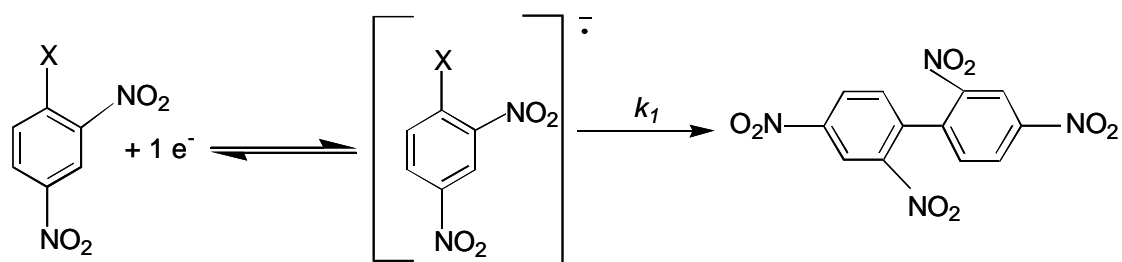

FULL PAPER

Mechanistic studies on the reactivity of halodinitrobenzene radical-anion

Illuminada Gallardo*, Gonzalo Guirado, & Jordi Marquet

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Iluminada Gallardo *, Gonzalo Guirado, Jordi Marquet

Departament de Química, Universitat Autònoma de Barcelona, E-08193 Bellaterra, Barcelona, Spain

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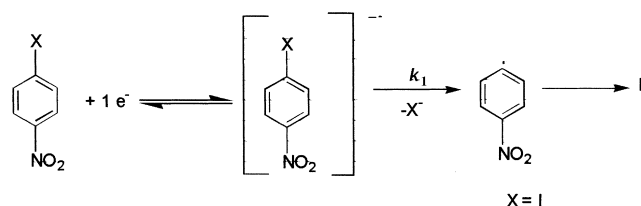
Abstract

The electrochemical behaviour of 1-F-2,4-dinitrobenzene, 1-Cl-2,4-dinitrobenzene and 1-Br-2,4-dinitrobenzene in DMF is described. The 1-F-2,4-dinitrobenzene radical anion dimerises *before* cleaving, whereas 1-Cl-2,4-dinitrobenzene and 1-Br-2,4-dinitrobenzene radical anions dimerise *after* cleavage. This change mechanism allows the obtention of 2,2',4,4'-tetranitrobiphenyl in a selective way, and with good efficiency. The electrochemical oxidation of σ -complexes is shown to be an alternative means of obtaining products that are difficult to obtain through traditional procedures. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Halodinitrobenzenes; Reduction; Mechanism; Electrochemistry; 2,2',4,4'-Tetranitrobiphenyl

1. Introduction

Unimolecular fragmentation of radical ions to yield radical and ions constitute key elementary steps in many electron transfer initiated processes [1,2]. It has been suggested [3] that reduction of certain unsaturated and aromatic halides involves initial addition of the electron to the π system, followed by cleavage of the σ bond to halogen. Several authors [4–6] have proposed that cleavage of C–X bonds in halogeno-aromatic radical anions may be seen as the result of electron transfer from the π^* radical anion to the σ^* by an orbital crossing. Therefore the complete process would consist of the addition of an electron to an electrophore of a complex molecule, followed by intra-molecular electron transfer, and the subsequent reaction of another part of the molecule. This behaviour has been recognised for a number of years as being characteristic of the halonitrobenzenes, for example, for the 4-nitrocompounds in acetonitrile [7–10]:



Cyclic voltammetric experiments have demonstrated that: (a) the nitroaromatic electrophore is undoubtedly the initial electron acceptor; (b) the carbon–halogen bond cleavage represented by k_1 formally represents a transference of the added electron from the π system to the orthogonal σ system; and (c) the decomposition rate k_1 depends on X, the order of the halogen mobility being $F < Cl < Br < I$ [11]. It is known from ESR experiments, that there is some coupling between the two systems [12–14], and this coupling presumably provides the mechanism by which bond cleavage takes place. The nitro group acts as an intramolecular catalyst for the removal of the halogen atom. Other examples of this behaviour have been recognised in the electrochemical reduction of bromotriphenylethylene [15], haloanthracenes [16], nitrobenzyl halides [17,18], halobenzophenones [19] and halobenzonitriles [20].

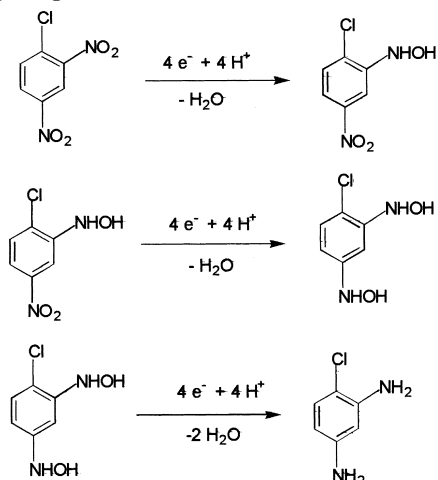
On the other hand, dimerisation of radical anions prior to C–F bond fragmentation has been postulated in some examples with relatively stable fluorine-substi-

* Corresponding author. Tel.: +34-93-5811927; fax: +34-93-5812920.

E-mail address: igg@klington.uab.es (I. Gallardo).

tuted radical anions: fluorobenzonitrile [21], pentafluoropyridine [22] and pentafluoronitrobenzene [23].

