

Reductively activated 'polar' nucleophilic aromatic substitution. A new mechanism in aromatic chemistry?

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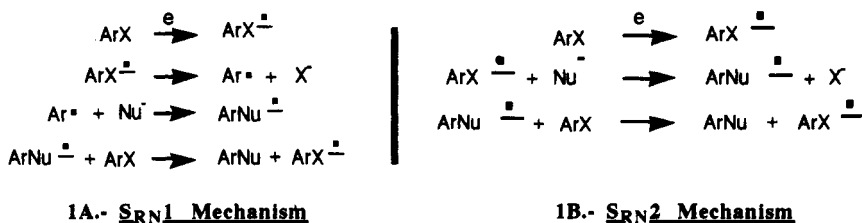
Abstract: Electrochemical studies indicate that although the reactions of *p*-dinitrobenzene and *p*-nitrobenzotrile with phenolate or phenol in DMF show radical features, they can not be attributed to the direct reaction of the nucleophile on the substrate radical anion. Mechanistic studies suggest that in spite of its different behavior in front of radical scavengers or irradiation, all polyfluoronitrobenzenes react with methanol in aqueous solution following a second stage rate determining "polar" S_NAr mechanism. The reported facts are not compatible with the previously proposed (for some of these reactions) $S_{RN}2$ mechanism. However, reductive activation is feasible in certain cases but substrate radical anion formation is not responsible for it. Topologically controlled coulombic interactions (TCCI) have been used to achieve reductively activated S_NAr reactions on otherwise unreactive nitrophenyl ethers. A mechanistic rationale is discussed.

1. INTRODUCTION.

Nucleophilic aromatic substitution reactions on aromatic compounds able to stabilize radical anions, such as dinitrobenzenes, nitrobenzophenones, nitrobenzotriles, polyfluoronitrobenzenes, etc., show normally radical features. However, radical anions of those compounds are stable toward dissociation and except for the very particular case of *o*-iodonitrobenzene (1) no example of the $S_{RN}1$ chain mechanism (2) for nitroaryl derivatives has so far been demonstrated (scheme 1A). One interpretation, proposed to justify the radical features of the reactions of dinitrochlorobenzenes with hydroxide ion, suggests the intermediacy of radical anions, formed through electron transfer from the nucleophile to the substrate (3), prior to the σ -complex (what we can call S_NAr -SET mechanism).

Abe and Ikegami (4) observed the presence of the corresponding radical anions in the reactions of dinitrobenzenes with OH^- in aqueous DMSO, and they postulated that the radical anions were intermediates in these reactions. Sammes *et al.* (5) have studied the displacement of nitro groups from *p*-dinitrobenzene and other nitrocompounds by various phenoxide ions in DMSO. These reactions yielded substituted diphenyl ethers. They showed that the reactions were inhibited by radical scavengers and they concluded that those reactions were radical in nature. Shein *et al.* (6) demonstrated the formation of *p*-dinitrobenzene radical anion when this substrate was reacted with a series of anion nucleophiles. On the other hand, it has been shown in the literature (7b) that the reactions of *p*-nitrobenzotrile with sodium ethoxide and phenoxide, although not stimulated by light could be inhibited by radical scavengers. Those results (and others) prompted Denney and Denney (7) to postulate the general operativity of a mechanism that included as a key step the reaction of a nucleophile with the radical anion derived from the aromatic substrate ($S_{RN}2$ type mechanism, scheme 1B). The $S_{RN}2$ mechanism was considered as an hypothesis in

the early literature but rejected on experimental grounds (8). This proposal (extended to many well demonstrated $S_{RN}1$ cases) has found strong resistance in the chemical community (9).



