above-mentioned compounds. Only dibenzoyl (18, $E_{\frac{1}{2}} = -0.85$ V) reacted instantaneously in deoxygenated benzene solution at room temperature giving rise to a strong spectrum of the radical anion, while di(2-pyridyl) ketone (13, $E_{\frac{1}{2}} = -1.47$ V) and fluorenone (14, $E_{\frac{1}{2}} = -1.29$ V) afforded the corresponding radical anions less readily. In fact fluorenone gave initially very weak signals the intensity of which increased with time, reaching a maximum *ca.* half an hour after mixing of the reactants. With 13, on the other hand, the spectrum of the radical anion could only be observed at higher temperature ($T \geq 50$ °C). These results can be explained in terms of a spontaneous electron transfer from the BH₄⁻ anion to the ketone taking place at a rate lower than that of compounds characterized by reduction potentials less negative than -1.0 V *vs.* SCE, and that can be accelerated by raising the temperature. In THF solution the process is easier and the spectrum of the fluorenone radical anion developed immediately after mixing, while that of di(2-pyridyl) ketone developed gradually with time even at room temperature. All other diaryl ketones having reduction potentials more negative than -1.5 V *vs.* SCE did not afford spectra of the radical anions either in benzene or in THF in the temperature range $25 \leq T \leq 60$ °C. Instead, EPR signals due to the corresponding radical anion were detected if the benzene or THF solution of the ketones 11, 12, 15, 16 and of the borohydride were irradiated with UV light. The formation of the radical anions of diaryl ketones during photolysis may, in principle, be explained in terms of photoinduced electron transfer [eqns. (2) and (3)]. Actually aromatic ketones are known



to have readily accessible triplet states the energy content of

Table 3 EPR spectral parameters of the radical adducts of $\text{BH}_3^{\cdot-}$ to ketones

Ketone	Coupling constants/G ^a	<i>g</i> -factor
11	$a(4 \text{ H}^m) 1.13, a(4 \text{ H}^o) 3.04, a(2 \text{ H}^p) 3.60, a(^{11}\text{B}) 3.60, a(\text{H}^{\text{BH}_3}) 0.88$	2.0031
12	$a(\text{H}^{4,4'}) 1.10, a(\text{H}^{5,5'}) 4.23, a(\text{H}^{3,3'}) 4.53, a(^{11}\text{B}) 3.54, a(\text{H}^{\text{BH}_3}) 0.67$	2.0041
15	$a(\text{H}^{4,5}) 0.48, a(\text{H}^{2,7}) 0.97, a(\text{H}^{3,6}) 3.75, a(\text{H}^{1,8}) 4.03, a(^{11}\text{B}) 4.23, a(\text{H}^{\text{BH}_3}) 0.61$	2.0033
16	$a(\text{H}^{4,5}) 0.13, a(\text{H}^{2,7}) 0.97, a(\text{H}^{3,6}) 3.48, a(\text{H}^{1,8}) 3.88, a(^{11}\text{B}) 5.42, a(\text{H}^{\text{BH}_3}) 0.30$	2.0037
17a	$a(3 \text{ H}^{\text{OMe}}) 0.42, a(2 \text{ H}^m) 1.47, a(2 \text{ H}^o) 4.41, a(3 \text{ H}^{\text{Me}}) 12.9, a(^{11}\text{B}) < 0.1, a(\text{H}^{\text{BH}_3}) 2.49$	2.0033

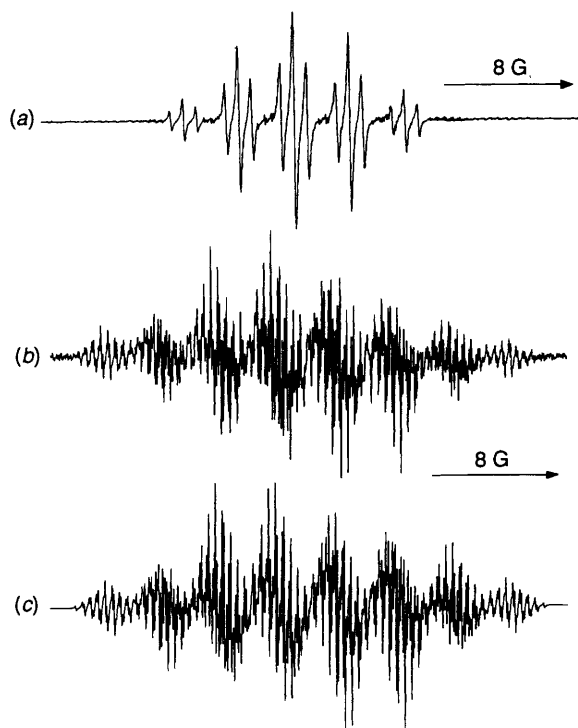
^a 1 G = 10⁻⁴ T.