The reduction of dinitrobenzenes involves two separate one-electron processes [24]: radical anion and dianion are stable (in the cyclic voltammetry experiments) and a third reduction wave is responsible for the nitroso group formation. The only bibliographical reference [25] on the electrochemical reduction of 1-halo-2,4-dinitrobenzenes, deals with the reduction in acid solution at room temperature for unsymmetrically substituted 1,3-dinitrobenzenes (1-X-2,4-dinitrobenzenes) the first reduction occurring at the 2-nitro group (X = Cl, Br, I). In 1-Cl-2,4-dinitrobenzene, the inductive effect from the chlorine on the 2-nitro group is probably responsible for this easier reduction:



It is interesting to emphasise that under these conditions no bond cleavage seems to take place.

In this article we intend to address a number of questions concerning the electrochemical behaviour of 1-halo-2,4-dinitrobenzenes in aprotic solvents, specially in which order and at which reduction level the follow-

ing events happen for the different substrates: nitro group reduction, carbon-halogen bond cleavage, and radical anion dimerisation.

In addition, and in a synthetic context, the dimerisation of radical anions previous to carbon-halogen bond breaking in these substrates can be very significant since the Ullmann method [26], the classical synthesis of biphenyls, has not been described for 2,2',4,4'-tetranitrobiphenyl that is obtained alternatively by nitration of biphenyl [27].

Thus, the redox behaviour in an aprotic solvent of a series of 1-halo-2,4-dinitrobenzenes such as: 1-F-2,4-dinitrobenzene (1-F-2,4-DNB), 1-Cl-2,4-dinitrobenzene (1-Cl-2,4-DNB) and 1-Br-2,4-dinitrobenzene (1-Br-2,4-DNB) is described and discussed in this paper.

2. Experimental

2.1. Chemicals

1-F-2,4-DNB, 1-Cl-2,4-DNB and 1-Br-2,4-DNB and DMF were from Aldrich Chemical Co. $n\text{Bu}_4\text{NBF}_4$ was from Fluka (puriss pa). Commercial products were of the highest purity available and were used as received. 2,2'-4,4'-Tetranitrobiphenyl was prepared as in Ref. [27].

2.2. Instrumentation and procedures

The instrumentation and electrochemical procedures were the same as described previously [23]. The potential is referred to a standard calomel electrode (SCE).

The inorganic anion concentration was determined by ionic chromatography (CLSI) [Metrohm 690 ion chromatograph 9 using a Hamilton PRP-X100 anion column (124 × 4.6 mm (i.d.)), with a solution of 2×10^{-3} M of phthalic acid and 10% acetone at pH 5 as the mobile phase [28].

3. Results and discussion

At a sufficiently high scan rate (v) in cyclic voltammetry, the compounds 1-X-2,4-dinitrobenzene, with X: F, Cl and Br show electrochemical behaviour analogous to 1,3-dinitrobenzene (1,3-DNB). That is, if there are no chemical reactions linked to electron transfer, the 1-X-2,4-DNB (at potentials more positive than -2.50 V where nitroso formation takes place), shows two successive one-electron waves corresponding to fast electron transfers, assigned to the formation of the radical-anion and of the dianion (Fig. 1). The lower limit for v to observe this behaviour depends on the halogen, thus for X = F, Cl it is 20 V s^{-1} and for X = Br it is 500 V s^{-1} .

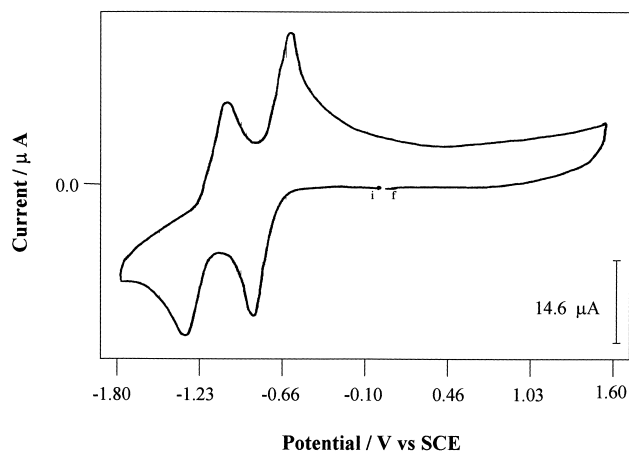
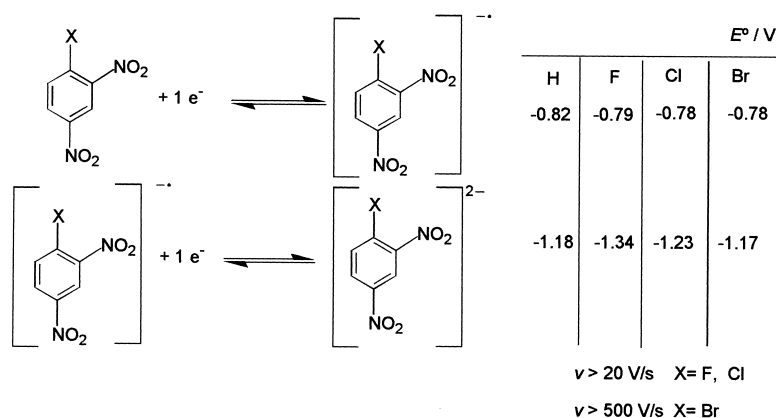


Fig. 1. Cyclic voltammetry of 1-Cl-2,4-dinitrobenzene (6.0 mM) in DMF + 0.1 M $n\text{Bu}_4\text{NBF}_4$ at 13°C . Scan rate 20 V s^{-1} , glassy carbon disk electrode (0.5 mm diameter). The scan is in the potential range: 0.00 / -1.80 / +1.60 / 0.00 V vs. SCE.



