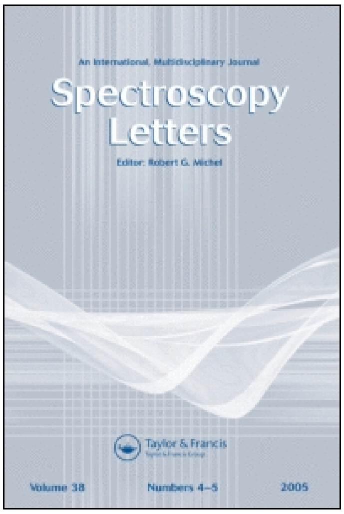

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# Cyclic Voltammetry and Electron Paramagnetic Resonance Study of the Electrochemical Reduction of P-Nitrobenzyl Bromide in Aprotic Solvents

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# CYCLIC VOLTAMMETRY AND ELECTRON PARAMAGNETIC RESONANCE STUDY OF THE ELECTROCHEMICAL REDUCTION OF P-NITROBENZYL BROMIDE IN APROTIC SOLVENTS.

**KEY WORDS:** Nitro radical, EPR, electrochemical reduction, aprotic solvents, electron-transfer.

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## ABSTRACT:

EPR has been used to investigate the radicals postulated as intermediates in the intramolecular electron transfer and dehalogenation of p-nitrobenzyl bromide (p-NBBr) in DMSO and DMFA at room temperature. The electrochemical behavior has been studied through the use of cyclic voltammetry. According to the postulated reaction mechanism, the one-electron reduction of p-nitrobenzyl bromide generates an anion radical which undergoes breakage of the C-Br bond followed by

intramolecular electron transfer. The free radical obtained is finally transformed into p-nitrotoluene.

## INTRODUCTION

The reduction of nitrobenzyl halides provides an adequate model for the analysis of intramolecular electron transfer, which is an important process in many biological and biopolymeric redox systems (1). One-electron reduction of aromatic compounds which contain an halogen and an electron-attracting substituent has been shown to produce initially an anion radical, leading subsequently to dehalogenation. Such processes have been suggested previously as intermediate steps in several organic substitution reactions. These phenomena have usually been investigated by analysis of UV-visible spectra (2) and by pulse radiolysis in aqueous solution (3,4,5).

In the present study, intramolecular electron transfer was analyzed by following the electrochemical behavior of p-nitrobenzyl bromide (p-NBBr) in dimethylsulfoxide (DMSO) and N,N-dimethylformamide (DMF) using cyclic voltammetry (CV), characterizing by EPR the anion radicals produced and their posterior fate. We are now reporting the direct formation of these stable products in aprotic solvents at room temperature for the first time. Before the present report, only information about the formation of the transient absorption spectra of the anion radicals in aqueous solutions (2) and also about matrix isolated radical anions at 77 K (6) had been published.

## EXPERIMENTAL SECTION

### Electron Spin Resonance

Free radicals were prepared by electrolytic reduction *in situ* and their EPR spectra were recorded on a Varian V-4502 spectrometer with a 100 KHz unit, a Varian V-1530 Klystron and a 9 inch Varian V-3400 electromagnet. The generated magnetic field was measured with a Varian E-500 gaussimeter and the microwave frequency was about 9.5 GHz.

The spectra were recorded on a Hewlet-Packard 7004 B X-Y plotter.

### Cyclic Voltammetry

The cyclic voltammograms were recorded at a glassy carbon electrode, using a saturated calomel electrode as reference and an auxiliary platinum wire electrode, on a CV-27 BAS voltammograph. The measurements were done at approximately a $1 \times 10^{-3}$ M concentration, at room temperature and under an inert atmosphere.

### Chemicals

The solvents used were spectroscopic grade, repurified by standard methods. Technical nitrogen was purified in the usual way. Tetraethylammonium perchlorate was from G. Frederick Smith Chemical Co. P-nitrobenzyl bromide was obtained from Sigma.

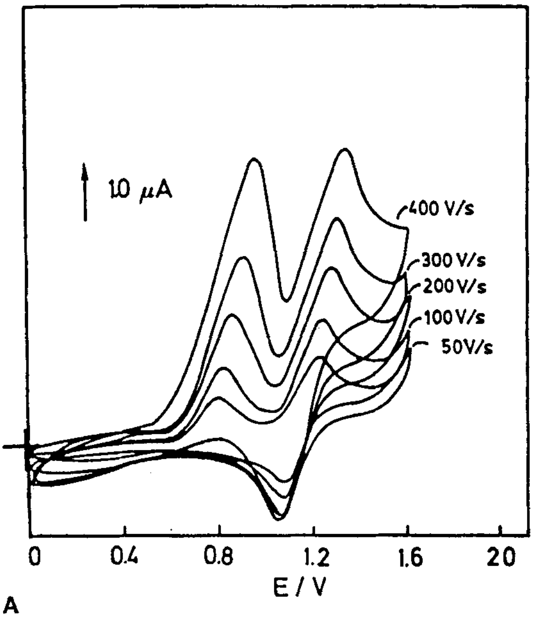

FIG. 1 A.- Cyclic voltammetry of p-NBBr in DMF a 25°C. First sweep at different scan rates.

