Cyclic voltammetric behaviour of the $O_2/O_2^{\bullet -}$ redox couple at a HMDE and its interaction with nisoldipine

M.E. Ortiz, L.J. Núñez-Vergara, J.A. Squella *

Bioelectrochemistry Laboratory, Chemical and Pharmaceutical Sciences Faculty, University of Chile, PO Box 233, Santiago 1, Chile

Abstract

We have studied the $O_2/O_2^{\bullet -}$ redox couple on the HMDE in DMSO aprotic media, obtaining optimal conditions of both oxygen concentration and scan rate in order to avoid oscillatory phenomena. By choosing the oxygen concentration and scan rate appropriately we obtained well-resolved reversible and reproducible cyclic voltammograms for the $O_2/O_2^{\bullet -}$ redox couple. A ΔE_p value of 63.0 ± 5.2 mV for scan rates between 0.6 and 10 V s^{-1} was obtained. The current ratio, I_{pa}/I_{pc}, depended on the scan rate, tending to one as the scan rate increased suggesting that oxygen reduction followed an EC mechanism with the second order superoxide disproportionation reaction as the chemical step. We have found a disproportionation constant value of 4.08×10^3 M^{-1} s^{-1} with a standard deviation of ± 208 and a coefficient of variation of 4.8%. Furthermore, we have used the cyclic voltammetric response of the $O_2/O_2^{\bullet -}$ redox couple in order to study the interaction of the dihydropyridine drug nisoldipine with superoxide. With the addition of nisoldipine, the cyclic voltammogram was changed indicating that $O_2^{\bullet -}$ reacts with nisoldipine within the time scale of the cyclic voltammetry. We have found that superoxide acts as a Brönsted base, deprotonating nisoldipine, and consequently nisoldipine acts by scavenging $O_2^{\bullet -}$.

Keywords: Superoxide; Cyclic voltammetry; Nisoldipine; Proton abstraction

1. Introduction

Research concerning the cellular origins and physiological consequences of free radicals now occupies thousands of investigators worldwide. Some of these scientists are examining the potential role of reactive oxygen species (superoxide anion, hydroxyl radical and hydrogen peroxide) in a long list of maladies, including atherosclerosis, cancer, inflammatory disease and cataracts. These highly reactive molecules have been suggested as agents not merely of disease, but also of the aging process itself. The superoxide anion, $O_2^{\bullet -}$, can be induced by electron transfer reaction in vivo to generate the other active oxygen species such as hydroxyl free radical and hydrogen peroxide.

Although the electrochemical reduction of oxygen to superoxide anion in aprotic solvents has been known since 1965 [1–5] there is still great interest in this type of research. Therefore, much research for screening bioactive compounds either to scavenge $O_2^{\bullet -}$ or to inhibit $O_2^{\bullet -}$ generation is of particular interest. As a consequence, such research requires the use of methods that may be able both to generate and detect $O_2^{\bullet -}$ in solutions. Photochemical, enzymatic, pulse radiation, chemical reaction followed by spectrophotometry as well as electron spin resonance (ESR) and electrochemical techniques have been employed for this purpose [6–10]. Among these techniques, the use of cyclic voltammetry for generation and detection of $O_2^{\bullet -}$ by the electrochemical reduction of molecular oxygen appears to be a convenient method mainly for two reasons. First, $O_2^{\bullet -}$ is derived from the direct electro-reduction of dissolved oxygen in a simple medium without other initial compounds that are used to generate $O_2^{\bullet -}$ by other means and so this method can ensure that the following reaction of $O_2^{\bullet -}$ is free from the influence of these initial compounds. Second, this method can instantly follow the reaction of $O_2^{\bullet -}$ with bioactive compounds at the electrode surface.

The electrochemical reduction of oxygen to superoxide has been studied for several media and electrode

E-mail address: asquella@ciq.uchile.cl (J.A. Squella).

materials. A first medium is the usual aprotic solvents [11–14], such as acetonitrile (AN), dimethylsulfoxide (DMSO) and *N*,*N*-dimethylformamide (DMF).