Scheme 1.

In the interval of potentials studied (without reaching the value where nitroso formation occurs) and at lower v , new reduction waves appear that indicate unequivocally the existence of new species formed by associated chemical reactions.

1-F-2,4-DNB show behaviour differentiated clearly from that of 1-Cl-2,4-DNB and from that of 1-Br-2,4-DNB. On the other hand, both 1-Cl-2,4-DNB and 1-Br-2,4-DNB are more similar in behaviour at the level of first electron transfer, though differing more at the second electron transfer level.

3.1. The electrochemical behaviour of 1-Cl-2,4-DNB and 1-Br-2,4-DNB

Within the range of concentrations studied (2–11 mM), no concentration effect was observed on either the form or the parameters of the voltammograms obtained.

3.1.1. $v > 20 \text{ V s}^{-1}$ for 1-Cl-2,4-DNB and $v > 500 \text{ V s}^{-1}$ for 1-Br-2,4-DNB (Fig. 1)

Two reversible one-electron waves are observed for the two compounds, which would be in agreement with the mechanism described in Scheme 1.

The difference in order of magnitude between the values of v indicate that reduced 1-Br-2,4-DNB is much more reactive than reduced 1-Cl-2,4-DNB.

3.1.2. 1-Br-2,4-DNB at $100 < v < 500 \text{ V s}^{-1}$ (Fig. 2)

The voltammograms present two reduction waves. The second wave increases in height (from one electron to almost three electrons). In addition, after the second wave, and on the return scan, we observe the oxidation peak for the Br^- ion ($E_p = +1.05 \text{ V}$) and the oxidation peak for the NO_2^- ion ($E_p = +0.59 \text{ V}$), which means that, after the second electron transfer, there is a chemical reaction. It is reasonable to suppose that this corresponds to the cleavage of the 1-Br-2,4-DNB dianion giving rise to Br^- and the 1,3-DNB anion. The rate

constant of this reaction is of the order of 10^4 s^{-1} . Given that the second wave grows in height, we suggest that the 1,3-DNB anion is protonated producing 1,3-DNB and, at the potential of this second wave, the 1,3-DNB that is formed undergoes two electron reduction giving 1,3-DNB $^{2-}$. It is known that 1,3-DNB $^{2-}$ evolves in part, and at this potential, giving rise to NO_2^- [29].

1-Cl-2,4-DNB does not show such behaviour (there is no variation in the second wave height, nor is the Cl^- ion detected in oxidation scans above to the potential of the second wave), allowing us to conclude that its dianion is stable with respect to the Cl^- ion loss reaction (Scheme 2).

3.1.3. 1-Br-2,4-DNB at $100 < v < 10 \text{ V s}^{-1}$ (Fig. 3a)

For the first wave we observe a height greater than one electron, and following this, we detect the presence of the Br^- ion; for the second wave (Fig. 3b) we observe a height which is twice that of the first wave, and following this we detect the presence of the NO_2^-

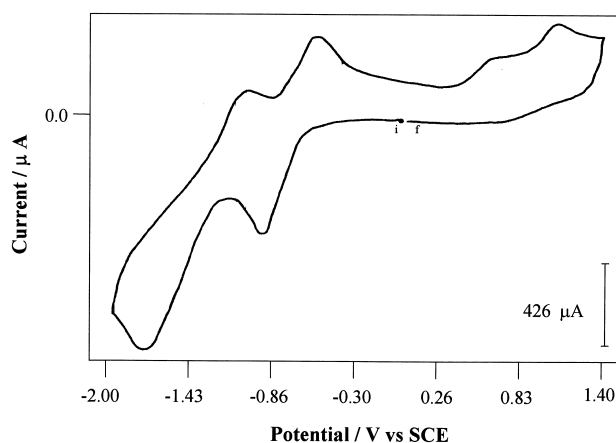


Fig. 2. Cyclic voltammetry of 1-Br-2,4-dinitrobenzene (10.0 mM) in DMF + 0.1 M $n\text{Bu}_4\text{NBF}_4$ at 13°C . Scan rate 100 V s^{-1} , glassy carbon disk electrode (0.5 mm diameter). The scan is in the potential range: 0.00/–2.00/+1.40/0.00 V vs. SCE.