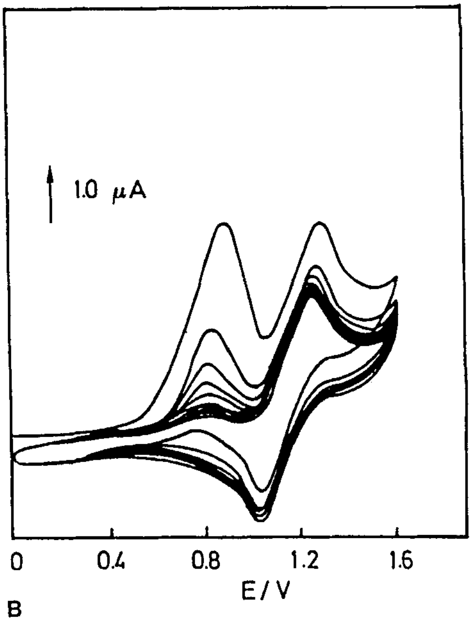

FIG. 1 B.- Cyclic voltammetry of p-NBBr in DMF a 25°C. Multiple scans at 200 mV $s^{-1}$.

TABLE 1

CV date for p-NBBr in DMSO and DMF vs saturated calomel electrode

| Solvent | | - Epc/V | Δ Ep/V |
|---|---|---|---|
| DMSO | wave I | 0,72 | - |
| | wave II | 1,26 | 0,063 |
| DMF | wawe I | 0,86 | |
| | wave II | 1,27 | 0,066 |

## RESULTS AND DISCUSSION

Linear sweep cyclic voltammograms of p-NBBr were recorded under identical conditions in DMSO and DMF. The scan was initiated always in the negative direction from 0.0 V. Figures 1A and 1B show the cyclic voltammograms, exhibiting two well defined reduction waves (Table 1).

The first cathodic wave (I), in both solvents, has no anodic response and presents irreversible behavior in the whole range of sweep rates used (20 - 500 V/s).

From this study it can be seen that ip increases linearly with the sweep rate and $ip/v^{1/2}$ is constant in the speed range observed. The Ep shifts catodically with increasing v. When successive sweeps are recorded (Fig 1B) the loss of the first cathodic wave is detected showing that chemical reactions are associated with the electrochemical process being studied.

Accordingly, the following mechanism can be put forth for the compound's electrochemical behavior in aprotic solvents.

In the initial step, reduction of the starting material originates the anion radical (p-NBBr$^{\overline{\cdot}}$) according to the following equation:

$$Br\text{-}CH_2\text{-}C_6H_4\text{-}NO_2 \;+\; e \;\Longleftrightarrow\; (Br\text{-}CH_2\text{-}C_6H_4\text{-}NO_2)^{\overline{\cdot}} \qquad (I)$$

A spectrum can be recorded in the EPR cavity, which presents an hyperfine structure deriving from the interaction of the unpaired electron with a nitrogen nucleus and three pairs of equivalent protons ( Fig 2). The values of the coupling constants corresponding to the spectrum of p-nitrobenzyl bromide anion radical in DMSO are the following: $a_N = 0.957$ mT, $a_H{}^o = 0.332$ mT, $a_H{}^m = 0.216$ mT, $a_H CH_2 = 0.083$ mT. The coupling constant for the halogen could not be detected (6).

In a second step, we postulate an intramolecular electron transfer with the resulting breakage of the C-Br bond, originating the p-nitrobenzyl radical and a bromide ion according to equation (II):

$$(Br\text{-}CH_2\text{-}C_6H_4\text{-}NO_2)^{\overline{\cdot}} \;\Longleftrightarrow\; {\cdot}CH_2\text{-}C_6H_4\text{-}NO_2 \;+\; Br^- \qquad (II)$$

This bond scission is favored by the strong electron affinity of the nitro group, which reduces charge density in the ring, as also happens with substituents such as CN and

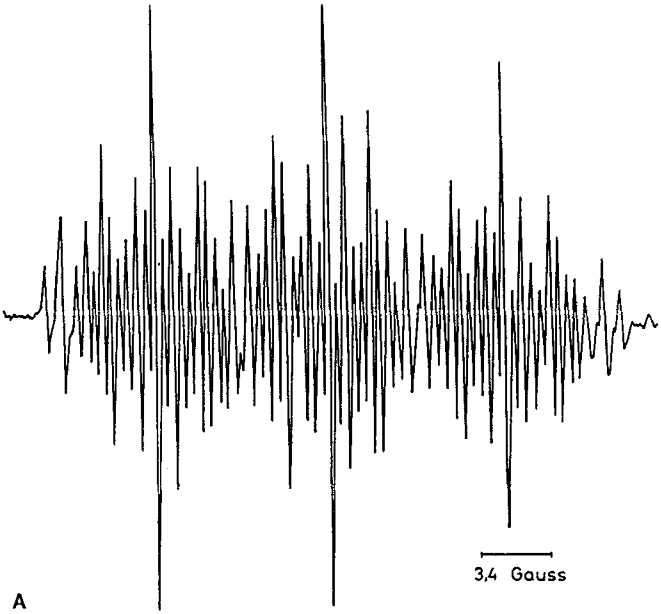

FIG. 2 A.- Experimental EPR spectrum of p-NBBr- radical in DMSO.