Scheme 1

Thermodynamic and kinetic considerations indicate that outer sphere electron transfer will be very slow in strongly endergonic processes as the ones here considered, and that in those endergonic processes a very fast follow up step is compulsory for the reaction to be feasible. This fast follow up step can be present in the S_{NAr} -SET scheme, but this is not the case in the $S_{RN}2$ type one, where a presumably high barrier radical anion - nucleophile reaction follows the first electron transfer step. It is worth to remember that an inner sphere electron transfer step had to be proposed (10) to solve a similar question concerning aliphatic $S_{RN}1$ processes initiated by nitronates. Therefore, we thought that even though the $S_{RN}2$ hypothesis was attractive, it deserved a closer examination. This lecture is divided in three parts. In the first one, we present some electrochemical studies on reactions previously assigned to the $S_{RN}2$ type mechanisms. The second one is devoted to the nucleophilic aromatic substitution reactions on polyfluoronitroaromatics, compounds we believed were the best candidates to react through the $S_{RN}2$ type mechanism. In the third part the reductive activation of S_{NAr} reactions is described and a mechanistic rationale discussed.

2. ELECTROCHEMICAL TESTING OF THE $S_{RN}2$ HYPOTHESIS (11).

The study was carried out on the reactions of *p*-dinitrobenzene (*p*-DNB) and *p*-nitrobenzotrile (*p*-NBN) with phenolate and phenol as examples of charged and uncharged nucleophiles respectively, in DMF as a solvent. Cyclic voltametry experiments in dry DMF show two reversible peaks corresponding to the first and the second reduction of the substrate in both cases (Fig. 1, *p*-DNB). The reaction of *p*-DNB with excess phenoxide ion in DMF was almost instantaneous, yielding 4-nitrophenyl phenyl ether, and no radical anion could be detected by UV/Vis spectroscopy. The reaction was slower when using $[\text{PhO}^-]/[\text{substrate}] < 1$. In Fig. 1 cyclic voltagrams of a blank reaction (cyclic voltametry performed after 10 min. of mixing, **blank** in Fig. 1) and of a reaction where a cyclic voltametry was performed every 30 seconds (cyclic voltagram after 10 min. of mixing is shown, **CV** in Fig. 1) are also compared. A new wave (with respect to the *p*-DNB voltagram), corresponding to the reduction of the substitution product, 4-nitrophenyl phenyl ether, is now present. However, the first reduction wave is still reversible in the presence of the nucleophile, and the relative intensity of this wave with respect to the one corresponding to the substitution product, is lower in the blank voltagram, indicating a faster evolution of the substitution reaction in the blank experiment. Those results strongly suggest that no direct reaction between the substrate radical anion and the nucleophile happens in our conditions.

Next, the *p*-DNB radical anion was electrochemically generated in DMF, and its possible reaction with phenoxide ion monitored by UV/Vis spectroscopy. *p*-DNB radical anion has a very characteristic (12) absorption spectra ($\lambda_{\text{max}} = 400 \text{ nm}$, $\lambda_{\text{max}} = 920 \text{ nm}$, this last band appears as a very useful terminal absorption in the UV/Vis spectrum, 800 nm , since our systems show no other absorptions in this part of the spectrum), and resulted to be stable in inert atmosphere. Addition of sodium phenolate to the radical anion solution produced no reduction of the intensity in the absorption spectra of the radical anion, thus confirming that direct reaction of the *p*-DNB radical anion with the phenolate nucleophile does not take place in DMF.

The reaction of *p*-nitrobenzotrile (*p*-NBN) with sodium phenoxide yielded 4-phenoxybenzotrile and it showed the same electrochemical features that the *p*-DNB reaction. However, the reaction resulted to be slower, and therefore some additional tests could be performed. Thus, a certain yield reduction was observed when the reaction was carried out in the presence of sulfur. Also, the reaction with air bubbling gives a much lower yield than the reaction in inert atmosphere. Those experiments confirm earlier reports (7b) on the influence of radical scavengers on the reaction. However, electrolysis at -0.9V (first reduction wave) resulted also in an important yield reduction indicating that external radical anion generation was deleterious for the substitution reaction. Our results eliminate the attack of the nucleophile on the substrate radical anion ($S_{RN}2$) as an operative step in the substitution mechanism of those reactions, but they confirm the radical nature of it.