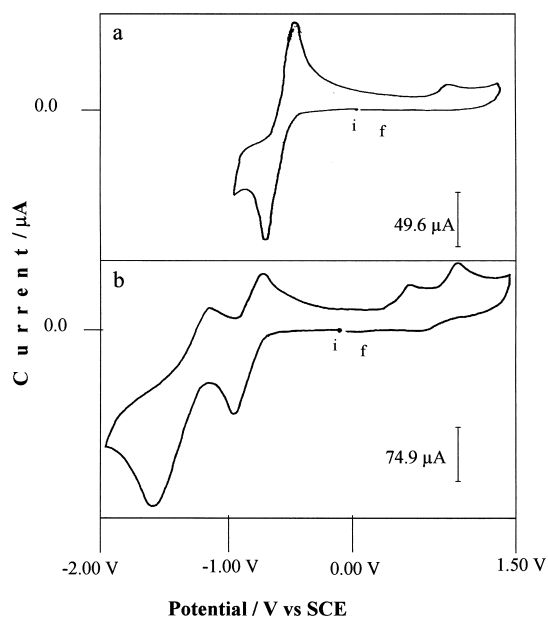
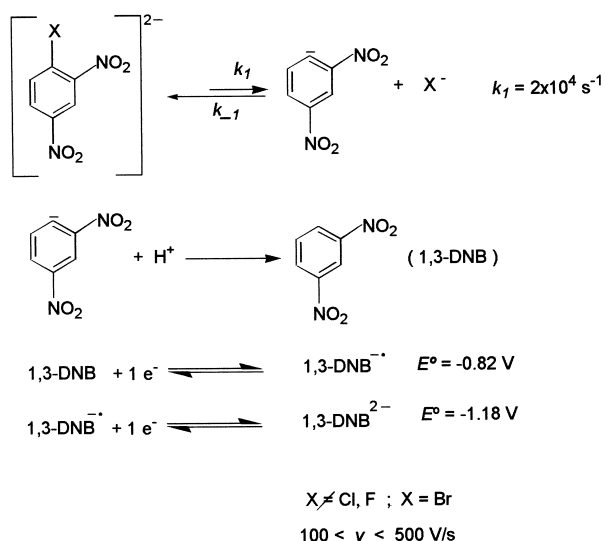


Fig. 3. Cyclic voltammetry of 1-Br-2,4-dinitrobenzene (10.0 mM) in DMF + 0.1 M $n\text{Bu}_4\text{NBF}_4$ at 13°C. Glassy carbon disk electrode (0.5 mm diameter). Scan rate 25 V s^{-1} . The scan is in the potential range: 0.00/−1.80/+1.40/0.00 V vs. SCE. Scan rate 50 V s^{-1} . The scan is in the potential range: 0.00/−1.80/+1.40/0.00 V vs. SCE.

ion in the oxidation. Therefore, in this case a cleavage reaction at the radical anion level takes place, and the observed features would be in agreement with that described in Scheme 3.

The 1,3-DNB radical obtained by the loss of the halide anion may follow two paths: (1) the abstraction of a hydrogen atom, in order to yield 1,3-DNB, and then at this potential to reduce to $1,3\text{-DNB}^{\bullet-}$; or (2) the acceptance of an electron, followed by protonation in order to yield 1,3-DNB, and then reduction at this potential. In both cases, the height of the first wave

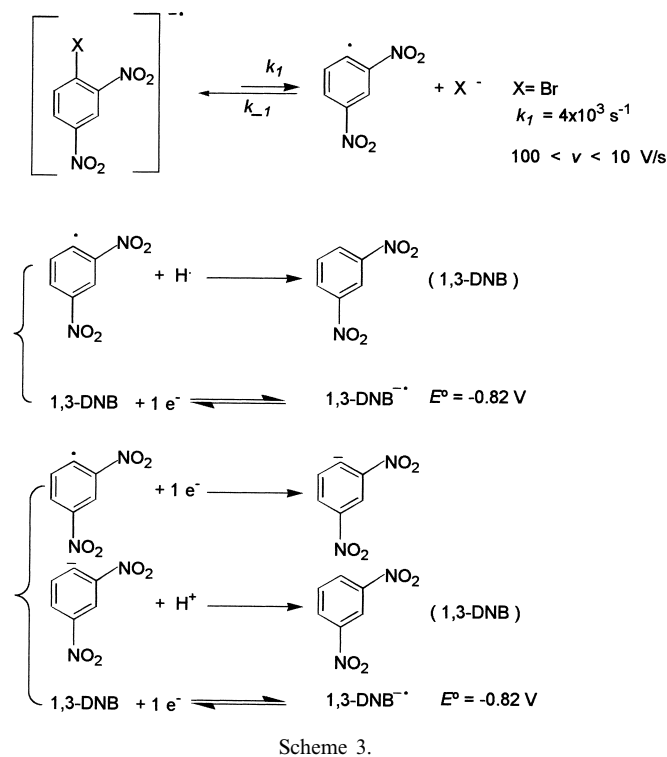
increases and, also in both cases, $1,3\text{-DNB}^{\bullet-}$ is obtained. The data available does not allow us to discern this point.

The second wave that appears within this scan rate range is due to the reduction of the unruptured 1-Br-2,4-DNB radical-anion and that of the $1,3\text{-DNB}^{\bullet-}$ which has been formed. This second wave is higher, due to the fact that the 1-Br-2,4-DNB dianion probably undergoes cleavage itself (Scheme 2).

3.1.4. At v lower than 20 V s^{-1} for 1-Cl-2,4-DNB and lower than 5 V s^{-1} for 1-Br-2,4-DNB (Fig. 4)

The voltammograms obtained are much more complex: the number of reduction waves has increased, showing new peaks for the two compounds studied at approximately −1.41 and −1.63 V (these new waves appear to be reversible). Additionally, the height of the first wave increases (to more than 1 electron mol^{-1}), and a new (chemically irreversible) oxidation wave appears, at +0.68 V for both compounds, as well as those corresponding to the oxidations of the Cl^- , Br^- and NO_2^- ions (+1.12, +0.89 and +0.50 V, respectively).

These new oxidation and reduction peaks are assigned to 2,2',4,4'-tetranitrobiphenyl (TNBP)¹ [29] which would have been formed through the dimerisation of the 1,3-DNB radical.



¹ TNBP present three reversible waves with E° : −0.68 V (corresponding to two electrons), −1.45 and −1.65 V and one oxidation wave with $E_p = +0.68 \text{ V}$.

