Solvent Effects on the Reduction Potentials of Nitroanilines

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The influence of a number of aprotic solvents on the electrochemical reduction of *ortho*- and *para*-nitroanilines and their *N*-methyl derivatives has been studied. The reduction potentials, depending fundamentally on the acceptor properties of the medium, decrease with increasing solvent acceptor number. A similar effect is produced by intramolecular hydrogen-bonding interactions in *ortho*-derivatives. Intermolecular hydrogen-bonding interactions, occurring with derivatives having 'free' N–H protons, are transmitted through the molecule, enhancing the sensitivity of the NO_2 group to the acceptor solvent.

As reported in the preceding paper,[1] the configuration of *ortho*- and *para*-nitro-*N*-methylanilines and of other derivatives of the same *N*-methylanilines appears to be at least in part modulated by the solvent, the degree of coplanarity of the NHR group and the ring being enhanced by the basicity of the medium. The first stage in the electroreduction of nitroanilines (generating the stable radical $RNO_2^{-\cdot}$, in which the electron is partially localized on the nitrogen of the NO_2 group [2,3]) offers the means of investigating, at the level of the NO_2 group, the effect of the medium on the nitroaniline produced by direct interaction with this group as well as by interactions transmitted through the aniline molecule. In order to obtain information about the influence of the medium on the behaviour of systems with a certain degree of delocalization, able to transmit molecular interactions, we have studied the influence of various aprotic solvents on the electroreduction of *ortho*- and *para*-nitroanilines and their *N*-methyl derivatives.

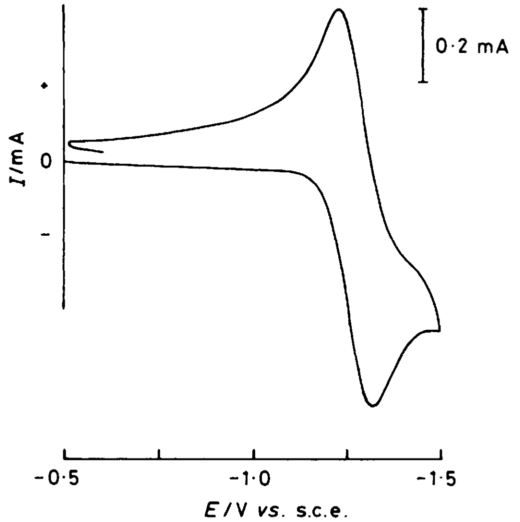


Figure 1. Reduction of 10^{-3}M-*ortho*-nitro-*N*-methylaniline by cyclic voltammetry in acetone (TEAP 0.1M) at a glassy carbon electrode (potential scan rate 0.5 V s^{-1})

Experimental

The *ortho*- and *para*-nitro-*N*-methylanilines were obtained by treating the *N*-tosyl derivatives of the primary nitroanilines with dimethyl sulphate, and subsequent treatment of the tosyl-*N*-methyl derivatives with a mixture of sulphuric and acetic acids (2:1).[4,5] The *ortho*- and *para*-nitro-*N,N*-dimethylanilines were synthesized from the appropriate nitro-halogeno-benzenes and dimethylamine hydrochloride.[6]

Solvents were purified by standard methods,[7] stored under argon, and protected from light. The water content of solvents and reagents was monitored by Karl Fischer titrations and kept below 5×10^{-4}M. The tetraethylammonium perchlorate (TEAP) used as background electrolyte (0.1M) was obtained commercially, recrystallized twice from water, and dried under vacuum.

Voltammetric data were obtained by cyclic voltammetry using a PARC 370 electrochemistry system in a glass cell with a glassy carbon working electrode, a platinum-wire auxiliary electrode, and an aqueous saturated calomel reference electrode (s.c.e.). The s.c.e. was connected to the working cell through a Luggin capillary as described elsewhere.[8] All measurements were performed in an argon atmosphere. The reported potentials, measured at the first cyclic voltammogram, are referred to the couple bisbiphenylchromium(I)–bisbiphenylchromium(0) used as inner reference redox system.[9]