A second is alkaline media in the presence of surfactants such as triphenylphosphine oxide (TPO) [15,16], α-quinoline [17,18] and isoquinoline [19,20]. More recently, Song et al. [21], developed a new medium system containing a water-soluble surfactant, sodium dodecyl sulfate (SDS) suitable for studying superoxide and its reaction in aqueous solution. On the other hand, the study of the $O_2/O_2^{\bullet -}$ couple as a function of electrode material has been carried out for platinum, gold, mercury and glassy carbon in several aprotic solvents [13], but the great majority of the work related to the cyclic voltammetry of the couple $O_2/O_2^{\bullet -}$ in aprotic media is restricted to platinum, gold and carbon electrodes [1,4,14,13]. Curiously, when mercury electrodes were used [4,13], generally Hg (Pt) was employed but never the normal hanging mercury drop electrode (HMDE). Probably, this is because of the recently described [22,23] oscillatory phenomena occurring in CVs of the $O_2/O_2^{\bullet -}$ couple on a HMDE in non-aqueous aprotic media. This oscillatory phenomenon produces strong distortion in the cyclic voltammograms so that quantitative reproducible measurements cannot be obtained.

In this work we employed a cyclic voltammetric method on a HMDE in non-aqueous aprotic media to study the couple $O_2/O_2^{\bullet -}$ and the interaction between superoxide and a well-known 1,4-dihydropyridine–calcium antagonist drug such as nisoldipine (Fig. 1). Previous studies have suggested [24–29] that these types of drugs provide an antioxidant protective effect that may contribute to their pharmacological activity. Thus, 1,4-dihydropyridine derivatives, in addition to their well-known effect on calcium metabolism, could themselves have an antioxidant effect. Specifically, it has been demonstrated that nisoldipine behaves as an antioxidant drug [29,30]. Consequently the feasibility that nisoldipine could exert a protective effect by direct reaction with superoxide anion is an interesting challenge to explore. To resolve this point cyclic voltammetry is a very useful tool.

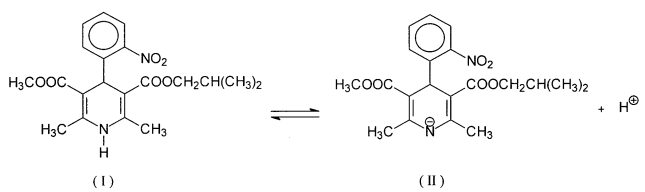

Fig. 1. Chemical structure of nisoldipine (I) and its anionic form (II).

2. Experimental

2.1. Reagents

The aprotic solvent, dimethylsulfoxide (DMSO) used in electrochemical experiments was purchased from Merck and was dried with 3-Å molecular sieves. Nisoldipine (100% chromatographically pure) was provided by Laboratorio Chile (Santiago, Chile). Unless different condition are given, all the experiments were carried out in aprotic (100% DMSO) media with 0.1 M tetrabutylammonium perchlorate (TBAP) purchased from Fluka. Oxygen (99.8% pure) and nitrogen (99.9% pure) were purchased from AGA (Santiago, Chile).

2.2. Apparatus and procedures

Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) experiments were performed with a BAS CV-50 W voltammetric analyzer. All the measurements were carried out in a three-electrode measuring cell. A hanging mercury drop electrode (HMDE), a platinum wire counter electrode and an Ag | AgCl | KCl(sat) reference electrode were used for the measurements. Alternatively Au and glassy carbon disc electrodes with areas of 0.02 and 0.071 cm^2, respectively, were also used. For measurements in oxygen media, O_2 gas was bubbled directly into the cell in order to obtain fixed concentrations of oxygen, and during the measurement, O_2 gas was flushed over the cell solution. In order to maintain a fixed oxygen concentration in the measurement cell an apparatus consisting of two flow-meters (Cole Palmer 316SS) for oxygen and nitrogen, respectively, equipped with needle valves were used. Given the oxygen solubility in DMSO containing 0.1 M TEAP [31] and by establishing oxygen and nitrogen flow rates, it was possible to determine the concentration of oxygen in the gas passing through the measurement cell [32]. All cyclic voltammograms were carried out at a constant temperature of 25 °C. The return-to-forward peak current ratio, I_{pa}/I_{pc}, for the oxygen/superoxide couple was measured for each cyclic voltammogram varying the scan rate from 0.05 up to 50 V s^{-1} according to the procedure described by Nicholson [33].

