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Acceleration of the Homogeneous and Electrochemical Reductions of Dioxygen in Aprotic Media by Ammonium Ions. Is the Driving Force a Function of NH_4^+ Concentration? What Is the Mechanism of the Reaction?

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Previous interpretation of homogeneous reduction of dioxygen by the anion radical of C_{60} in aprotic medium in the presence of NH_4^+ , which is based on an electron-transfer driving force depending on NH_4^+ concentration is not tenable because, from first principles, the driving force does not depend on reactant concentrations. Data have been interpreted in a framework of an electron-proton transfer mechanism. An examination of the electrochemical reduction of dioxygen in the presence of NH_4^+ shows that the mechanism is stepwise and allows the determination of key thermodynamic and kinetic parameters. With $\text{C}_{60}^{\bullet-}$ as a homogeneous electron donor, in the framework of the same stepwise mechanism, electron transfer acts as a pre-equilibrium while protonation by NH_4^+ is rate-determining. In all cases, a second electron transfer, which requires less energy than the first, leads after protonation by NH_4^+ to hydrogen peroxide.

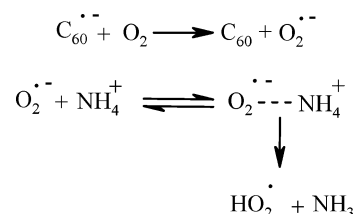
In spite of decades of active research,^{1a} the mechanisms of dioxygen reduction are not fully understood yet.^{1b} This is true for electrocatalysis² but also for electrochemical reduction on inactive electrodes and for homogeneous reductions. Recent additional work has, for example, been necessary to clarify the role of water and other weak acids in the reduction of superoxide ions produced by prior reduction of dioxygen.³ Design and analysis of biomimetic systems are investigated more actively than ever.⁴ In the area of homogeneous reductions, interesting data have been reported recently⁵ concerning the effect of ammonium ions on the reduction of dioxygen by the anion radical of C_{60} in an aprotic medium, namely, a dimethylsulfoxide (DMSO)/chlorobenzene (PhCl) 1:1 mixture. It was observed that the second-order rate constant of electron transfer from $\text{C}_{60}^{\bullet-}$ to O_2 increases with the concentration of NH_4^+ in a linear manner. As a clue to the interpretation of these data, some ESR evidence was given on the formation of a 1:1 complex between $\text{O}_2^{\bullet-}$ and NH_4^+ in the frozen solvent mixture, the complex being too weak to be observed at room temperature. On the basis of this observation, the NH_4^+ concentration effect was interpreted in the framework of the mechanism shown in Scheme 1 by application of the Marcus quadratic relationship between the activation free energy, ΔG^\ddagger , and the driving force, $-\Delta G^0$ ⁶

$$\Delta G^\ddagger = \frac{\lambda}{4} \left(1 + \frac{\Delta G^0}{\lambda} \right)^2 \quad (1)$$

introducing the reorganization energy, λ . To match the linear concentration effect of NH_4^+ , both the driving force and the reorganization energy were deemed to increase with the concentration of NH_4^+ .

This interpretation is incorrect for two essential reasons. First, driving forces do not depend on the concentrations of the

SCHEME 1



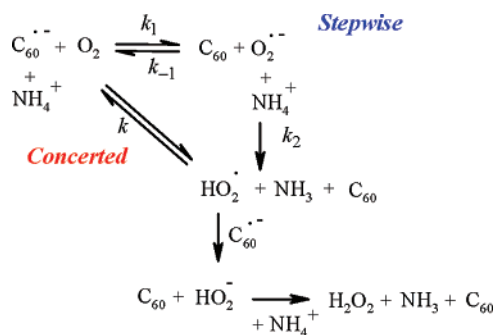
reactants but are defined from their chemical potentials taken in their standard states (μ^0):⁷

$$\Delta G_{\text{C}_{60}^{\bullet-} + \text{O}_2 + \text{NH}_4^+ / \text{C}_{60} + \text{O}_2^{\bullet-} \cdots \text{NH}_4^+}^0 = \mu_{\text{C}_{60}}^0 + \mu_{\text{O}_2^{\bullet-} \cdots \text{NH}_4^+}^0 - \mu_{\text{C}_{60}^{\bullet-}}^0 - \mu_{\text{O}_2}^0 - \mu_{\text{NH}_4^+}^0$$

In addition, in the framework of Scheme 1, NH_4^+ interferes after the first, *irreversible*, electron transfer and therefore has no influence on the rate constant.