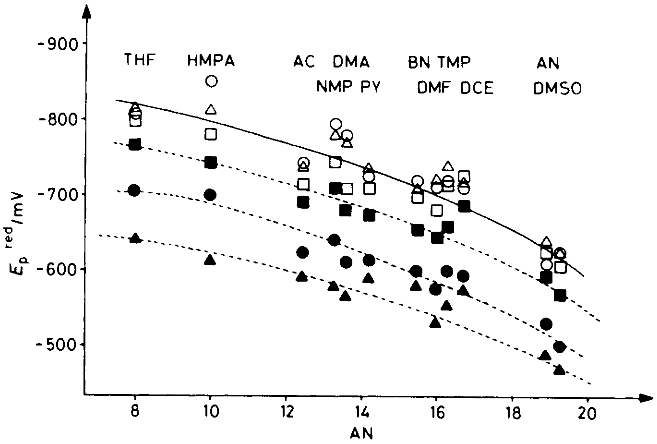


Figure 2. Effect of the acceptor properties of the solvents on the reduction-peak potentials of nitroanilines: (○) *p*-nitroaniline; (△) *p*-nitro-*N*-methylaniline; (□) *p*-nitro-*N,N*-dimethylaniline; (●) *o*-nitroaniline; (▲) *o*-nitro-*N*-methylaniline; (■) *o*-nitro-*N,N*-dimethylaniline [potential values referred to bisbiphenylchromium(I)–(0)]

Results

The first cathodic reductions of *ortho*- and *para*-nitroaniline and of their *N*-methyl and *N,N*-dimethyl derivatives in various

Table 1. Reduction-peak potential values of nitroanilines in various aprotic solvents

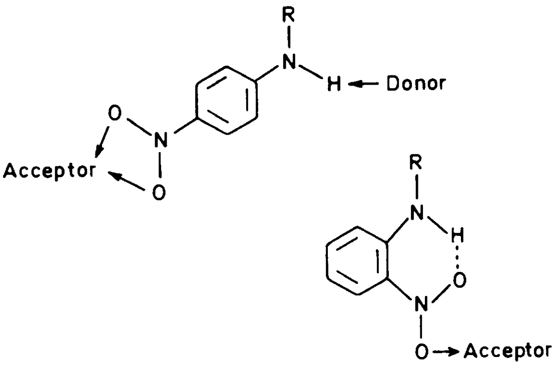
			E_p^{red}/mV					
			Nitroaniline		Nitro-*N*-methylaniline		Nitro-*N*,*N*-dimethylaniline	
Solvent	AN[a]	DN[b]	*ortho*	*para*	*ortho*	*para*	*ortho*	*para*
Tetrahydrofuran (THF)	8	20	−705	−805	−640	−815	−765	−800
Hexamethylphosphoramide (HMPA)	10	38.8	−700	−850	−615	−810	−745	−780
Acetone (AC)	12.5	17	−625	−745	−590	−740	−690	−715
N-Methylpyrrolidone (NMP)	13.3	27.3	−640	−795	−580	−780	−710	−745
Dimethylacetamide (DMA)	13.6	27.3	−610	−780	−565	−775	−680	−710
Pyridine (PY)	14.2	33	−615	−725	−590	−735	−685	−710
Benzonitrile (BN)	15.5	11.9	−600	−720	−580	−710	−655	−700
Dimethylformamide (DMF)	16	26.6	−585	−710	−530	−720	−645	−680
Trimethyl phosphate (TMP)	16.3	23	−600	−720	−555	−740	−660	−715
1,2-Dichloroethane (DCE)	16.7	0	−595	−710	−575	−720	−685	−725
Acetonitrile (AN)	18.9	14.1	−530	−610	−490	−640	−595	−625
Dimethyl sulphoxide (DMSO)	19.3	29.8	−500	−625	−470	−625	−570	−610

[a] Solvent acceptor number from ref. 11. [b] Solvent donor number from ref. 11.

Table 2. Estimated reduction-peak potentials for nitroanilines in an inert medium (AN = 0)[a]

	E_p^{red}/mV	
	ortho	*para*
Nitroaniline	−799	−900
Nitro-*N*-methylaniline	−708	−901
Nitro-*N*,*N*-dimethylaniline	−852	−867

[a] Potential values were estimated from data in Table 1 according to the relationship $E_p^{red} = a_0 + a_1$AN obtained for nitroanilines in low-acceptor media (AN < 17, without considering HMPA).



Scheme 1.

aprotic solvents were studied by cyclic voltammetry at room temperature (20 ± 1 °C). A typical cyclic voltammogram is reproduced in Figure 1.

According to standard reversibility criteria,[10] the observed electrochemical reduction (formation of the anion radical $RNO_2^{-\bullet}$) corresponds to a reversible diffusion-controlled one-electron process. The potentials of the reduction peaks (E_p^{red}) in the first cyclic voltammogram for the solutions studied are summarized in Table 1. The value of E_p^{red} depends on both the aniline substituent and the nature of the solvent. However, as the potential shows a relatively clear dependence on the acceptor properties of the medium, expressed as the solvent acceptor number AN[11] (Figure 2), the potentials E_p^{red} of the various derivatives in a hypothetical inert medium can be estimated, and therefore compared under similar conditions (Table 2).