2.3. Controlled potential electrolysis

Controlled potential electrolysis (CPE) was carried out using a mercury pool cathode ($A = 10.18$ cm^2). The applied potential (-1000 mV) was obtained using a WENKING POS 88 potentiostat as a source. This electrolysis was carried out in a two-compartment cell with the counter electrode separate from the pool electrode. In the three-electrode system, an Ag | AgCl | KCl(sat) electrode was used as the reference

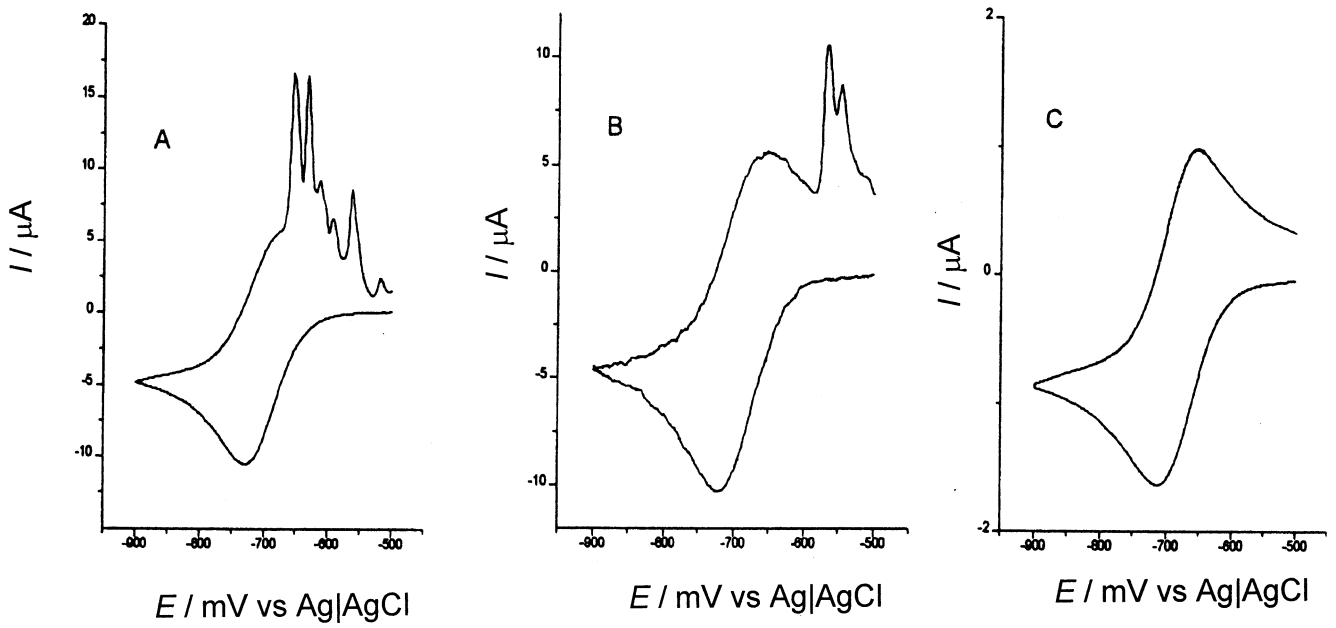

Fig. 2. CVs of the $O_2/O_2^{\bullet -}$ redox couple in O_2 + DMSO solutions at different oxygen concentrations at the HMDE. (A) 2.1×10^{-3} M (B) 1.1×10^{-3} M (C) 2.08×10^{-4} M. Sweep rate: 0.1 V s^{-1}.

electrode. Before each experiment, the solutions were first degassed with nitrogen, and then saturated with oxygen. The solution was stirred continuously for 10 min of electrolysis. CPE was followed by DPV or CV methods for proving the generation of superoxide radical anion and by DPV to follow the reaction of nisoldipine.

The concentration of superoxide anion generated by controlled potential electrolysis of an oxygen-saturated solution in DMSO was determined by the total charge used in the reaction.

3. Results and discussion

In spite of there being much work related to the study of the redox reaction of $O_2/O_2^{\bullet -}$ only two studies were carried out on the hanging mercury drop electrode (HMDE). Specifically, these studies [22,23] deal with the current oscillatory phenomena observed in the redox reaction of $O_2/O_2^{\bullet -}$ couple on the HMDE in acetone media [22] and in non-aqueous aprotic media [23]. We selected the HMDE to carry out a comprehensive study on the electrochemical generation and later interaction of the superoxide anion with the xenobiotic, nisoldipine.