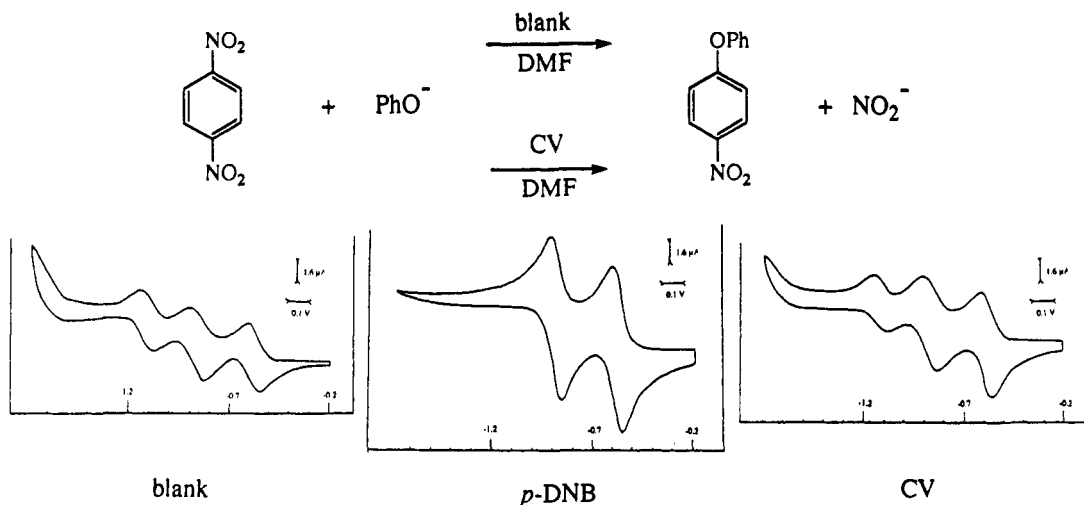
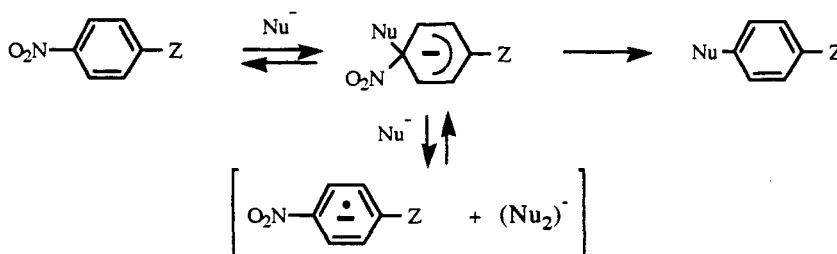


Fig. 1. Cyclic voltgrams (0.1V/s) of *p*-DNB in DMF (*p*-DNB) and of DMF solutions of *p*-DNB and of sodium phenolate after 10 min. of mixing (**blank**), and at the same time but running a cyclic voltammetry every 30 seconds (**CV**).



Scheme 2

A first explanation for the so far reported facts would be to consider the $S_{N}Ar$ -SET mechanism. Against it goes the previously commented endergonicity of the electron transfer step and the absence of stimulation by light. However such a mechanism has been proposed in the literature for even less favorable cases that use hydroxide ion as a reductant (3b,c). A variation to this mechanism, that would circumvent those objections, would be to consider an inner sphere electron transfer process ($S_{N}Ar$ /Inner-SET, scheme 2). In this mechanism, the radical anion would be produced by homolytic fragmentation of the intermediate σ -complex, perhaps with the help from another nucleophile molecule following the scheme proposed by Wasgestian (12b) to justify the appearance of the radical anion when *p*-dinitrobenzene is placed in the presence of cyanide. In this scheme, the radical anion would be in equilibrium with the σ -complex, justifying the observed radical features of all these processes, but not participating in the direct pathway from reagents to products.

