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Mechanistic Studies on the Electrochemical Reductive Coupling of some Polyhalogenonitrobenzenes. A New Example of a Radical Anion Dimerization

Claude P. Andrieux[a],* Anna Batlle, Martirio Espín, Iluminada Gallardo,* Ziqi Jiang and Jorge Marquet*

Departament de Química. Universitat Autònoma de Barcelona. 08193 Bellaterra. Barcelona. Spain.

[a] Laboratoire d'Electrochimie Moleculaire. Université Paris 7. 2 place Jussieu. 75251 Paris Cedex 05. France

Abstract: Coupling processes with loss of one halogen atom per ring are observed when heavily substituted polyhalogenonitrobenzenes (polyfluoro- and polychloro-) are electrochemically reduced in DMF. Product analyses and cyclic voltametry mechanistic studies suggest that in the particular case of pentafluoronitrobenzene, direct dimerization of the radical anions occurs prior to C-F bond fragmentation. On the contrary, reduction of the nitro group is the only observed process when less substituted polyhalogenonitrobenzenes are used in the same conditions. Nitro group reduction is also the main process for all the studied polyhalogenonitrobenzenes when the reactions are carried out in protic solvents.

INTRODUCTION

The frequently reported way in which halogenated aromatic radical anions evolve is the unimolecular fragmentation of the carbon-halogen bond to give an aryl radical and the halide ions. Several electrochemical studies on relatively long-lived radical anions such as halogenonitrobenzenes[1] and halogenobenzonitriles[2] have clearly established that the identity of the halogen and the other substituents in the phenyl ring have a marked influence on the rate of this process. As expected on the basis of the C-X bond energies, the order of the halogen mobility is F<Cl<Br<I. Dimerization prior to C-F bond fragmentation has been postulated[3] in some examples with fluorine susbtituted relatively stable radical anions (fluorobenzonitrile[3a] and pentafluoropyridine[3b] radical anions).

In aprotic solvents the electrochemical reduction of nitrobenzene is a classical example of the initial formation of a stable anion radical[4]. At all sweep rates that can be used in linear sweep voltammetry, between 0.05 and 100 $V.s^{-1}$, the first reduction wave appears as chemically reversible. This first one electron wave at -1.06 V vs SCE in DMF, is followed by a broad two electron wave where the reduction of the initial product leads to the radical anion of the corresponding nitroso-compound characterized by its oxidation peak during the reverse anodic sweep at -0.80 V vs SCE at 0.1 $V.s^{-1}$. This behavior is quite similar in water-methanol mixture (1:5) in neutral medium, but the difference between the first and the second waves is strongly reduced.

The monosubstitution on the benzene ring of nitrobenzene by different halogens does not modify the reduction scheme[1], with the exception of iodine. In this case the lifetime of the radical anion is only 1.5 s in acetonitrile, leading in the first electron process to the cleavage of the carbon-iodine bond[1].

It should be noticed that in the cases where the first radical anion show a good stability (for example 4-fluoronitro-benzene), the second step of the electrochemical reduction leads also to a nitroso compound as visualized by the anodic peak obtained at more positive potential than the oxidation peak of the radical anion.

Very few reports exist on the reductive electrochemical behavior of polyfluoronitrobenzenes. The appearance of a peculiar behavior upon increasing the number of fluorine substituents on the nitrobenzene system, could be expected on the basis of some literature reports[5,6]. Thus, the production of a dimeric compound with loss of the fluorine atoms in para position by electrochemical reduction of pentafluoronitrobenzene (PFNB) in acetonitrile was recently described[7] (without experimental details neither mechanistic interpretations). In addition, some of us have recently reported that PFNB undergoes electrochemically catalysed $S_{RN}2$ reactions in front of a variety of nucleophiles[8]. All this considered, we decided to carry out a systematic study on the electrochemical behavior of polyfluoronitroaromatic compounds and some related polychloroderivatives.