Fig. 2 shows the cyclic voltammograms (CVs) obtained on the HMDE at different oxygen concentration solutions in DMSO containing 0.1 M tetra(*n*-butyl)ammonium perchlorate (TBAP). Surprisingly we found that the oscillatory phenomenon is also observed when DMSO is used as the solvent. This finding is in disagreement with that found in previous work [22,23] wherein the oscillatory phenomenon was not observed with DMSO as the solvent. However if we compare cyclic voltammograms for solutions with different oxygen concentrations, we can appreciate (Fig. 2A–C) that when the oxygen concentration decreases, the oscillatory phenomenon also diminishes and finally disappears completely. Furthermore, we have also observed a dependence between the sweep rate and the presence of the current oscillations. In Fig. 3A–C we observe that, as the sweep rate increases, the current oscillations in the voltammograms disappear. In order to obtain the optimal conditions of oxygen concentration and scan rate we have recorded many voltammograms changing both parameters and examining the appearance and disappearance of the current oscillation phenomenon. As can be seen in Fig. 4 we have obtained a curve that describe the interface between oscillatory and non-oscillatory areas. This curve fits very well ($r^2 = 1$) with the following equation:

$$v = 0.064 - 0.297c + 1.218c^2 - 1.121c^3 + 0.544c^4 \qquad (1)$$

where v is the scan rate (V s^{-1}) and c is the concentration (mM). Consequently, by choosing the oxygen concentration and scan rate appropriately we can obtain well-resolved reversible cyclic voltammograms for the $O_2/O_2^{\bullet -}$ couple.

In Fig. 5 we show CVs for the $O_2/O_2^{\bullet -}$ couple obtained for a 1.1×10^{-3} M oxygen solution at different scan rates. We have obtained a ΔE_p value of 63 ± 5.2 mV for a scan rate range between 0.6 and 10 V s^{-1}, corresponding to the reversible one electron reduction of oxygen to produce superoxide anion radical. As can be seen in the inset of Fig. 5 the current ratio,

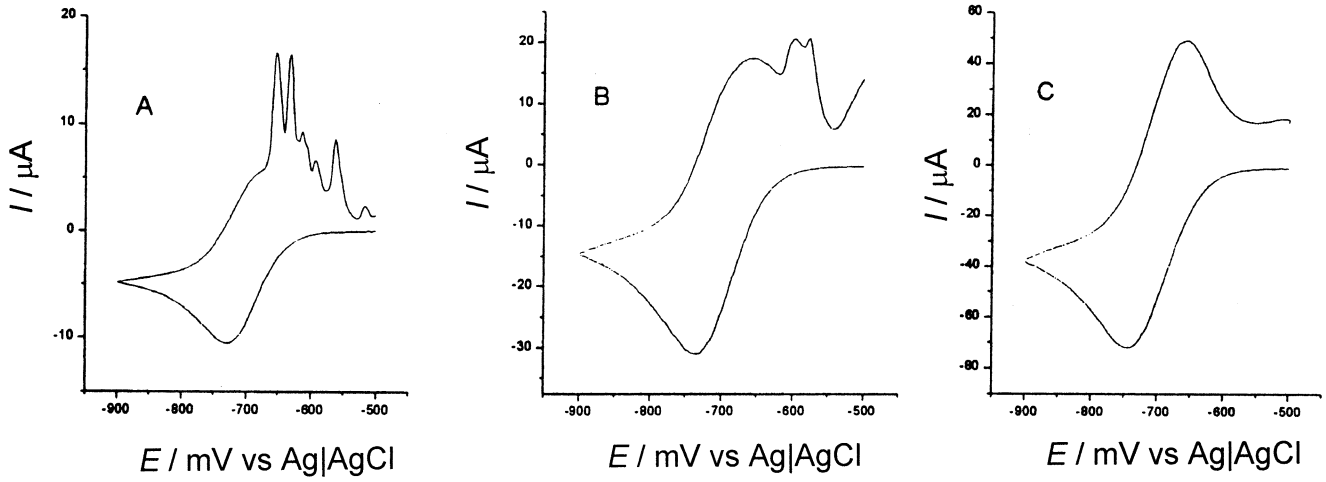

Fig. 3. CVs of the $O_2/O_2^{\bullet -}$ redox couple at the HMDE in O_2-saturated DMSO solution at different sweep rates. (A) 0.1 V s^{-1} (B) 1 V s^{-1} (C) 7 V s^{-1}.

