Voltammetric determination of the heterogeneous charge transfer rate constant for superoxide formation at a glassy carbon electrode in aprotic medium

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Abstract

A detailed investigation on the electrochemical reduction of oxygen was carried out using cyclic voltammetry at a glassy carbon electrode in dimethylsulphoxide (DMSO) containing 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. A diffusion-limited, quasi-reversible one-electron peak corresponding to the oxygen-superoxide anion couple is seen. The quasi-reversibility was supported by the ΔE_p and I_p behavior with the square root of the scan rate, which is typical for a quasi-reversible process. We have used the theory developed by Nicholson for a study of the electrode reaction kinetics in order to measure a precise and reproducible value for the standard rate constant, k^0, of the quasi-reversible reduction of oxygen to superoxide anion. The k^0 mean value obtained was 9.3×10^{-2} with a standard deviation of $\pm 0.4 \times 10^{-2}$ cm s^{-1}, and a coefficient of variation of 4.6%. The k^0 value obtained was compared with both a previous value found in the literature and with simulated curves.

1. Introduction

Superoxide ($O_2^- {}^\bullet$), the product of the one-electron reduction of molecular oxygen (Eq. (1)) is one of the reactive oxygen species easily produced and is implicated in several harmful biological processes such as lipid peroxidation and protein denaturation.

$$O_2 + e^- \rightarrow O_2^- {}^\bullet \tag{1}$$
$$2O_2^- {}^\bullet \rightarrow O_2 + O_2^{2-} \tag{2}$$

On the other hand, $O_2^- {}^\bullet$ reacts in many different ways, e.g. as a Brønsted base, an oxidant, a nucleophile, a one-electron reductant and a radical, in aprotic media [1–3]. Because of its versatility, electrochemical techniques (especially cyclic voltammetry) have been employed for studying its generation, detection and reactivity towards different compounds [4–8] at different electrodes. In the study of electrode reaction mechanisms it is important to know the kinetic parameters of the processes involved and so it is useful to be able to obtain a rapid estimation of electron transfer rates experimentally.

There is much work related to the study of the redox reaction of $O_2/O_2^- {}^\bullet$, but the majority of this is related to the dismutation process (Eq. (2)) and only a few studies are related to the kinetics of the electrochemical step, wherein the calculation of the heterogeneous charge transfer rate constant at a glassy carbon electrode was the main objective [9,10].

In previous work we have found [4] that, at a mercury electrode, the heterogeneous rate constant (k^0) of the one-electron reduction of oxygen to produce superoxide is sufficiently high to appear reversible on the time scale of the cyclic voltammetric experiment. However, when the electrode is glassy carbon the results are different and rather contradictory. One paper [9] reveals that oxygen is reduced to superoxide in a one-electron reversible step but in another paper [10] the same transfer is found to be quasi-reversible. We have not found any work in the literature relating to the precision

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and exactitude of the k^0 values obtained experimentally. In this paper we have used the procedure described by Nicholson [11] in order to obtain a reliable k^0 value for the redox couple O_2/O_2^- $^\bullet$ (Eq. (1)) in DMSO and 0.1 M TBAP. We have developed a comprehensive study involving a large series of measurements at different scan rates in order to investigate the reproducibility, exactitude and precision of the k^0 value. Furthermore, we have used cyclic voltammetric simulation to verify the k^0 value obtained.

2. Experimental

2.1. Reagents

The aprotic solvent, dimethylsulfoxide (DMSO), used in the electrochemical experiments was purchased from Merck and was dried with 3 Å molecular sieves. All the electrochemical experiments were carried out in aprotic media (100% DMSO) 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) experiments were performed with a BAS CV-50 W voltammetric analyzer. All the measurements were carried out in a three-electrode measuring cell. A glassy carbon disc electrode with an area of 0.071 cm^2, a platinum wire counter electrode and a Ag | AgCl | NaCl(sat) reference electrode were used for the measurements. The glassy carbon disk working electrode was polished using successively 0.3 and 0.05 μm alumina powder on a polishing cloth before each experiment.

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 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. Knowing the oxygen solubility in DMSO containing 0.1 M TEAP [12] and by establishing the oxygen and nitrogen flow rates, it was possible to determine the concentration of oxygen in the gas passing through the measurement cell [13]. All cyclic voltammograms were recorded 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 [14].