We are thus left with two possibilities (Scheme 2): either a concerted associative mechanism in which NH_4^+ is involved

SCHEME 2



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in a termolecular reaction or a stepwise process in which the initial electron transfer is followed by the reaction with NH_4^+ . The converse mechanism, proton transfer followed by electron transfer, need not be considered because dioxygen has no affinity for NH_4^+ .⁵

In the concerted case, the rate law is given by

$$\frac{d[\text{C}_{60}^{\bullet-}]}{dt} = -2k[\text{O}_2][\text{NH}_4^+][\text{C}_{60}^{\bullet-}]$$

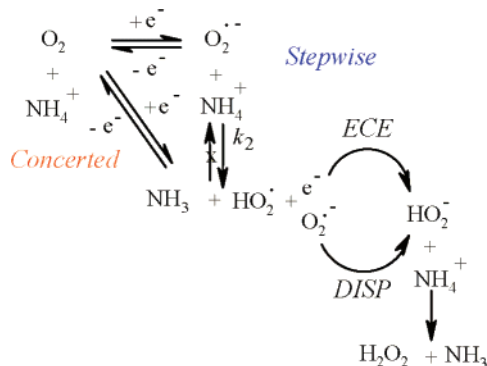
with a driving force

$$\Delta G_{\text{C}_{60}^{\bullet-} + \text{O}_2 + \text{NH}_4^+ / \text{C}_{60} + \text{HO}_2^{\bullet} + \text{NH}_3} = \mu_{\text{C}_{60}}^0 + \mu_{\text{HO}_2^{\bullet}}^0 + \mu_{\text{NH}_3}^0 - \mu_{\text{C}_{60}^{\bullet-}}^0 - \mu_{\text{O}_2}^0 - \mu_{\text{NH}_4^+}^0$$

(which is independent of all reactant concentrations, including $[\text{NH}_4^+]$). It follows that the apparent second-order rate constant is proportional to $[\text{NH}_4^+]$ as observed experimentally. The factor 2 in the above equation is a stoichiometric factor indicating that a second molecule of $\text{C}_{60}^{\bullet-}$ is consumed by the strongly downhill reduction of the HO_2^{\bullet} molecule that has been generated by electron transfer from a first $\text{C}_{60}^{\bullet-}$ molecule, followed by protonation by NH_4^+ (Scheme 2).

As discussed later on, the stepwise mechanism in Scheme 2 may also be compatible with the experimental data. To help solve the problem, we detour through the reductive electrochemistry of dioxygen in the presence of NH_4^+ , for which the same mechanistic dichotomy applies. Here too, a second electron transfer, which requires less energy than the first, has to be considered, leading eventually to hydrogen peroxide (Scheme 3), similarly to previous observations made with other weak Brønsted acids such as phenol.⁸

SCHEME 3



The first electrode material we tried was platinum because it was reported⁵ to give rise to reversible cyclic voltammograms of dioxygen in the presence of NH_4^+ , from which a perfectly linear E_{ap}^0 versus $\log[\text{NH}_4^+]$ plot, with a 60 mV per log unit slope (from 0.003 to 0.3 M NH_4^+), was derived (E_{ap}^0 vs $\log[\text{NH}_4^+]$ is the apparent standard potential obtained as the midpoint between the cathodic and anodic peak potentials).⁹ In fact, no such reversible behavior is observed on a platinum electrode as attested by Figure 1a. Starting from a reversible slow charge-transfer wave, a totally irreversible plateau-shaped wave is obtained rapidly upon addition of NH_4^+ . After an initial positive shift, the location of this wave quickly becomes independent of the concentration of NH_4^+ . A second wave develops simultaneously, corresponding to the direct reduction of NH_4^+ . These results are not surprising in view of the well-known electrocatalytic properties of platinum toward dioxygen