I_{pa}/I_{pc}, depends on the scan rate, tending to one as the scan rate increases. This diagnostic criterion fulfils the requirements for an irreversible chemical reaction following a reversible charge transfer step, i.e. an EC_i process [34]. Furthermore an increase in the oxygen concentration results in a decrease of I_{pa}/I_{pc}. This result is a diagnostic criterion suitable to demonstrate that the rate of the chemical step is not first-order [35]. Consequently the chemical step can be ascribed to the well-known [36] second-order disproportionation reaction of the superoxide anion to complete the EC_i mechanism according to the following equations:

$$O_2 + e^- \leftrightarrow O_2^{\bullet -} \quad (2)$$

$$2O_2^{\bullet -} \rightarrow O_2 + O_2^{-2} \quad (3)$$

The second-order rate constant of the disproportionation reaction was assessed from cyclic voltammograms according to the procedure of Olmstead and Nicholson [37] as is detailed in a previous paper [38]. Confirming the second order character of the following chemical reaction (superoxide disproportionation), plots of the kinetic parameter, ω, versus the time constant, τ, were linear (Fig. 6). From the slope of this straight line we obtained the second order rate constant, k_2, for the decay of the superoxide anion radical. We found a k_2 value of 4.38×10^3 M^{-1} s^{-1} with a standard deviation of ± 208 and a coefficient of variation of 4.8% for ten independent sets of experiments.

In order to study the interaction of the xenobiotic nisoldipine with superoxide we have examined the effect of adding this drug on the cyclic voltammetric response of the $O_2/O_2^{\bullet -}$ couple. Fig. 7 shows the cyclic voltammograms of various concentrations of nisoldipine solutions in oxygenated DMSO containing 0.1 M TBAP. Also Fig. 7D shows a cyclic voltammogram of a solution of nisoldipine in non-oxygenated solution, which shows that nisoldipine does not produce any electrochemical signal in this potential zone. With the addition of nisoldipine, the oxidation peak current of $O_2^{\bullet -}$ (anodic current, oxygen regeneration) decreases, while the reduction current (cathodic current, $O_2^{\bullet -}$ formation) increases. These data suggest that nisoldipine reacts with $O_2^{\bullet -}$, that is, it scavenges $O_2^{\bullet -}$ in DMSO, in a concentration-dependent way. Furthermore, from the experiments in Fig. 7 we can conclude that the addition of nisoldipine to an oxygen solution in DMSO causes the one-electron process to become a two-electron reduction. The two-electron reduction mechanism can be ascribed as follows:

$$2(O_2 + e^- \rightarrow O_2^{\bullet -}) \quad (4)$$

$$2O_2^{\bullet -} + 2NIS{-}NH \rightarrow 2HO_2^{\bullet} + 2NIS{-}N^- \quad (5)$$

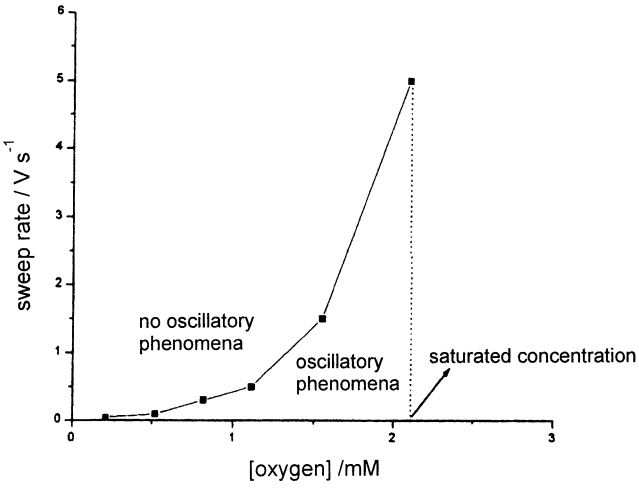

Fig. 4. Curve showing the dependence of the oscillatory phenomena on both sweep rate and oxygen concentration in DMSO at the HMDE.