Fig. 1(a) EPR spectrum of the radical anion of **15** generated by irradiating a benzene solution of the ketone and Bu_4NBH_4 ; (b) experimental and (c) simulated EPR spectra of the adduct of the borane radical anion, $\text{BH}_3^{\cdot-}$, to **15** obtained on photolysis of the same solution containing some di-*tert*-butyl peroxide

which is high enough with respect to that of the ground state, to make reaction (3) strongly exoergonic.²²

When using an aryl alkyl ketone such as 4-methoxyacetophenone (**17a**) we observed, upon photolysis, a very complex spectrum due to a radical species identified, on the basis of its spectral parameters, as the adduct to the carbonyl oxygen of the borane anion radical, $\text{BH}_3^{\cdot-}$.

Spectra of similar, hitherto undetected, radical adducts were also obtained with the diaryl ketones **11**, **12** and **15**, **16** when di-*tert*-butyl peroxide was added to the solution during photolysis (see Table 3). As an example Fig. 1(a) shows the EPR spectrum of the radical anion of xanthen-9-one (**15**) and Fig. 1(b) that of the corresponding $\text{BH}_3^{\cdot-}$ adduct.

These adducts are thought to be formed by reaction [eqn. (6)] with the ketone of $\text{BH}_3^{\cdot-}$ generated *via* hydrogen abstraction from BH_4^- , either by the photoexcited **17a** or by *tert*-butoxyl radicals derived from photolysis of the peroxide [eqns. (4)–(5)].

The photoinduced formation of the radical anions from **11**, **12**, **15**, **16** which has been explained in terms of reactions (2) and (3), might alternatively be due to ET [eqn. (7)] from the borane radical anion, $\text{BH}_3^{\cdot-}$, formed in reaction (5).

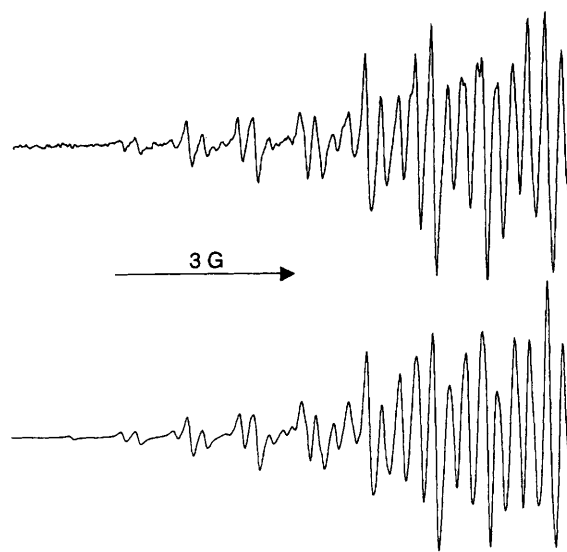
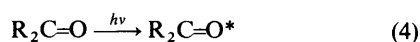
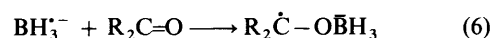
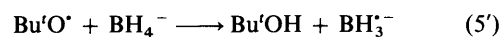
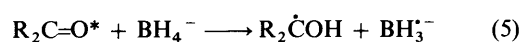
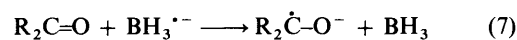


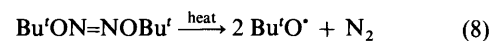
Fig. 2 Experimental and simulated initial low-field part of the spectrum of the $\text{BH}_3^{\cdot-}$ adduct to **11** in benzene solution containing some di-*tert*-butyl peroxide.



In order to check this possibility these ketones have been thermally reacted (*ca.* 50 °C) with the borohydride in benzene



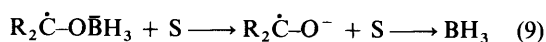
solution in the presence of *tert*-butyl hyponitrite. Above room temperature this thermolabile compound is a source of butoxyl radicals [eqn. (8)] which in turn may give rise to $\text{BH}_3^{\cdot-}$ in the dark.



In the absence of spontaneous reaction of all of the ketones with Bu_4NBH_4 , the EPR spectra of the $\text{BH}_3^{\cdot-}$ adducts were initially observed, however, the spectral patterns changed with time owing to the appearance of signals due to the radical anions. This behaviour indicates that addition prevails over electron transfer (7).

The slow growth of the radical anion seems to be due to the reaction [eqn. (9)] of the adduct with some species (S) the formation of which is concurrent with that of the adduct itself. We believe that this species is *tert*-butyl alcohol originating when the butoxyl radical abstracts hydrogen from BH_4^- .

In fact if a drop of *tert*-butyl alcohol is added to the sample under examination, the EPR spectrum of the adduct is immediately replaced by that of the radical anion.



With 4-methoxyacetophenone (**17a**) addition of *tert*-butyl alcohol to the solution led to the disappearance of the spectrum of the BH_3^- adduct without the concomitant appearance of the spectrum of the radical anion. This is presumably due to the short lifetime of the latter radical which does not accumulate in solution as does the analogous species derived from diaryl ketones.