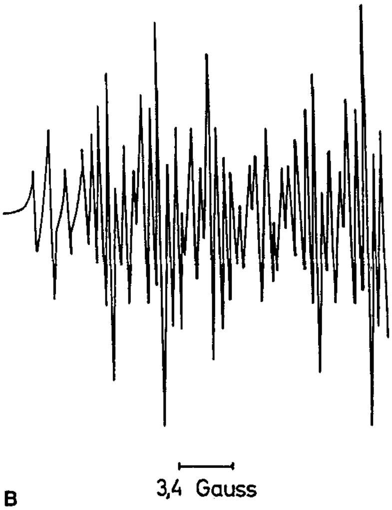

FIG. 2 B.- Simulated spectrum of p-NBBr- in DMSO.

$COCH_3$ (3). In addition, the electron accepting ability of bromine facilitates formation of the bromide ion and the corresponding C-Br bond breakage (4).

The reduction of the p-nitrobenzyl radical $\cdot CH_2-C_6H_4-NO_2$ may also occur through H-atom abstraction (7), with the concomitant formation of p-nitrotoluene, according to equation (III).

$$\cdot CH_2-C_6H_4-NO_2 + CH_3-SO-CH_3 \text{------>} CH_3-C_6H_4-NO_2 + CH_3-SO-CH_2\cdot \qquad \text{(III)}$$

When the first potential scan is performed in the range of seep rates used, no alterations are observed maintains the first wave irreversible. On the contrary, by repeated cycles involving the second cathodic peak, the first wave diminishes progressively and eventually disappears. The experimental data are consistent with the hypothesis that the irreversibility of the first wave is due to chemical reactions associated with the electrochemical process.

The second voltammetric wave (II), corresponds to a reversible couple over the whole range of sweep rates, the difference between the anodic and cathodic peak potentials being 60 mV for sweep rates in the range 20 -500 mV $s^{-1}$. The current function $ip/v^{1/2}$ is constant for both couples, indicating that the processes are diffusion controlled. This couple may be assigned to a reductive process involving the transfer of one electron (equation IV) with formation of the

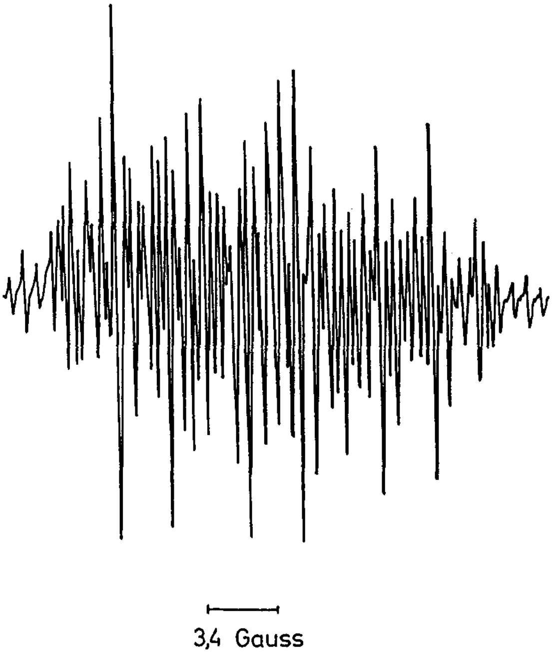

FIG. 3.- Experimental spectrum of p-nitrotoluene anion radical in DMF.

p-nitrotoluene anion radical, a stable species which can be detected by EPR:

$$CH_3-C_6H_4-NO_2 + e \dashrightarrow ( CH_3-C_6H_4-NO_2 )^{\cdot-} \tag{IV}$$

The radical obtained in DMF shows a well resolved spectrum (Fig 3) which was analyzed and simulated in terms of a triplet due to the nitrogen nucleus, a triplet due to the C-2 and C-6 aromatic ring protons, another due to the C-3 and C-5 protons, and a quadruplet due to the methyl protons. The same hyperfine pattern is seen in DMSO. The coupling constants correspond to those already reported for the spectrum of p-nitrotoluene (8).

The results give additional support for the intermediacy of these anion radicals in many reactions of the parent substrates in several organic substitutions at room temperature (2,3,4). The EPR studies at room temperature permit to prove the formation of these anion radicals and their following destiny. The use of cyclic voltammetry and electron spin resonance permits to infer that small molecules like p-nitrobenzyl bromide are good models for the study of electron transfer mechanisms, suggesting the possibility of extending these results to more complex systems.

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