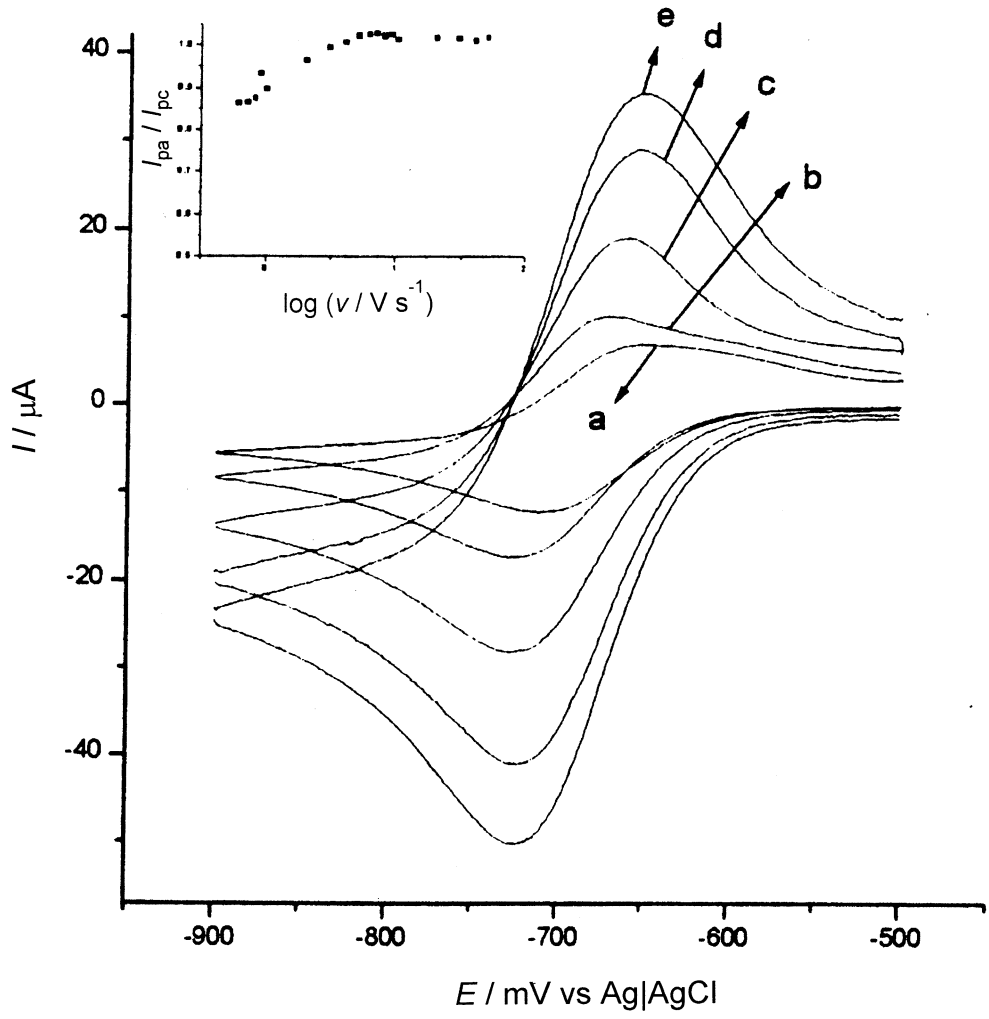

Fig. 5. CVs of the $O_2/O_2^{\bullet -}$ redox couple at different sweep rates. (a) 0.6 V s^{-1}; (b) 1 V s^{-1}; (c) 3 V s^{-1}; (d) 7 V s^{-1}; (e) 10 V s^{-1}. Inset: I_{pa}/I_{pc} ratio for the $O_2/O_2^{\bullet -}$ couple at different sweep rate values.