Next we decided to test the possibility that the reaction between a radical anion and a nucleophile were feasible with neutral nucleophiles. Thus, we compared the results of cyclic voltammetry experiments of *p*-DNB and *p*-NBN in DMF and in the presence and in the absence of phenol (Fig. 2). The first reduction wave does not show any variation (keeping its reversibility in the presence of phenol), confirming that radical anions do not react with nucleophiles. However, some variations were observed at the second reduction wave level, we shall come back to this in the last part of the article.

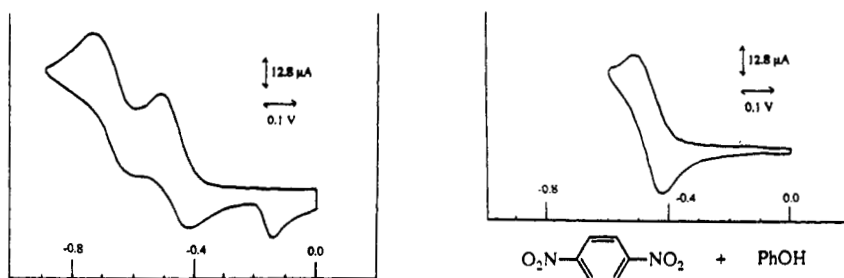


Fig. 2. Cyclic voltammogram (0.1 V/s) of a solution of *p*-DNB and phenol in DMF.

3. LOOKING FOR SPECIFIC EXAMPLES OF $S_{RN}2$ MECHANISM (13,14).

In order to confirm (or not) the existence of such a mechanism, polyfluoronitrobenzenes were considered as substrates in aqueous solution as reaction media. The addition of the well known stability of the nitroaromatic radical anions towards the fragmentation (probably increased in water solution) to the strength of the C-F bond should help to cancel the possible $S_{RN}1$ mechanism and the dehalogenation reaction. On the other hand, theoretical calculations (AM1 semiempirical method) indicated that the excess net charge in the highly substituted polyfluoronitrobenzenes was mainly placed in the substituents, leaving the phenyl ring almost neutral. Of course, this was the ideal situation for the hypothetical attack of a nucleophile on a radical anion.

TABLE 1. Reactions of PFNB with nucleophiles (13).



NuH	Conditions	Additives	(yield _{add} /yield _{blank})
MeOH	MeOH/H ₂ O (9:1) K ₂ CO ₃ , r. t. 10 min	Galvinoxyl (1)	0.47
		Galvinoxyl (0.25)	0.80
MeOH	MeOH/H ₂ O (2:1) K ₂ CO ₃ , r. t. 10 min	1,3-DNB (1)	0.39
		1,3-DNB (0.25)	0.76
MeOH	MeOH/H ₂ O (2:1), r. t. NaHCO ₃ , 20 min	hν	>10 ²
C ₆ H ₅ OH	CH ₃ CN/H ₂ O (5:1) K ₂ CO ₃ , r. t. 5 min	Galvinoxyl (1)	0.44
		Galvinoxyl (0.5)	0.55
		1,3-DNB (0.5)	0.90

In Table 1 (taken from ref. 13) the behavior of pentafluoronitrobenzene (PFNB) in front of nucleophiles (methanol and phenol), in slightly basic media, is summarized. Those reactions showed sensitivity to the presence of radical scavengers, and they were photostimulated. However, the operativity of an $S_{RN}1$ mechanism was discarded since the PFNB is very stable (15) with respect to fragmentation (it even dimerizes before undergoing any cleavage), methanol and phenol acted as nucleophiles through the oxygen atom, and the reactions were relatively insensitive to the presence of oxygen. In the beginning we attributed those contradictory facts to the operativity of an $S_{RN}2$ mechanism (13). However, the results and conclusions described in the previous part of this paper have prompted us to give a closer look to the reactions of pentafluoronitrobenzene comparing them with the ones of some others polyfluoronitrobenzenes. Here we will describe some results of a mechanistic study on the thermal reactions of 3,4-difluoronitrobenzene (DFNB), 2,3,4,5-tetrafluoronitrobenzene (TFNB), and pentafluoronitrobenzene (PFNB) with methanol, and on the corresponding photochemically and electrochemically stimulated (next part of the paper) reactions. Those new results have forced us to abandon the $S_{RN}2$ hypothesis for the reactions of polyfluoronitrobenzenes with nucleophiles (14).