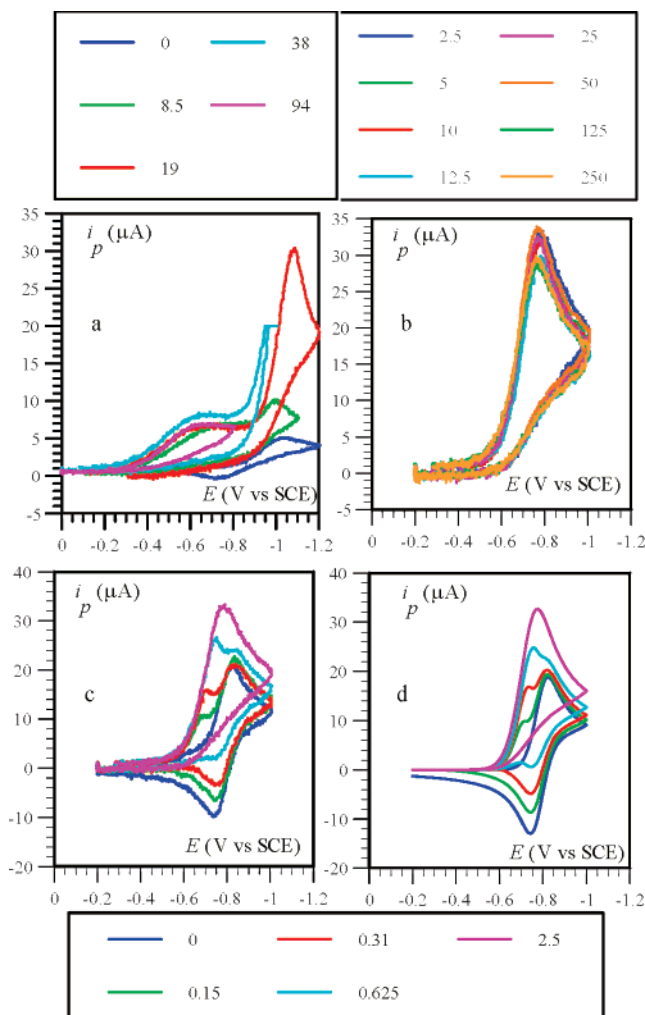


Figure 1. Cyclic voltammograms of O_2 from an air-saturated (2.4 mM) solution as a function of NH_4BF_4 concentration in 1:1 DMSO/ PhCl + 0.1 M $[\text{NBu}_4\text{BF}_4]$ at a platinum electrode (a); in DMSO with $[\text{NH}_4\text{BF}_4] + [\text{NBu}_4\text{BF}_4] = 0.5$ M, at a glassy carbon electrode¹² (b,c); d is the simulation of c. Scan rate, 0.2 V/s; temperature = 24 °C. The numbers in the inserts are the concentrations of $[\text{NH}_4\text{BF}_4]$ in millimoles.

reduction in the presence of proton donors^{1a} and also toward proton reduction.¹⁰

We thus switched to glassy carbon, an electrode material that is not expected to chemically interfere in the course of the reduction. The results are shown in Figure 1b–d. In the absence of NH_4^+ , the dioxygen one-electron wave is chemically reversible but electrochemically irreversible.¹¹ From its shape, height, and location, we obtained the following characteristics: standard potential $E_{\text{O}_2/\text{O}_2^{\bullet-}}^0 = -0.782$ V versus SCE; transfer coefficient $\alpha = 0.5$; diffusion coefficient $D = 4 \times 10^{-5}$ cm² s⁻¹ and standard rate constant $k_s = 0.033$ cm s⁻¹. Upon addition of NH_4BF_4 , the wave loses its reversibility and increases in height, rapidly reaching a two-electron stoichiometry. The peak then obtained does not vary any longer upon increasing the concentration of NH_4^+ . This observation rules out the concerted mechanism. Indeed, because NH_4^+ is a reactant the electrochemical rate law for the concerted pathway writes

$$\frac{I}{F} = k_s \exp\left[-\frac{\alpha F}{RT}(E - E_{\text{O}_2 + \text{NH}_4^+ / \text{HO}_2^{\bullet} + \text{NH}_3}^0)\right][\text{O}_2][\text{NH}_4^+]$$