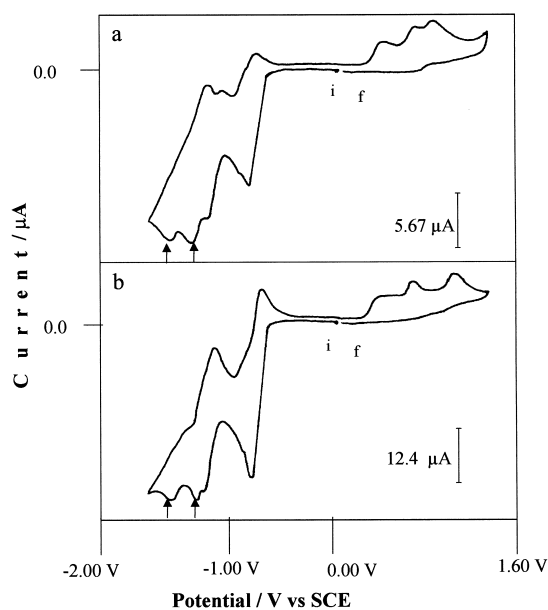


Fig. 4. Cyclic voltammetry in DMF + 0.1 M $n\text{Bu}_4\text{NBF}_4$ at 13°C. Glassy carbon disk electrode (0.5 mm diameter). 1-Br-2,4-dinitrobenzene (10.0 mM). Scan rate 0.3 V s^{-1} . The scan is in the potential range: $0.00/-1.80/+1.40/0.00 \text{ V vs. SCE}$. 1-Cl-2,4-dinitrobenzene (7.8 mM). Scan rate 0.3 V s^{-1} . The scan is in the potential range: $0.00/-1.80/+1.50/0.00 \text{ V vs. SCE}$.

2,2',4,4'-tetranitrobiphenyl (prepared through an alternative synthesis) to solutions of 1-Cl-2,4-DNB and 1-Br-2,4-DNB cause the increase of the newly-found peaks (Scheme 4).

Additions of water in amounts greater than $105 \mu\text{l}$ (1.20 mM) to a solution of 1-Cl-2,4-DNB cause the disappearance of the 2,2',4,4'-tetranitrobiphenyl peaks, which demonstrates that the dimerisation proposed in Scheme 4 occurs only when all the protons in the medium have been consumed by the 1,3-DNB ion (Scheme 3).

Electrolysis at a controlled potential for 1-Cl-2,4-DNB and for 1-Br-2,4-DNB, after the first electronic transfer at -0.88 V (passing 2F, in order to form the 2,2',4,4'-tetranitrobiphenyl dianion) allows for the identification and quantification of the presence of Cl^- and Br^- ions. Additional electrolysis at controlled potential after the first electronic transference at -0.88 V (in order to form the 2,2',4,4'-tetranitrobiphenyl dianion) and exhaustive oxidation at $+0.80 \text{ V}$ (in order to oxidise this dianion to a neutral species) highlights the formation of 2,2',4,4'-tetranitrobiphenyl. Table 1 summarises the results obtained.

Table 1 shows clearly the higher proportion of 1,3-DNB derived from 1-Br-2,4-DNB, a fact that is perfectly justifiable in terms of the mechanism proposed and the value of the rate constants. Thus, the 1-Br-2,4-DNB radical-anion breaks quickly, and therefore close to the electrode, and the charge transference reaction

on the 1,3-DNB radical is more favoured than dimerisation [30].

To conclude, both 1-Cl-2,4-DNB and 1-Br-2,4-DNB, at low v , and subsequent to the first electron transfer, have as their determining rate step: the first-order chemical reaction (we should have in mind that there is no concentration effect) giving rise to a halide anion and the corresponding 1,3-DNB radical. 1,3-DNB, nitrobenzene and TNBP are formed in the two cases. Nevertheless, the TNBP formation is slightly favoured from 1-Cl-2,4-DNB. At high scan rates, and therefore in the absence of linked chemical reactions, the behaviour is of the 1,3-DNB type.

3.2. The electrochemical behaviour of 1-F-2,4-DNB

At v greater than 20 V s^{-1} (Fig. 1, Scheme 1), a 1,3-DNB type behaviour is observed.

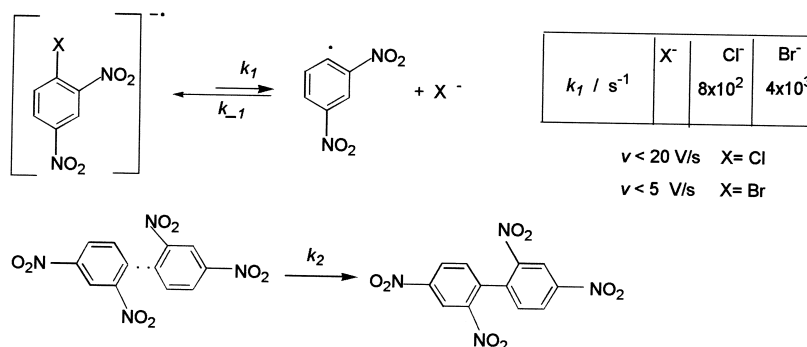
When $v < 1 \text{ V s}^{-1}$, (Fig. 5a) the number of reduction peaks increase, and a single oxidation peak appears. The increase of the first reduction peak is observed, and the appearance of two new reversible reduction peaks with E° at -1.35 and -1.56 V . In oxidation, one appears alone (only after the first reduction), at $+0.71 \text{ V}$. It is not possible to observe the F^- ion oxidation in cyclic voltammetry [31].