Discussion

Since the reduction of nitroanilines involves the addition of one electron, partially localized on the N atom of the NO_2 group,[3] the first reduction potential of the nitroaniline is fundamentally determined by the stability of the radical $RNO_2^{-\bullet}$. Every substituent or medium effect that contributes to a charge transfer from the NO_2 group to the ring or to the environment will therefore stabilize this anion, thus favouring the reduction process. The interactions of the anion radicals with the medium should be similar to those described for the neutral nitroanilines, but somewhat stronger, especially in electrophilic media.

Unsubstituted and partially substituted nitroanilines are known to interact with donor as well as with acceptor solvents; these interactions affect the electronic structures of the molecules and thus produce solvatochromic effects[12] (Scheme 1). Similar effects are produced by intramolecular interactions in the *ortho*-nitroanilines.[13] Moreover, as established from i.r. studies of these and other anilines in various media,[1] not only the electronic but also the molecular configurations of the substrates are influenced by the nature and strength of both intra- and inter-molecular interactions.

Although solvent and substituent effects are strongly related, the relatively predominant influence of the acceptor properties of the solvent on the reduction potentials of the anilines studied (see Figure 2) allows us to estimate the potential values in an inert medium (AN = 0) and thus to discuss separately the effects of the substituents (Table 2).

The degree of substitution at the amino group has a clear influence on the redox behaviour of the *ortho*-derivatives, whereas for the *para*-derivatives this influence is scarcely observed; the small differences between the E_p^{red} values for these compounds are essentially within the experimental error. Thus, although the presence of an amino group as substituent considerably affects the reduction potentials of nitroaromatic compounds [$E_{1/2}$ of nitrobenzene in acetonitrile with respect to bisbiphenylchromium(I) is −0.370 V], the differences between the inductive effects on the nitro group of the different amino groups appear to be not very significant. The different reduction potentials observed for *ortho*-nitroanilines, in general lower than those of the *para*-derivatives, could therefore be attributed to the effect of intramolecular interactions. In fact, *ortho*-

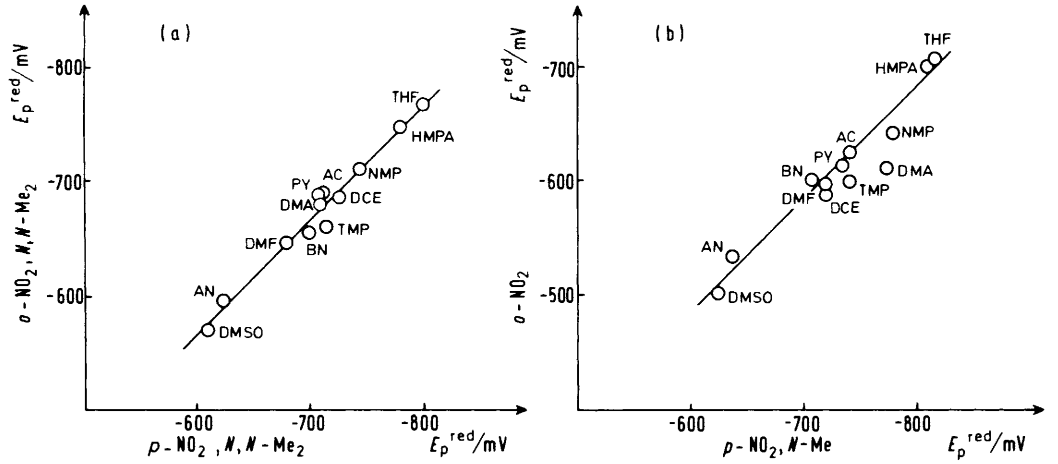


Figure 3. Comparison of the reduction-peak potentials of some nitroanilines in various solvents: (a) *ortho*-nitro-*N*,*N*-dimethylaniline with *para*-nitro-*N*,*N*-dimethylaniline; (b) *ortho*-nitroaniline with *para*-nitro-*N*-methylaniline [potential values referred to bisbiphenylchromium(I)–(0)]