The standard heterogeneous charge transfer rate constant (k^0) associated with the redox process of Eq. (1) was calculated from the peak-to-peak separation (ΔE_p) of the cyclic voltammogram according to the method described by Nicholson [11]. All the measurements were *IR* compensated with positive-feedback circuitry to make sure a minimized uncompensated resistance. E_λ was selected at least $90/n$ mV beyond the cathodic peak, where n is the number of electrons involved in the reaction.

Simulated CV curves were obtained using DIGISIM$^\circledR$ 2.1 CV (BAS) Simulator for Windows software. The software was run using a Gateway 2000 PC.

3. Results and discussion

Cyclic voltammograms of a saturated O_2 DMSO + 0.1 M TBAP solution at a glassy carbon electrode at different scan rates, were recorded between 0.05 V and 50 V s^{-1}. For all experiments the negative sweep started at -400 mV and finished at -1000 mV versus Ag | AgCl | NaCl(sat). In Fig. 1 we can observe CVs for the oxygen/superoxide couple obtained in an oxygen saturated DMSO solution at various potential scan rates. The return-to-forward peak current ratio, I_{pa}/I_{pc}, and the ΔE_p values for the O_2/O_2^- $^\bullet$ couple were measured for each single cyclic voltammogram. The separation between the anodic and cathodic peaks (Table 1) was larger than that expected for a reversible one-electron process of a freely diffusing species, in-
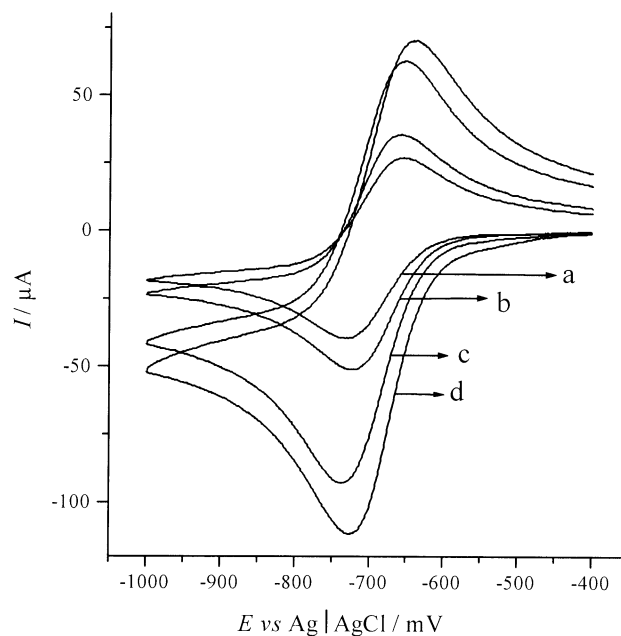

Fig. 1. CVs of the O_2/O_2^- $^\bullet$ redox couple in oxygen-saturated DMSO solution at different sweep rates. (a) 0.05 V s^{-1}, (b) 0.09 V s^{-1}, (c) 0.3 V s^{-1}, (d) 0.5 V s^{-1}.

Table 1
Determination of k^0 from cyclic voltammetry for the reduction of O_2 to $O_2^- \cdot$ in an oxygen-saturated DMSO+0.1 M TBAP solution at glassy carbon

Sweep rate/V s^{-1}	ΔE_p/mV	ψ	k^0/cm s^{-1}
0.1	70	2.38	0.081
0.2	72.5	1.96	0.093
0.4	78.6	1.39	0.093
0.7	83.6	1.02	0.091
0.9	85.8	0.93	0.094
1	88.2	0.86	0.092
1.1	88.8	0.86	0.096
1.5	93.2	0.72	0.094
1.6	94.2	0.71	0.096
1.7	94.2	0.71	0.098
1.8	96.8	0.64	0.091
2.2	99.2	0.60	0.095

Mean±S.D.: 0.093±0.004; CV: 4.6%.