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (6)$$

giving the following overall reaction:

$$O_2 + 2NIS{-}NH + 2e^- \rightarrow 2NIS{-}N^- + H_2O_2 \quad (7)$$

where NIS–NH and NIS–N^- represent nisoldipine and the anionic form of nisoldipine respectively (species I and II in Fig. 1). Similar effects were reported by other authors when moderately weak acids such as phenol [13] or certain aromatic ketones [39] were present in excess. However to date no work has reported this effect in dihydropyridine compounds. In the present study superoxide anion acts as a Brönsted base deprotonating nisoldipine and nisoldipine acts by scavenging $O_2^{\bullet -}$. Although the primary reactive mode of $O_2^{\bullet -}$ is as a base, it is able to facilitate oxidations carried out by O_2 in a sequence of steps initiated by proton abstraction [40], following a mechanism analogous to that of base-catalyzed auto-oxidations [41,42].

In order to prove that superoxide acts by proton abstraction, producing nisoldipine anion we carried out the following experiments. First, we electrogenerated superoxide anion exhaustively by controlled potential electrolysis (CPE) in a DMSO oxygenated solution containing 0.1 M TBAP at a mercury pool cathode. Second, we added increasing quantities of the previ-

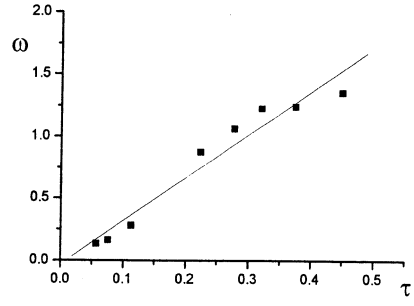

Fig. 6. Plot of the kinetic parameter, ω, with the time constant, τ, for the $O_2/O_2^{\bullet -}$ redox couple.

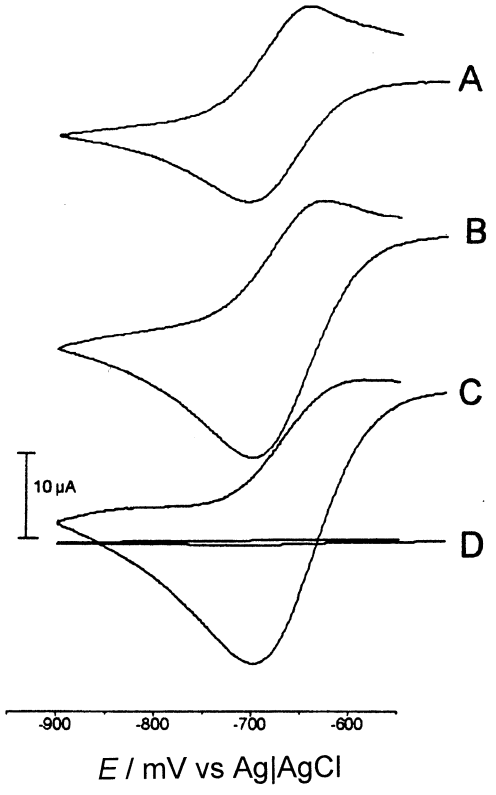

Fig. 7. CVs of the $O_2/O_2^{\bullet -}$ redox couple in the presence of different nisoldipine concentrations. (A) Without nisoldipine; (B) 5 mM; (C) 10 mM. Curve (D) shows the CV of 1 mM nisoldipine without oxygen. Sweep rate: 1 V s^{-1}.

ously formed superoxide solution to a cell containing 1 mM nisoldipine in DMSO + 0.1 M TBAP solution and then we followed the response of the nisoldipine signal using differential pulse voltammetry. In Fig. 8A we show the voltammogram corresponding to a nisoldipine solution (without added superoxide) showing two voltammetric peaks, i.e. one main peak at − 1215 mV and a minor peak at − 1430 mV. The voltammetric change as a consequence of adding superoxide is shown in Fig. 8B,C. In these figures we can observe that, when superoxide is added, the voltammetric signal at − 1215 mV disappears and the peak at − 1430 mV increases considerably. The gradual disappearance of the peak at − 1215 mV is related directly to the quantity of superoxide added. These results suggest a change of the electroactive species as a consequence of adding superoxide. On the other hand we repeated the same experiment described in Fig. 8, but instead of superoxide, we added the base tetrabutylammonium hydroxide (TBAH). As can be observed in Fig. 9 we obtained the same behavior, suggesting that superoxide acts as a base, changing the electroactive species. Moreover in a previous paper [43] we have proved that for 4-(nitrophenyl) substituted 1,4-dihydropyridine compounds in aprotic media, the ionized (II) and unionized (I) forms are in equilibrium according to the equation in Fig. 1. The equilibrium was displaced by adding a base, and both ionized and unionized species were determined