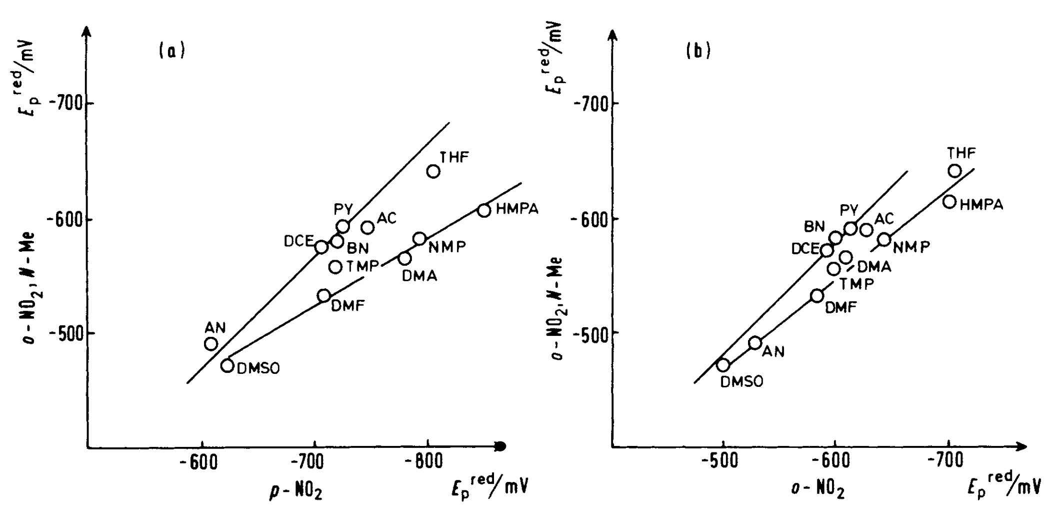


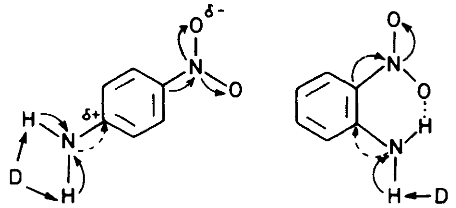
Figure 4. Comparison of the reduction peak potentials of some nitroanilines in various solvents: (a) *ortho*-nitro-*N*-methylaniline with *para*-nitroaniline; (b) *ortho*-nitro-*N*-methylaniline with *ortho*-nitroaniline [potential values referred to bisbiphenylchromium(I)–(0)]

nitroaniline and *ortho*-nitro-*N*-methylaniline, for which the formation of intramolecular hydrogen bonds is possible, are more easily reduced than *ortho*-nitro-*N*,*N*-dimethylaniline, the reduction potential of which, estimated for an inert medium, is in turn only slightly below those of the *para*-nitro derivatives. The higher stability of the anion radical of *ortho*-nitro-*N*-methylaniline relative to its *ortho*-nitroaniline analogue, inferred from their reduction potentials, implies a strengthening of the intramolecular hydrogen bond in the substituted species caused by the presence of the methyl group.

Although the influence of the medium on the electroreduction of nitroanilines is certainly a function of several solvent properties, the results reported in Figure 2 indicate a predominant effect of the electrophilic character of the solvents, thus reflecting the importance of a direct solute–solvent interaction through the NO_2 group. As already stated, such an interaction would preferentially stabilize the reduced anionic form, decreasing the reduction potential with increasing solvent acceptor strength. Other interactions (for instance, intermolecular hydrogen bonding for derivatives with primary and secondary amino groups) are scarcely observed, though they certainly contribute to the relatively high dispersion in the plots shown in Figure 2.

However, the relative sensitivity of the different nitroanilines to the solvent (graphically illustrated by comparing the solvent shifts of the potentials for pairs of compounds as shown in Figures 3 and 4) also appears in some cases to depend, to a certain extent, on the donor properties of the medium. Many of these graphic comparisons indicate approximately linear relationships, with slopes near unity (Figure 3), pointing to an equivalent influence of the medium on the reduction potentials of the compounds compared. However, there are other systems for which this behaviour is observed only in solvents with moderate and low donor strength (DN $<$ 23). In strong donor solvents nearly linear relationships are also obtained but the slopes are different from unity, indicating different behaviour of the two species (Figure 4). This tendency is especially noticeable in the comparison of the reduction potentials of *ortho*-nitro-*N*-methylanilines with those of other derivatives capable of acting as intermolecular hydrogen-bond donors. *ortho*-Nitro-*N*-methylaniline displays in high donor-strength solvents a lower relative sensitivity to the influence of the medium (slope 0.60 and 0.80 in Figure 4). Nevertheless, as suggested by the sequence of potentials in the different solvents, this sensitivity, in low as well as in high donor-strength media, is always related to the interaction of the aniline with the electrophilic sites of the solvent molecules. The donor properties of the medium only modulate such an interaction.

The enhanced sensitivity to the solvent of the compounds with 'free' N–H acidic protons relative to that of the *ortho*-*N*-methyl derivative can be explained by considering the interactions shown in Scheme 2. As indicated by the arrows, hydrogen-bond interaction with donor solvents produces charge displacements that, in agreement with previous i.r. studies of these and other anilines,[1] lead to a greater degree of coplanarity of the amine group with the ring; simultaneously, this produces a charge transfer to the NO_2 group. This charge increment will lead to a greater nucleophilicity of the NO_2 oxygen atoms, thus explaining the enhanced sensitivity to the medium induced by the hydrogen-bonding interactions between the aniline and the donor solvent.



Scheme 2.

Acknowledgements

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