The reactions of DFNB and TFNB, with methanol in aqueous solution and in the presence of carbonate as a base produced 3-fluoro-4-methoxynitrobenzene (62% yield) and 4-methoxy-2,3,5-trifluoronitrobenzene (81% yield) respectively and they were studied in the absence and in the presence of radical scavengers (variable concentrations of *m*-dinitrobenzene and of galvinoxyl). No effect was observed in any case. Comparison of those results with the reported ones for the corresponding reaction of PFNB (Table 1) resulted surprising, specially in the case of TFNB (considering the original $S_{RN}2$ proposal) since its first and second reduction potentials in MeOH/H₂O ($E^{\circ}/V = -0.76$, and $E_{p2}/V = -1.10$, vs. SCE) were very similar to the ones reported for PFNB ($E^{\circ}/V = -0.66$, and $E_{p2}/V = -1.10$, vs. SCE) (13).

Kinetic studies were carried out on the reaction of TFNB (as an example of reaction insensitive to the presence of radical scavengers) and on the reaction of PFNB (as the best candidate to react following an $S_{RN}2$ type pathway). Good pseudo-first order kinetics were obtained in all the cases (indicating that probably those are not chain reactions). Those reactions behave as typical examples of general base catalyzed nucleophilic aromatic substitutions. Thus, no reaction is observed in the absence of base, however, using a phosphate buffer (pH 7 in both cases) the reactions go to products at measurable rates. This result suggests (16) a nucleophilic aromatic substitution mechanistic scheme with a limiting second stage. This is a typical scheme when activated fluoroaromatics react with neutral nucleophiles (17), and in our case this situation seems to be even more evident since the σ -complex is expected to be rather stable. The measured activation parameters have the expected values (18) for second stage rate determining S_NAr reactions carried out in aqueous solutions and resulted to be very similar in both reactions.

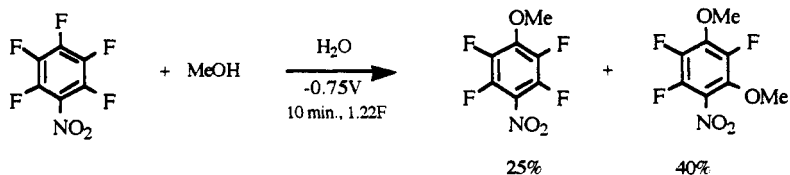
The high similarity between the kinetic behavior of the PFNB and TFNB reactions with methanol has forced us to postulate a common mechanism for both reactions. However, the reaction of PFNB shows a significant sensitivity to the presence of radical scavengers (see Table 1) while the corresponding reaction with TFNB does not. The obvious interpretation is that radicals are present in the reaction of PFNB but they are not in the direct pathway between reagents and products. This leads us again to a Wasgestian (12b) type mechanistic scheme (scheme 2). Since the second step is rate determining in our nucleophilic aromatic substitution reactions, the σ -complex will be in equilibrium with the starting materials and also with the radical anion. Depending on this second equilibrium position, the presence of the corresponding radical anion will be apparent (6), and the reaction will show sensitivity to the radical scavengers (case of PFNB), or not (case of TFNB).

Another interesting difference between the reactivity of PFNB and TFNB is their response to photochemical activation. We had previously published (13) that the reactions of PFNB with methanol in aqueous solution, and in the presence of sodium bicarbonate as a base, could be stimulated by UV light. A similar result was impossible to achieve with TFNB or DFNB. Now we have established the nature of the UV light activation in the PFNB case as pseudostimulation. Good pseudozero order kinetics were obtained at several temperatures (no change of the rate constant with the temperature) in the reactions of PFNB with methanol in the presence of NaHCO₃ and under UV irradiation, indicating that no stimulation

of a ground state chain reaction was happening. On the contrary, under UV light the reaction becomes a typical photochemical reaction, its rate only depending on the number of absorbed photons. This result indirectly supports the mechanism hypothesis postulated in scheme 2 for the ground state reactions.