With THF instead of benzene as the solvent, photolysis of mixtures of the ketones **11**, **12**, **15**, **16** and Bu_4NBH_4 , either in the presence or in the absence of di-*tert*-butyl peroxide, afforded only the spectra of the corresponding radical anions, while the thermal reaction in the presence of *tert*-butyl hyponitrite did not lead to the appearance of any EPR signals. In the former case, the radical anions are formed *via* photoinduced electron transfer, whereas in the latter the butoxyl radicals are possibly intercepted by solvent molecules and do not undergo hydrogen abstraction from BH_4^- .

Heteroaromatic Bases.—Nitrogen-containing heteroaromatic bases having relatively high reduction potentials also react spontaneously with Bu_4NBH_4 in benzene or THF to give the corresponding radical anions. This is the case with phenazine (**19**, $E_1 = -1.20$ V) and tetraazanaphthalene (**20**, $E_1 = -1.06$ V), but not with benzo[*c*]cinnoline (**22**, $E_1 = -1.50$ V), benzo[2,1,3]thiadiazole (**21**, $E_1 = -1.49$ V) and pyrazine (**23**, $E_1 = -2.12$). The EPR spectra of the anion of **19** after some time started to show the presence of additional lines due to a second species which, however, did not completely replace that initially observed. This second species showed a spectrum much wider than that of the radical anion, as would be expected for a complex between the heteroaromatic base and borane, BH_3 . As already mentioned compounds **21**–**23** did not afford the radical anions when reacted with borohydride; however, intense EPR signals were detected upon irradiation with UV light. In the case of benzo[*c*]cinnoline the spectrum was that of the corresponding radical anion, while **21** and **23** afforded very wide and complex spectra which have not yet been fully interpreted. There is, however, little doubt that they are due to paramagnetic species where the nitrogen atoms ligate one or two borane units. Further studies are underway unambiguously to identify these species and to elucidate their mechanism of formation.

Conclusions

The reaction of tetrabutylammonium borohydride with a number of compounds characterized by reduction potentials ranging from *ca.* -2 to $+0.25$ V with respect to the saturated calomel electrode (SCE) has been investigated both in benzene and tetrahydrofuran or dimethoxyethane.

Our results indicate that the reduction potential of the organic compounds above which spontaneous electron transfer (ET) from the BH_4^- anion takes place, is close to -1.5 V in THF or DME and slightly less negative in benzene solution. Actually spontaneous formation of radical anions has been observed only with substrates having reduction potentials above this limit. With less easily reducible compounds, electron transfer is sometimes induced photochemically, while in other cases, the photoexcited derivatives react by abstracting a hydrogen atom from the borohydride. The resulting borane radical anion may then undergo addition to an unexcited molecule affording easily detectable radical adducts.

Experimental

1,4,5,8-Tetraazanaphthalene²⁴ and *tert*-butyl hyponitrite²⁵ were prepared as described in the literature. All other compounds were commercially available and were used after standard purification procedures.

EPR Spectra.—The EPR spectra were recorded on a Bruker ESP 300 spectrometer equipped with an NMR gaussmeter for field calibration and a Hewlett Packard 5350B microwave frequency counter for the determination of the *g*-factors, which were corrected with respect to that of perylene radical cation in concentrated H_2SO_4 ($g = 2.0025_8$). Photolysis was carried out by focusing the light from a 500 W high-pressure mercury lamp on the EPR cavity. Digitized EPR spectra were transferred to an AT-486 (33 MHz) personal computer, in order to analyse complex spectra by means of autocorrelation²⁶ or cepstral²⁷ techniques.

A typical sample consisted of a deoxygenated benzene, THF or DME solution of the unsaturated compound (*ca.* 0.1 mol dm^{-3}) containing Bu_4NBH_4 (*ca.* 0.4 mol dm^{-3}) and, when necessary, some di-*tert*-butyl peroxide or *tert*-butyl hyponitrite. In order to achieve optimum resolution, the concentration of the radicals had sometimes to be lowered by dilution.

Electrochemistry.—Electrochemical measurements were made in acetonitrile (ACN, Merck Uvasol reagent grade), used as received, with 0.1 mol dm^{-3} $(C_2H_5)_4NBF_4$ as the supporting electrolyte. Experiments were performed at 25 ± 0.1 °C, by using a conventional three-electrode cell. Platinum was used as working and counter-electrode. A saturated calomel electrode (SCE), separated from the test solution by 0.1 mol dm^{-3} $(C_2H_5)_4NBF_4$ solution in ACN sandwiched between fritted disks, was used as reference electrode for all potentials.

Cyclic voltammetric measurements were carried out, at a scan rate of 0.4 V s^{-1} , with an AMEL 552 potentiostat, a 568 programmable function generator, a 731 integrator, a 836 *x/y* recorder and a Nicolet 3091 digital oscilloscope. The minimization of the effect of uncompensated resistance was achieved with a positive feedback network of the potentiostat.

Acknowledgements

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