dicating that the redox reaction of the $O_2/O_2^- \cdot$ couple in this medium is only quasi-reversible. We have carried out an exhaustive determination of ΔE_p values at different scan rates finding a linear behavior between ΔE_p and the square root of the scan rate (Fig. 2) which agrees very well with the theory for a typical quasi-reversible process [11]. In fact, according to this theory, the kinetic parameter ψ varies linearly with $v^{1/2}$ and ΔE_p approaches linearity for small ψ; consequently in this zone ΔE_p should vary linearly with $v^{1/2}$. On the other hand the I_{pa}/I_{pc} values were very close to unity, giving an α value = 0.5 for this quasi-reversible process. The quasi-reversibility for this process was also confirmed from the I_{pa} versus $v^{1/2}$ plot, which exhibits an apparent linear trend when it is plotted in a narrow range of scan rates [15] (Fig. 3). With the above results we can be sure
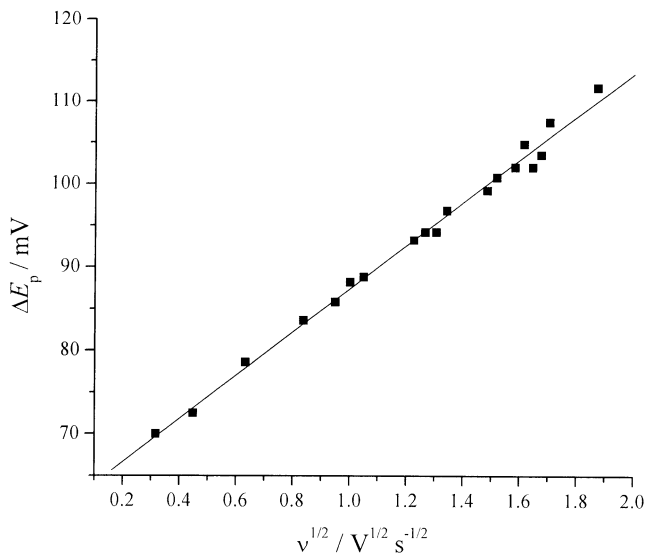

Fig. 2. Quasi-reversible ΔE_p variation with the scan rate for the $O_2/O_2^- \cdot$ redox couple in O_2 saturated DMSO+0.1 M TBAP solution at a glassy carbon electrode.
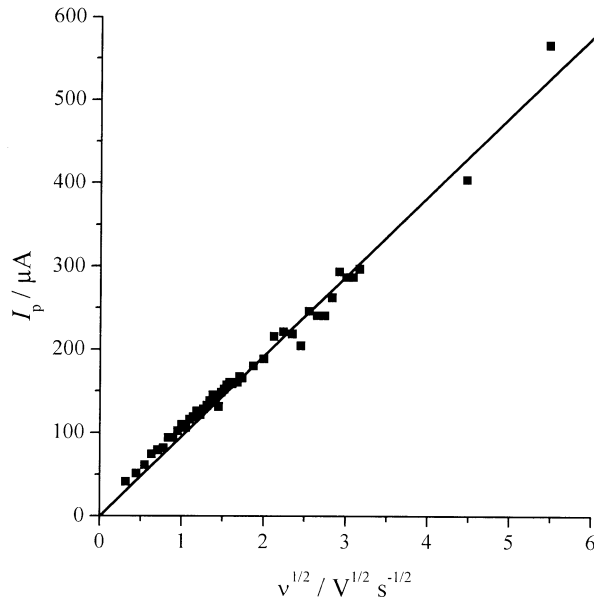

Fig. 3. Quasi-reversible peak current variation with the scan rate for the $O_2/O_2^- \cdot$ redox couple in O_2 saturated DMSO+0.1 M TBAP solution at a glassy carbon electrode.

that any possible uncompensated resistance is sufficiently small that the resulting voltage drops are negligible compared to the ΔE_p attributable to kinetic effects.

Under these conditions of quasi-reversibility it may be possible to study the kinetics of the electrode reaction, and the separation of the peak potentials, ΔE_p, should be a measure of the standard rate constant for electron transfer. These ΔE_p values were introduced in the working curve described by Nicholson [11] for obtaining the transfer parameter, ψ, and then the standard heterogeneous charge transfer rate constant for the electron transfer process according to the following equation [16]:

$$\psi = \frac{(D_0/D_R)^{(\alpha/2)} k^0}{D_0 \pi v (nF/RT)^{1/2}} \qquad (3)$$

To convert experimentally determined values of ψ to k^0, the diffusion coefficients for O_2 and $O_2^- \cdot$ of Collins et al. [8] were used, and a value of α equal to 0.5 was also used.

Results for the reduction of oxygen saturated in DMSO+0.1 M TBAP solution for some selected scan rates are summarized in Table 1.