RESULTS AND DISCUSSION

Electrochemical reduction of difluoronitrobenzenes

The introduction of a second fluorine on the benzene ring does not modify the behavior described for 4-fluoronitrobenzene[1]. Thus, a small positive shift of the standard potential E^o of the couple substrate/radical anion is observed in DMF when comparing 3,5-difluoronitrobenzene (-0.80 V vs SCE) with 3-fluoronitro-benzene (-0.91 V vs SCE) being those radical anions stable whatever the sweep rate used. On the other hand, formation of species attributed to the nitroso-compound radical anion in the second reduction step is always observed in DMF as in methanol-water mixture (Fig.1 (a) and (b)).
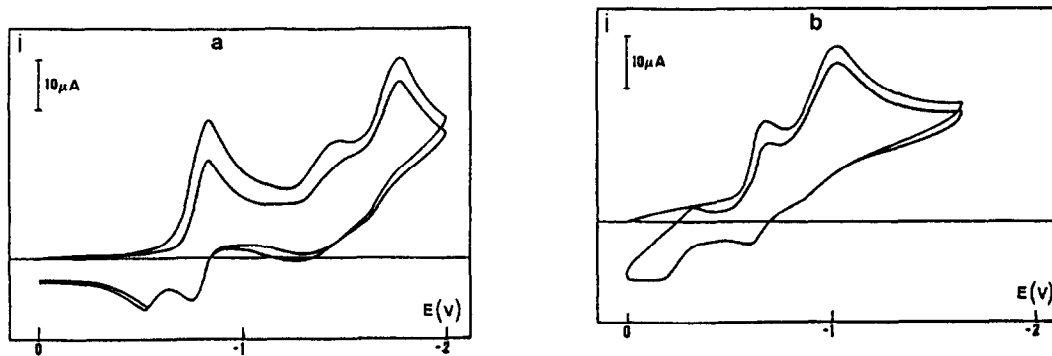

Fig.1.-   Voltammetry of 3,5-difluoronitrobenzene 2.0 mM in DMF (a) and in water-methanol mixture (b). 0.1 V.s^{-1}. Glassy carbon electrode.

The same behavior is obtained with 3,4-difluoronitrobenzene with standard potential E^o=-0.91 V vs SCE.

Electrochemical reduction of pentafluorobenzene (PFNB)

In DMF, this fully fluoro-substituted compound shows a completely different behaviour. The first step remains a chemically reversible one electron process only if the sweep rate is increased up to 10 V.s^{-1}. At lower sweep rates the number of electrons involved in the reduction increases and a new anodic wave, only 150 mV more positive that the preceding one, appears as this latter one decreases (Fig.2).
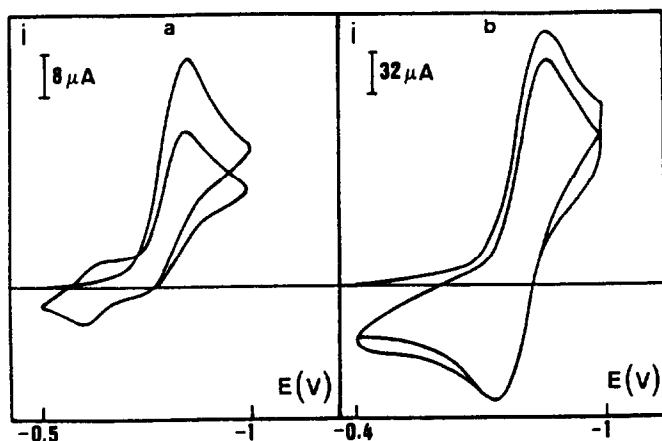

Fig.2.-   Voltammetry of pentafluoronitrobenzene (PFNB) 1.48 mM in DMF
at 0.1 V.s^{-1} (a) and 10 V.s^{-1} (b). Glassy carbon electrode.

It must be emphazised that this new reversible wave is obtained at the level of the first reduction process, not observing the nitroso couple obtained with less substituted nitrocompounds. Moreover, in experiments at high sweep rate (where a stable radical anion is obtained) and using a large sweep (down to -2 V vs SCE in DMF) in order to observe the second reduction, no formation of nitroso-compound is detected (we have verified on mono- and difluoro-compounds that at a sweep rate as 10 V-s^{-1} the nitroso-compound is always formed and observable by its oxido-reduction peaks).

The formation of the dimer (I), scheme 1, with loss of the para fluorine atom, on the substrate, at the level the first reduction step as described by Selivanova et al.[7] is confirmed by the following experiments.

a) The electrochemical study of the chemically prepared dimer[9] leads to a single two electron reversible reduction wave at the same potential that the new reversible wave observed at low sweep rate by reduction of the pentafluoronitrobenzene (Ep= -0.60 V and -0.66 V for anodic and cathodic peak potential). The less

difficult reduction of the dimer as compared to the initial substrate explains the increase of the electron number until 2 for the reduction at very low sweep rate. On the other hand, the fact of obtaining only one two electron wave for a dinitrodiphenyl compound while the dinitrobenzene itself gives two one electron waves is in agreement with the same observation for non fluoro-compounds[10].