4. REDUCTIVE ACTIVATION OF "POLAR" NUCLEOPHILIC AROMATIC SUBSTITUTION.

In spite of the fact that those reactions (PFNB and TFNB) show all the features of second stage rate determining "polar" S_NAr reactions, and that radicals do not seem to be involved in the direct pathway from reagents to products, they can be reductively activated (13,14). This activation had been previously studied (13) by us for the reaction of PFNB with methanol and phenol in the presence of sodium bicarbonate. We have also studied the reactions of PFNB and TFNB with methanol in the absence of any added base (scheme 3, PFNB as example). In these conditions the unstimulated reactions have a negligible rate. However, under cathodic stimulation, a 25% yield of 4-methoxy-2,3,5,6-tetrafluoronitrobenzene and 40% yield of 2,4-dimethoxy-3,5,6-trifluoronitrobenzene were obtained in the PFNB case (-0.75V vs. SCE, 65% total substitution yield, 10 min., 1.22 faradays, room temperature), and a 26% of 4-methoxy-2,3,5-trifluoronitrobenzene in the TFNB case (-0.8V vs. SCE, 10 min., 1.18 faradays, room temperature). In this last case, only traces of the disubstitution product were present in the reaction crude. The corresponding reaction of DFNB resulted unsuccessful being nitro group reduction the only detected process.



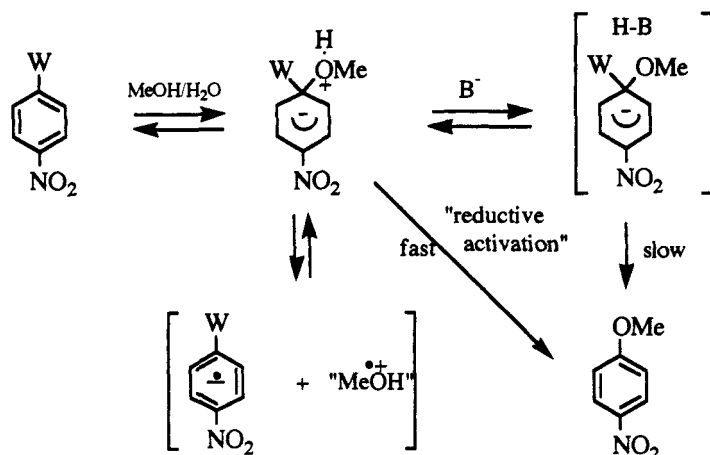
Scheme 3

A very related situation is found in the reactions of *p*-DNB and *p*-NBN with phenol in DMF. Electrolysis of the reaction mixture at -0.9V (vs. SCE, glassy carbon electrode, second reduction wave) in the case of *p*-DNB led to the monosubstitution product in 28% yield in 10 min. (4.6 faradays). A blank experiment gave no reaction. However, reactions carried out with *p*-NBN using different potentials (-1.3V, and -1.55V, vs. SCE) were unsuccessful, being nitro group reduction products the only observed reaction (11).

The reported facts indicate that a modest sensitivity of a reaction to the presence of radical scavengers or to light irradiation not necessarily means the operativity of a chain radical process. On the other hand, a S_NAr mechanism with the second step as a rate determining step seems to be a necessary condition for the reductive activation to be feasible. The $S_{RN}2$ mechanistic scheme is not at all appropriate to justify those facts.