The formation of 2,2',4,4'-tetranitrobiphenyl by dimerisation (in a mechanism similar to that of Scheme 4 with $\text{X} = \text{F}$) could well be proposed, given the appearance both of new reduction peaks, and also an oxidation peak ($+0.71 \text{ V}$). However, in a close examination, the behaviour observed is significantly different from what we have just described for 1-Cl, and 1-Br-2,4-DNB, thus:

1. There is a concentration effect that suggests the operation of a bimolecular process. A study on the form and characteristics of voltammograms in terms of the 1-F-2,4-DNB concentration (within the 2–11 mM range) [32] allows us to conclude that the rate determining step of the reaction is the dimerisation of the radical-anion formed after the first electron transfer, and to calculate the dimerisation constant: $k = 800 \text{ M}^{-1} \text{ s}^{-1}$.
2. Conversely to what happened with 1-Cl, and 1-Br-2,4-DNB, upon addition of 2,2',4,4'-tetranitrobiphenyl to a solution of 1-F-2,4-DNB, the newly-existing peaks do not increase significantly, but rather there is the appearance of new peaks.

Therefore 1-F-2,4-DNB at $v < 1 \text{ V s}^{-1}$, and at the first wave potential level, a mechanism such as the one described in Scheme 5 is proposed:

The compound formed by the coupling of the two 1-F-2,4-DNB radical anions is a dianion. Intermediates of this type are known as σ complexes or Meisenheimer's complexes [33,34]. The σ complex is capable of



Scheme 4.

Table 1
Electrolysis of 1-X-2,4-dinitrobenzenes^a

	Yields				
	1	2			
X (%)	1-X-2,4-DNB (%)	1,3-DNB (%)	C ₆ H ₅ NO ₂ (%)	TNBP (%)	
1-Br-2,4-DNB ^b	90.0	10.0	50.0	5.0	25.0
1-Cl-2,4-DNB ^b	85.0	15.0	43.5	7.3	36.2
1-F-2,4-DNB ^{b,c,d}	95.0				85.0

^a Electrolysis (2 F) of 1-Br-2,4-DNB, 1-Cl-2,4-DNB, 1-F-2,4-DNB (10 mM) at -0.88 , -0.88 , -1.00 V, respectively. 2, electrolysis (2 F) of 1-Br-2,4-DNB, 1-Cl-2,4-DNB, 1-F-2,4-DNB (15.7, 15.1, 15.3 mM at -0.88 , -0.88 and -0.90 V, respectively and exhaustive oxidation at 0.80 V). Working electrode: graphite.

^b Anions and organic compounds analysed by cyclic voltammetry.

^c Anions analysed by ionic chromatography (CLSI).

^d Organic compounds analysed by gas chromatography/mass spectroscopy.

being reduced in two consecutive reversible one-electron steps with E° at -0.87 and -1.06 V (see following paragraph) resulting in a species with four negative but stable charges at this potential². This behaviour would account for the fact that the first wave increases in height.

Electrolysis (after passage of 2.3F) at a potential of -0.90 V for 1-F-2,4-DNB solutions allow for the formation of the σ complex. The analysis of the electrolysed solution by ionic chromatography (CLSI) indicated that no fluoride anion is present, and in registering the voltammogram (Fig. 6, dotted line) first with a reduction scan, we are able only to observe the waves at -0.94 and -1.09 and $+0.71$ V, corresponding to the reduction of the σ complex, and there is no wave corresponding to the reduction of 2,2',4,4'-tetranitrobiphenyl. If an oxidation scan is registered first, however (Fig. 6, solid line), its oxidation wave appears at $+0.71$ V, and that for the 2,2',4,4'-tetranitrobiphenyl reduction appears at -0.68 V. The analysis of 1-F-2,4-DNB solution first electrolysed at -0.90 V,

² Ab initio calculations for studied molecules have been performed to demonstrate the stability of M^{4-} . The addition of the fifth electron leads to the cleavage of the molecule [35].