b) PFNB electrolysis at -1.0 V vs SCE clearly indicates that in the beginning of the reduction a two electron process is involved. A chromatographic analysis of the solution, and comparison with an authentical sample obtained by an alternative procedure[9], shows that the main reaction product is (I). Upon longer electrolysis, the dianion of (I) leads to further reduced dimeric compounds (II) and (III), scheme 1.
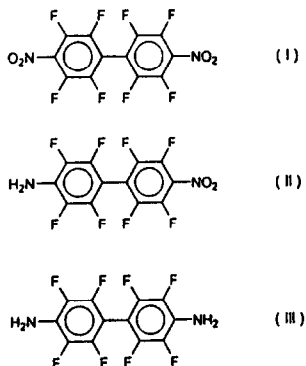
Scheme 1

That a second order kinetic process is involved after the first electron exchange is indicated by the concentration effect on the reaction kinetics (Fig. 3) and by the slope of -23 mV for the variation of the peak potential as a function of a decade of sweep rate, very near to the theoretical value -20 mV[11].
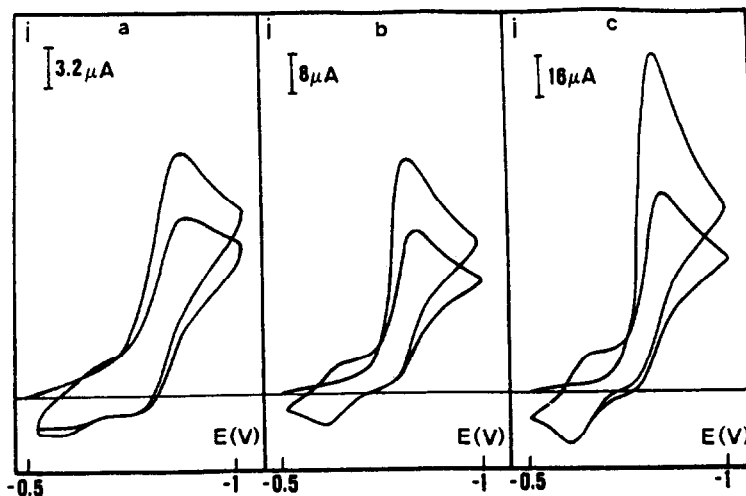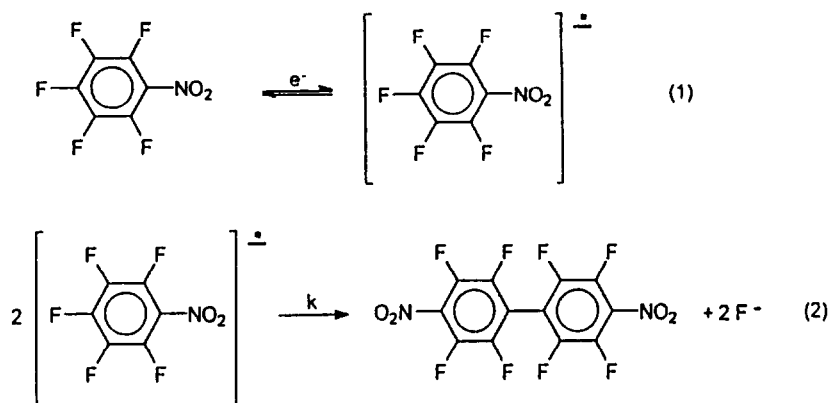

Fig.3.-   Concentration effect on the formation of octafluoro, 4-4'-dinitrobiphenyl in DMF
(a) 0.74 mM, (b) 1.48 mM, (c) 4.44 mM.

These two observations rule out the possibility of a cleavage of the fluorine-carbon bond in a step preceding dimerization. A mechanistic proposal in agreement with all the experimental facts is described in scheme 2.

Scheme 2

The dimerization rate constant is found to be $(3.8 \pm 0.8) \times 10^5 \ M^{-1} \ s^{-1}$, measured according to ref.11 for a radical-radical coupling.

In water-methanol mixture the observed behaviour is absolutely different. The radical anion appears as more stable and whatever the used sweep rate the first reduction wave appears as chemically reversible. Moreover, the second reduction step leads as for less substituted compounds to the characteristic wave of the nitroso-compounds. The comparison of the results in DMF and in water-methanol mixture seems to indicate a change in the electronic density distribution in the radical anion of the pentafluoronitrobenzene depending on the used medium. Due to the strong solvation effect of the methanol-water solvent over the nitro-group, the para position would be much less reactive. On the other hand, in an aprotic medium as DMF, dimerization would be possible due to the strong electron withdrawing effect of the five fluoro substituents.