We can therefore conclude that reductive stimulation of nucleophilic aromatic substitution is feasible in some particular cases, but that the radical anion formation is not responsible for it. A first interpretation for this reductive activation would be to consider that the substrate dianion formed after the second reduction is basic enough to catalyze the substitution process (a related explanation was given by Chambers and Adams (19) to justify the appearance of nitrophenols in the electrochemical reduction of dinitrobenzenes in not completely dried DMF). However, this scheme would lead to the appearance of relatively large amounts of starting material reduction products (the natural evolution of the protonated dianion), and in our stimulated reaction only very minor amounts of them can be detected. An alternative explanation would include the reduction of the zwitterionic σ -complex (20) that would immediately cleave (the reduction potentials of the zwitterionic σ -complexes should be similar to the ones of the radical anions, thus making difficult their detection by cyclic voltametry). The activation in this last hypothesis would be

due to the increase of the σ -complex fragmentation rate (this step is the rate determining step in our reactions with neutral nucleophiles) (16). A general mechanistic scheme for the reaction described is indicated in scheme 4.



Scheme 4

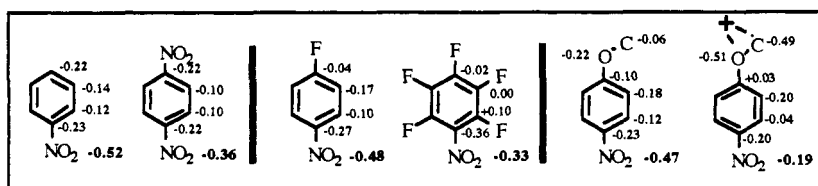
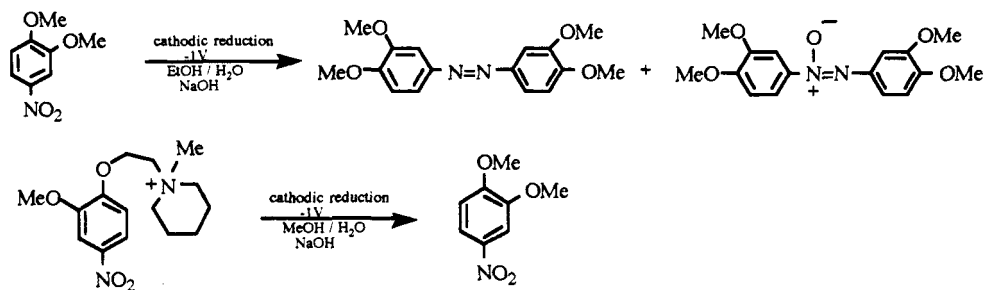


Fig 3.- Radical anion net charges.



Scheme 5

From the few known examples where the reductive activation was operative, compared with those where it was not, some general trends appear. In addition to a second stage rate determining mechanism for the unactivated substitution, the radical anion must be poorly basic (electrochemical nitro group reduction starts in most cases by protonation of the radical anion). In Fig. 3, the theoretically calculated net charges (AM1 semiempirical method) for different radical anions are shown. It is interesting to note that those substrates able to undergo the "reductively activated S_NAr reaction" are those that show a low electronic density in the nitro group of the corresponding radical anion. Therefore, the "topologically controlled coulombic interactions (TCCI effect)" that we have developed in another context (21), have been used to reduce the electronic density in the nitro group of radical anions. Also in Fig. 3, the effect of

placing a positive charge opposite to the nitro group in the radical anion of nitroanisole is shown. As expected, the electronic density on the nitro group is now very low, and this should translate in a lower basicity of the radical anion. In scheme 5, the reactivity under reductive conditions, in the presence of alcohols, of 4-nitroveratrole and 1-(N-methylpiperidino)-2-(2-methoxy-4-nitrophenoxy)ethane (TCCI effect) in aqueous solution is compared (22). In the first case only nitro group reduction products are obtained while when the TCCI effect is present, substitution is obtained in not deoxygenated solutions. When the reaction was carried out in inert atmosphere products resulting from substitution plus nitro group reduction were obtained. In any case, the convenience of a low basicity of the radical anion for the reductively activated S_NAr reaction to be observed was confirmed, being also those experiments new examples of the power of the TCCI approach in the developing of novel reactivity (23).

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