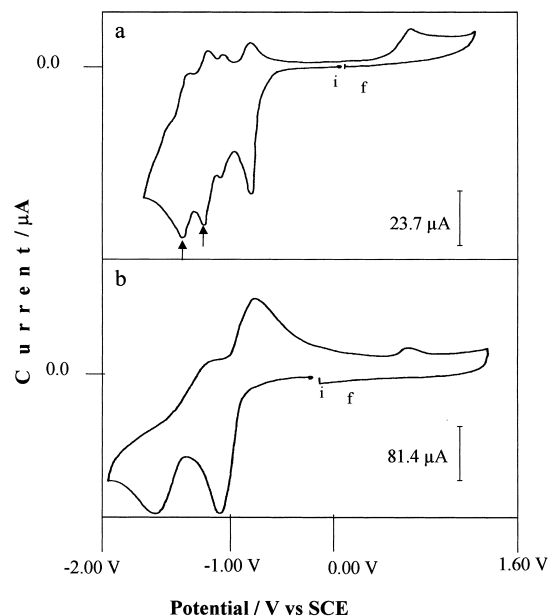
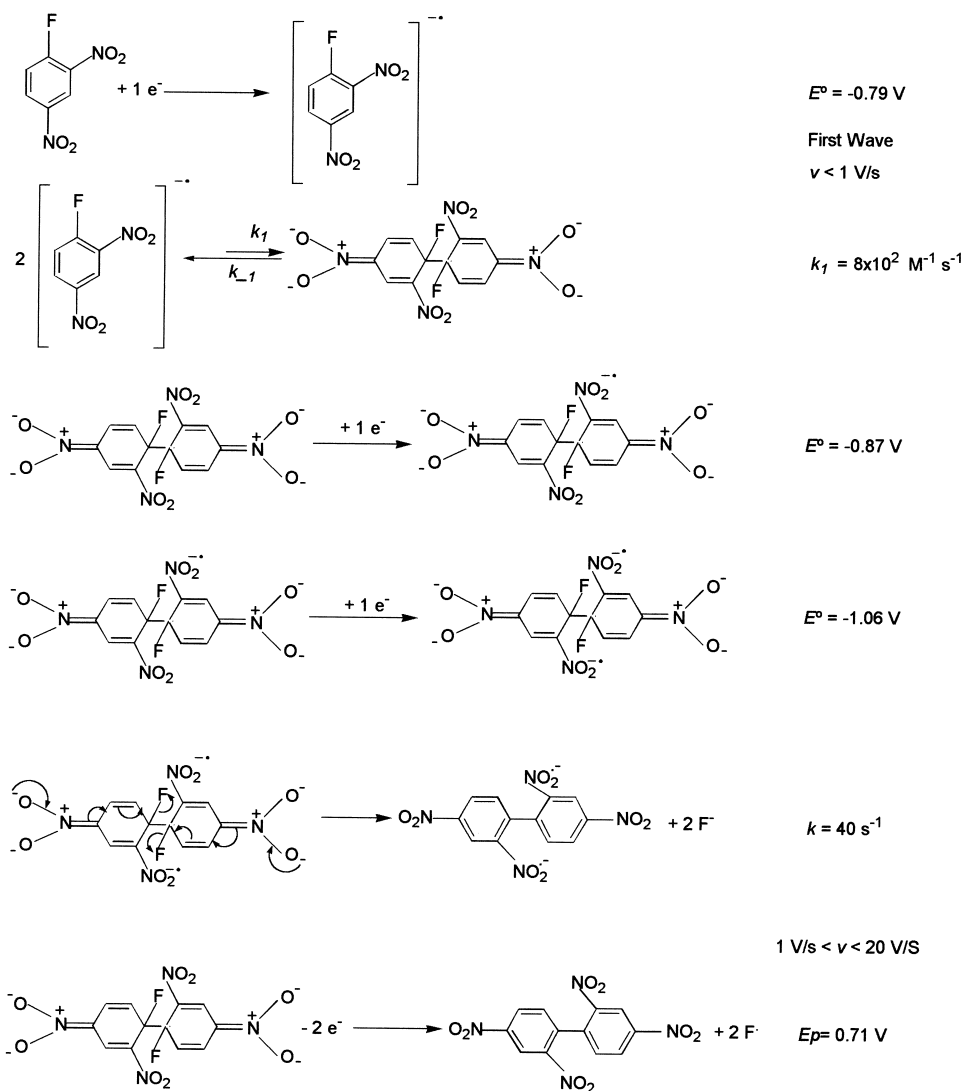


Fig. 5. Cyclic voltammetry of 1-F-2,4-dinitrobenzene (10.0 mM) in DMF + 0.1 M $n\text{Bu}_4\text{NBF}_4$ at 13°C . Glassy carbon disk electrode (0.5 mm diameter). Scan rate 0.3 V s^{-1} . The scan is in the potential range: $0.00/-1.80/+1.50/0.00$ V vs. SCE. Scan rate 10 V s^{-1} . The scan is in the potential range: $0.00/-2.00/+1.50/0.00$ V vs. SCE.



Scheme 5.

after passage of 2.3 F, then electrolysed at a potential of +0.80 V, beyond 2 F and by this means oxidising it, allows us to obtain 2,2',4,4'-tetranitrobiphenyl (85%) quantitatively. Neither 1,3-DNB nor 1-F-2,4-DNB are identified (see Table 1). The loss of F atom after oxidation of the doubly reduced σ -complex seems to be related to the second step of the well-known radical *ipso* substitution in aromatic compounds [36].

The analysis of a 1-F-2,4-DNB solution electrolysed at -1.00 V , after passage of 2.5 F allows us to identify and quantify the presence of the F^- ion by ionic chromatography (CLSI) (99%). The voltammogram of the electrolysed solution in this case is different since the peaks at -0.94 and -1.09 V , characteristics of the σ -complex, are not observed.

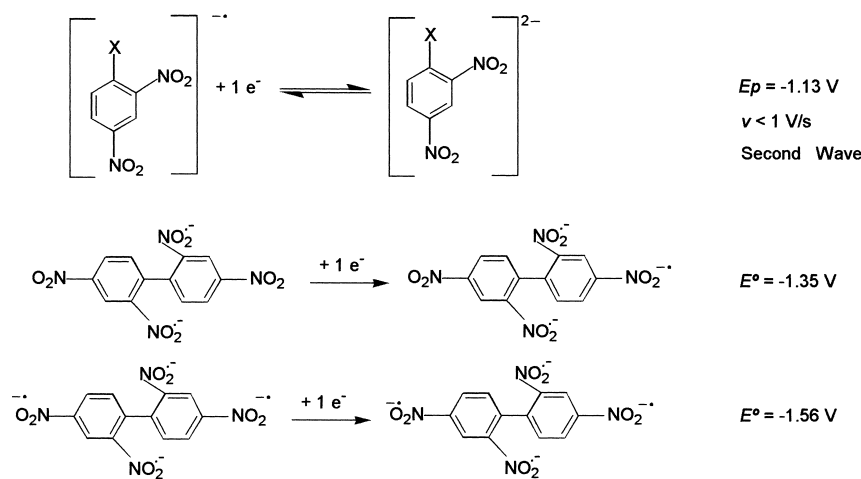
At potentials corresponding to the second wave, and $v < 1 \text{ V s}^{-1}$, we observe the reduction wave for the 1-F-2,4-DNB radical-anion that has not dimerised ($E^\circ = -1.34 \text{ V}$), and two small reduction waves ($E^\circ = -1.35 \text{ V}$

and $E^\circ = -1.56 \text{ V}$), which we attribute to the two successive one-electron reductions from the product formed by the loss of the F^- ions from the σ complex, doubly reduced, in line with what is described in Scheme 6.