Electrochemical reduction of other polyhalogenonitrobenzenes

Next we decided to compare the behavior of pentafluoronitrobenzene (PFNB) and pentachloronitrobenzene (PClNB). Interesting differences in behavior are observed in DMF. These differences are not important at the level of the first radical anion life-time (a change in the behavior is always obtained around 10 $V.s^{-1}$) but a different mechanism seems to be involved in the evolution of pentachloronitrobenzene radical anion. The kinetics of the reaction do not show any substrate concentration effect and the variations of the peak potential, about -30 mV by decade of sweep rate, indicate a first order chemical reaction after the initial transfer, which could be assigned to the cleavage of one carbon-chlorine bond. This result is supported by the analysis (HPLC-MS) of the electrolysis products. Besides an octachlorodinitrobiphenyl, a tetrachloro-nitrobenzene is also obtained as a minor product. Thus, our results strongly suggest that cleavage of the chlorine-carbon bond occurs before dimerization or further reduction. A similar mechanistic change has been

proposed in the literature[3b] to explain the observed differences between the electrochemical reduction of pentafluoro and pentachloropyridine.

This interesting different behavior between PFNB and PClNB led us to study 2,3,4,5-tetrafluoronitrobenzene. This compound shows a similar behavior. The first radical anion is stable, being so even at a sweep rate of 1 V.s^{-1}, preventing any kinetic determinations. Yet, by electrolysis in DMF medium, a dimeric compound resulting from loss of one halogen atom is obtained (GC-MS analysis of the reaction crudes), formation of nitroso derivative at the level of the second reduction step not being observed. The presence of four fluorine atoms on the benzene ring seems sufficient for the observed lacking of second reduction process on the nitrogroup in DMF. This hypothesis is confirmed by the study of the reduction of the two following sustrates: 4-methoxy-2,3,5,6-tetrafluoronitrobenzene and 4-phenoxy-2,3,5,6-tetrafluoronitrobenzene. These two compound lead to stable radical anions in the first reduction step and to no nitroso-compound in the second one. For the first of them, the electrolysis at -2 V vs SCE clearly shows (analysis of the reaction crudes by GC-MS) the formation of dimeric products with only three fluorine atoms per ring.

In water-methanol as a solvent, stable radical anions are observed in the first reduction for all the studied compounds, while formation of the radical anions of the corresponding nitroso-compounds occurs at the level of the second step of reduction.

CONCLUSIONS

The studied polyhalogenonitrobenzenes present in water-methanol mixture a very similar behavior to nitrobenzene itself and characteristic of the reduction of the nitro-group. The first wave remains chemically reversible whatever the sweep rate used and at the level of the second step the radical anion of the corresponding nitroso compound is formed.

In an aprotic medium as DMF a strong difference is observed between the less substituted compounds (mono and difluoronitrobenzenes) on one hand, and the more heavily substituted ones (penta and tetrahalogenonitrobenzenes) on the other hand. In the first cases, similar results to the described ones in protic medium are obtained. On the contrary, coupling processes with loss of one halogen atom by ring is observed in the more substituted cases. Kinetic results indicate that for PFNB dimerization preceeds the loss of fluorine atoms, and therefore, coupling of the radical anions is postulated. On the contrary PClNB leads to the corresponding dimer with previous breaking of the C-Cl bond at the same reduction level.

This behaviour seems to be related to the observed absence of the second nitro group reduction (no production of nitroso derivative) in the cases where dimerization is observed.

EXPERIMENTAL

Electrochemical measurements

The electrochemical cell and measurement procedures for CV have been described previously[12]. All potentials are reported *vs.* an aqueous saturated calomel electrode and glassy carbon is used as working electrode.

Electrolysis reactions were carried out by using a P.A.R. 273A potentiostat.

<u>Materials</u>

DMF (Fluka p.a.) and BF_4NBu_4 (Fluka puriss.) were used without purification.

4-fluoronitrobenzene (Aldrich), 3,5-difluoronitrobenzene (Aldrich), 3,4-difluoronitrobenzene (Aldrich), 2,3,4,5-tetra-fluorobenzene (Aldrich) and pentafluoronitrobenzene (Aldrich) were available commercially and were used without purification.

4-Methoxytetrafluoronitrobenzene was prepared following the method reported by Tatlow[13].