From our results, a mean value of $9.3 \times 10^{-2} \pm 0.4 \times 10^{-2}$ cm s^{-1} (CV = 4.6%) for the heterogeneous charge transfer rate constant was obtained. This value is in disagreement with that found in a previous work [9], wherein a value equal to 3.2×10^{-2} cm s^{-1} for the reduction of oxygen to superoxide ion in DMSO+0.1 M TBAP solution at a glassy carbon electrode was reported. Obviously a threefold difference is too much

for the same reaction at the same interface; consequently one of these values is erroneous. A relevant aspect in order to support our experimental results is that we have carried out a great number of independent measurements at different sweep rates validating our results statistically. In fact we have found a k^0 value wherein the reproducibility, exactitude and precision were determined, but in the previous paper the authors give only one value for the constant with no evidence of the error in the measurement. Another difference with the previously reported value [9] is that, according to our findings, the process was proved to be quasi-reversible, whereas in the previous paper the authors claimed a reversible one-electron peak for the oxygen reduction to superoxide ion under the same conditions.

In another previous paper [10] a still more different value for k^0 was reported for the reduction of oxygen to superoxide ion in aprotic medium but the difference in this case can be explained by the different nature of the solvent. In fact these authors reported values of 6.9×10^{-3} and 3.4×10^{-3} cm s^{-1} for quinoline and isoquinoline as the aprotic solvent, respectively.

Furthermore, in order to check the value that we obtained for the heterogeneous charge transfer rate constant, k^0, a simulation procedure was used wherein simulated cyclic voltammograms using the k^0 value obtained were compared with the experimental CVs. To obtain the simulated curve we used a mechanism according to the above Eqs. (1) and (2). For Eq. (1) we used an E^0 redox potential of -675 mV, $\alpha = 0.5$ and a k^0 value of 0.094 cm s^{-1}. For Eq. (2) we used $K_{eq} = 0.8$ with $k_f = 7000$ M^{-1} s^{-1} and $k_b = 8750$ M^{-1} s^{-1}. The double layer capacity was adjusted to 2.8×10^{-6} F. We also considered diffusion coefficients of 7.49×10^{-5} and 11.46×10^{-5} cm^2 s^{-1} for oxygen and superoxide, respectively. As can be seen (Fig. 4) we obtained a good correlation between the experimental and simulated cyclic voltammograms, confirming the validity of the heterogeneous charge transfer rate constant value.

4. Conclusions

The redox reaction of the $O_2/O_2^{-\bullet}$ couple at the GCE in DMSO solutions containing 0.1 M TBAP has been observed as a quasi-reversible electrode process on the time scale of the cyclic voltammetry. Using the theory developed by Nicholson [11] for the measurement of the quasi-reversible electrode reaction kinetics, we have evaluated the heterogeneous charge transfer rate constant from a great number of independent measurements at different sweep rates obtaining a statistically validated value of 9.3×10^{-2} cm s^{-1} (CV = 4.6%). This value differs from some previous values reported in the literature for the same reaction.
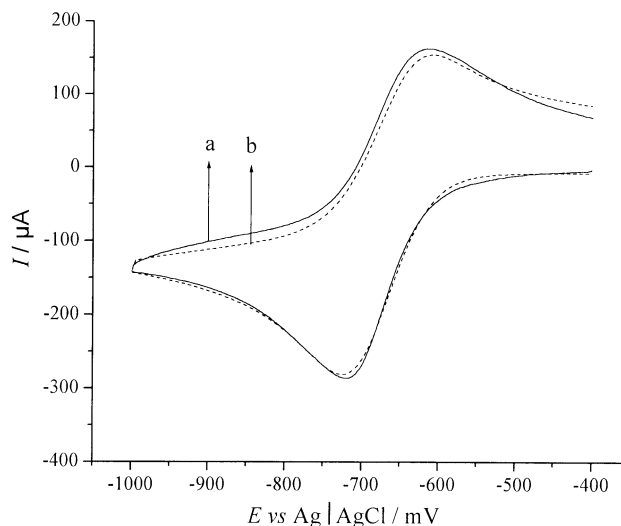

Fig. 4. CV of the $O_2/O_2^{-\bullet}$ redox couple in 1 mM O_2 in DMSO + 0.1 M TBAP solution, (b) simulated cyclic voltammogram of the $O_2/O_2^{-\bullet}$ redox couple. Sweep rate: 2.8 V s^{-1}.

The experimental cyclic voltammograms adjusted very well when compared with simulated ones using the kinetic constant obtained.

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