For $20 > v > 1 \text{ V s}^{-1}$, the 1-F-2,4-DNB voltammogram (Fig. 5b), maintains a reversible first reduction wave ($E^\circ = -0.79 \text{ V}$) of a height greater than $1 \text{ e}^- \text{ mol}^{-1}$, a reversible second wave ($E^\circ = -1.34 \text{ V}$) with a height that corresponds almost exactly to $1 \text{ e}^- \text{ mol}^{-1}$, and without any further reduction waves. Nevertheless, the oxidation wave at $+0.71 \text{ V}$ is maintained. This behaviour is understandable if we accept that the doubly reduced σ complex is stable.

4. Conclusions

The redox behaviour, in an aprotic solvent, of a series of 1-F-2,4-dinitrobenzene, 1-Cl-2,4-dinitrobenzene and



Scheme 6.

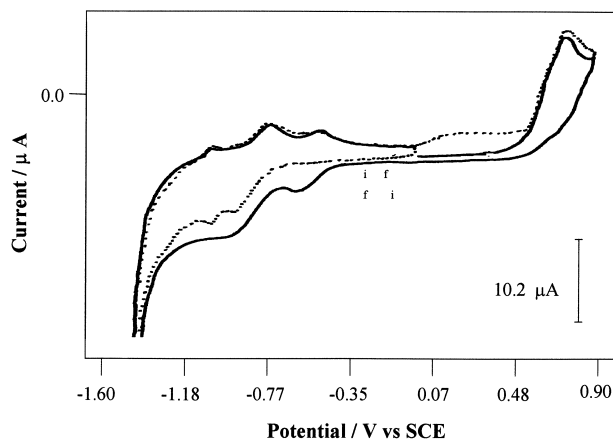


Fig. 6. Cyclic voltammetry after the reduction of 1-F-2,4-dinitrobenzene (10.0 mM) in DMF + 0.1 M $n\text{Bu}_4\text{NBF}_4$ at 13°C at -0.90 V passing 2.3 F. Scan rate 1.0 V s^{-1} . The scan is in the potential range: $0.00/-1.50/+0.90/0.00 \text{ V vs. SCE}$ (dotted line). The scan is in the potential range: $0.00/+0.90/-1.50/0.00 \text{ V vs. SCE}$ (solid line).

1-Br-2,4-dinitrobenzene was investigated in this study. In spite of the structural similarities, there were significant differences between the cyclic voltammograms in the three species. Thus, 1-Cl-2,4-DNB and 1-Br-2,4-DNB cleave the halogen-carbon bond at the first reduction level ($k = 8 \times 10^2$ and $4 \times 10^3 \text{ s}^{-1}$, respectively). On the other hand, 1-F-2,4-DNB following the first electronic transfer and unlike 1-Cl-2,4-DNB and 1-Br-2,4-DNB, dimerises before breaking ($k = 8 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$). This change in mechanism allows 2,2',4,4'-tetranitrobiphenyl to be obtained in a very selective way, and with excellent efficiency.

The observed reactivity can be related to the ability of the aromatic radical anions to undergo cleavage of the carbon halogen bond. The order $\text{F} < \text{Cl} < \text{Br}$ is the same as reported in the literature [5] for mono-nitro compounds with the peculiarity that in our case the stable fluoride radical anion dimerises. Savéant [37] has

provided the theoretical background to analyse the relative fragmentation reactivity of the radical anions. Thus, leaving apart entropy effects (that must be very similar in all the cases), in this model the fragmentative reactivity is a function of the bond dissociation energy of the neutral substrate (D_{RX}), the standard redox potential of the pair substrate/radical anion ($E_{\text{RX}/\text{RX}^{\cdot-}}^\circ$) and the standard redox potential of the pair radical/leaving group anion ($E_{\text{X}^{\cdot-}/\text{X}^-}^\circ$):

$$\Delta G_{(\text{RX}^{\cdot-} \rightarrow \text{R}^{\cdot} + \text{X}^-)}^\circ = D_{(\text{RX})} + E_{(\text{RX}/\text{RX}^{\cdot-})}^\circ - E_{(\text{X}^{\cdot-}/\text{X}^-)}^\circ + T\Delta S_{(\text{RX}^{\cdot-} \rightarrow \text{R}^{\cdot} + \text{X}^-)}^\circ$$

Taking into account that $E_{(\text{RX}/\text{RX}^{\cdot-})}^\circ$ is rather similar in all cases, and that $E_{(\text{Br}^{\cdot-}/\text{Br}^-)}^\circ = 1.48 \text{ V}$ versus SCE in DMF [26], and $E_{(\text{F}^{\cdot-}/\text{F}^-)}^\circ = 2.20 \text{ V}$ versus SCE in ACN [21] (this term, favours the cleavage of the C-F bond), it becomes clear that the bond dissociation energy ($D_{(\text{RX})}$) is the dominant factor responsible for the order of reactivity observed.

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