4-Phenoxytetrafluoronitrobenzene. A mixure of PFNB (0.639 g, 3.0 mmol), phenol (0.283 g, 3.0 mmol) and potassium carbonate (0.415 g, 3.0 mmol) was dissolved in a mixture of 50 ml of acetonitrile and 10 ml of water and kept at room temperature for 20 minutes. After that, the solvent was partially evaporated, and the aqueous solution was extracted with chloroform. The organic layer was dried and evaporated an the residue was chromatographed through silica-gel using hexane-$CHCl_3$ (10:1) as eluent. 4-phenoxytetrafluoronitrobenzene was obtained as an oil in 72% yield (0.623 g). IR (film) 3065, 1638, 1595, 1560, 1490, 1349, 1293, 1202, 1166, 1110, 1012, 773, 688 cm^{-1}; ^{1}HNMR (CDCl3): δ7.36-7.39 (2H), 7.25-7.18 (1H), 7.00-7.02 (2H); ^{13}CNMR (CDCl3): δ156.37, (142.72, 140.13) (J_{C-F}=259 Hz), (140.39, 137.80) (J_{C-F}=259 Hz), 139.95, 130.04, 124.81, 115.99; MS m/e (relative intensity) 287 (M$^+$, 99), 241 (9), 213 (13), 193 (20), 163 (3), 151 (1), 117 (2), 77 (100), 51 (31); Calcd.for $C_{12}H_5F_4NO_3$: C, 50.17; H, 1.76; N, 4.88; Found: C, 50.29; H, 1.79; N, 4.84.

4'4-Dinitrooctafluorobifenil, m.p. 83-84°C (Lit[2] 83-84.5°C) was obtained by oxidation of 4,4'diaminooctafluorobifenil (commercial sample) with pertrifluoroacetic acid, following the standard[14] procedure.

Electrolysis of Pentafluoronitrobenzene.- A solution of pentafluoronitrobenzene (500 mg, 4.70 mmol) in 150 ml of acetonitrile (0.1 M Et_4NBF_4 as supporting electrolite) was electrolysed using -1.00 V as applied potential with glassy carbon as electrode and under inert (N_2) atmosphere. After 59 coulombs (0.13 eq.) were consumed, the reaction was stopped. The solvent was evaporated affording a residue that was analyzed by gas-chromatography. The analysis showed the presence of traces of 4,4'-dinitrooctafluorobiphenyl (comparison with an authentical sample) but the very low conversion prevented any isolation attempt.

The electrolysis was repeated stopping the reaction after consuption of 227 coulombs (0.5 eq.). In this case, after following the same working up, the gas-chromatography analisis indicated mainly the presence of 4,4'-dinitrooctafluorobiphenyl (minor) and another product (major). The residue was chromatographed through silica-gel using hexane/$CHCl_3$) (2:1) as eluent, isolating 4-Amino-4'-nitrooctafluorobiphenyl in 11% yield (45 mg), mp 151.5-153.5 IR (KBr) 3536, 3431, 1672, 1602, 1553, 1511, 1483, 1356, 1265,1145, 1103, 1005, 943, 723 cm^{-1}; ^{1}HNMR (CDCl$_3$) δ 4.34 (d, 2H); MS, m/e (relative intensity) 358 (M$^+$, 100), 312 (92), 292 (73), 265 (79), 223 (13), 192 (10), 165 (14), 117 (15), 93 (14), 46 (12).

When the experiment was repeated stopping the reaction after consumption of 454 couloms (1 eq.), the gas-chromatography analysis indicated that main product was 4'4-diaminoocta-fluorobiphenyl (comparison with a commercial sample), 4'4-dinitrooctafluorobiphenyl not being present in the sample.

Electrolysis of Pentachloronitrobenzene (-1.2 V, coulomb consumption 1 eq.), Tetrafluoronitrobenzene

(-1.0 V, 1 eq.), 4-Metoxytetrafluoronitrobenzene (-2.0 V, 2 eq.). The same procedure just described was followed in all the cases, with the indicated applied potential and coulombs consumption. After working up, the samples were directly analysed by HPLC / MS (case pentachloronitrobenzene) or GC / MS (cases tetrafluoronitrobenzene and 4-methoxytetrafluoronitrobenzene). The detected products in each case were the following:

Pentachloronitrobenzene electrolysis: Starting material, one tetrachloronitrobenzene (MS, m/e 261, 259, 215, 203), and one aminonitrooctachlorobiphenyl (MS, m/e 486, 256, 229).

Tetrafluoronitrobenzene electrolysis. Starting material and one aminonitrohexafluorobiphenyl (MS, m/e 322, 276, 256, 229).

4-Methoxytetrafluoronitrobenzene electrolysis. Starting material and one aminonitrodimethoxyhexafluoronitrobenzene (MS, m/e, 382, 318, 303, 275).

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