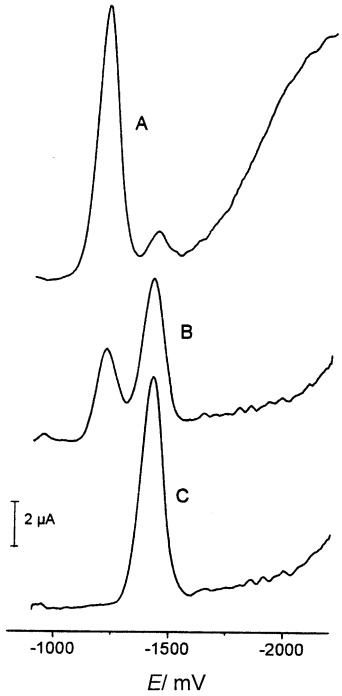

Fig. 8. DPV of 1 mM nisoldipine in DMSO + 0.1 M TBAP at different concentrations of electrogenerated superoxide. (A) Without superoxide; (B) 6.3×10^{-6} M; (C) 1.26×10^{-5} M.

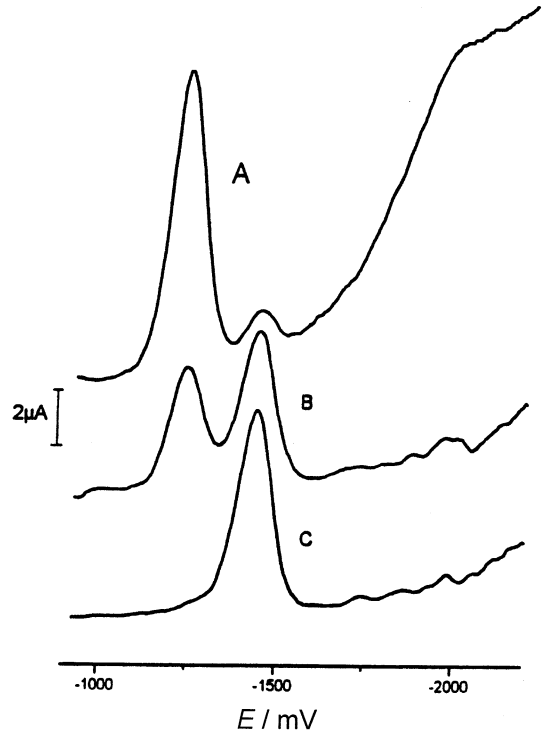

Fig. 9. DPV of 1 mM nisoldipine in DMSO + 0.1 M TBAP with different concentrations of tetrabutylammonium hydroxide. (A) Without base; (B) 5×10^{-5} M; (C) 1×10^{-4} M.

selectively using electrochemical and spectrophotometric methods. Considering these previous results we can explain the above observed effect of adding superoxide (Fig. 8) as due to the existence of two species of nisoldipine, i.e. ionized and unionized. In fact the peak observed at -1215 mV is due to the reduction of the unionized form of nisoldipine and the peak at -1430 mV is due to the ionized form. This assignment is in accord with the well-known fact that negatively charged species are more difficult to reduce than the corresponding uncharged species. Consequently the correct interpretation of the experiments observed in Fig. 8 is in line with the equation proposed above in Eq. (4).

4. Conclusions

We have investigated the current oscillation phenomenon, which arises in the redox reaction of $O_2/O_2^{\bullet -}$ couple at the HMDE in aprotic media and we have found the optimal working conditions of sweep rate and oxygen concentration in order to prevent the oscillation phenomena from occurring. Furthermore the results of CV measurements reported in this paper provide conclusive evidence that the presence of nisoldipine influences the $O_2/O_2^{\bullet -}$ redox couple by interaction between superoxide anion and nisoldipine. The results show that this interaction can be explained by the proposal that superoxide acts by proton abstraction producing nisoldipine anion. The rate of the proton abstraction is sufficiently rapid to the point that it can be observed and studied within the time-scale of cyclic voltammetry.

Acknowledgements

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