(I , current density; k_s , standard rate constant; α , transfer coefficient) and thus the peak potential is expected to vary as¹¹

$$E_p = E_{O_2+NH_4^+/O_2^{\bullet-}+NH_3}^0 - 0.78 \frac{RT}{\alpha F} + \frac{RT}{\alpha F} \ln \left(k_s \sqrt{\frac{RT}{\alpha F \nu D}} [NH_4^+] \right)$$

that is, to shift positively by 120 mV per decade of NH_4^+ at 298K for $\alpha = 0.5$.

In the framework of the stepwise mechanism, the passage to a two-electron stoichiometry results from the fact that the protonated radical, HO_2^{\bullet} is much easier to reduce than the starting molecule ($E_{HO_2^{\bullet}/HO_2^-}^0 \approx 0$ V vs SCE¹³), leading to a classical ECE–disproportionation mechanism.¹⁴ Protonation of the superoxide radical by NH_4^+ is slightly downhill ($pK_{A,NH_4^+} = 10.5^{15}$ and $pK_{A,HO_2^{\bullet}} \approx 11.7^8$). Because the second electron transfer is strongly downhill (by ca. 0.8 eV), the forward protonation is the rate-determining step of the ECE–disproportionation process. The rate constant, k_2 , can be determined as follows. For substoichiometric amounts of NH_4^+ , before the two-electron stoichiometry is reached, the voltammograms shows a pre-peak (Figure 1c). From its location, one obtains $k_2 = 10^7$ M⁻¹ s⁻¹ (see the simulated curves in Figure 1d).¹⁶ The independence of the two-electron wave from $[NH_4^+]$ results from the rate constant of the protonation step, k_2 , being large enough to make the forward electron transfer rate-determining. This was corroborated by simulation using the previously determined values of the various parameters: $E_{O_2/O_2^{\bullet-}}^0 = -0.782$ V versus SCE; $\alpha = 0.5$; $D = 4 \times 10^{-5}$ cm² s⁻¹, $k_s = 0.033$ cm s⁻¹, $k_2 = 10^7$ M⁻¹ s⁻¹, $E_{HO_2^{\bullet}/HO_2^-}^0 \approx 0$ V versus SCE.

The main conclusion of this electrochemical detour is that the reduction of dioxygen in the presence of NH_4^+ does not proceed along a concerted pathway but rather follows the electron-first, proton-second stepwise pathway.

The same is expected for the homogeneous reduction by $C_{60}^{\bullet-}$ (Scheme 2). How then can the linear acceleration of the reaction by NH_4^+ be interpreted? For the same reasons as in the electrochemical reaction, the protonation step may be regarded as irreversible. We also note that the initial electron-transfer reaction is very uphill (by 0.332 eV because $E_{C_{60}^{\bullet-}/C_{60}}^0 = -0.45$ V vs SCE⁵). It is therefore possible that electron transfer may act as a pre-equilibrium toward a rate-determining protonation step. At steady state, the kinetics is described by

$$-\frac{d[C_{60}^{\bullet-}]}{dt} = 2k_1 \frac{k_2[NH_4^+]}{k_{-1}[C_{60}] + k_2[NH_4^+]} [O_2][C_{60}^{\bullet-}] \quad (2)$$

where k_{-1} should be close to the diffusion limit ($k_{diff} \approx 10^9$ M⁻¹ s⁻¹) in view of the large exergonicity of the backward electron transfer. The factor 2 in the above equation is the same stoichiometric factor as already introduced in the concerted case. As seen earlier, $k_2 \approx 10^7$ M⁻¹ s⁻¹ in DMSO. Repeating the experiment in 1:1 DMSO–PhCl led to $k_2 \approx 5 \times 10^6$ M⁻¹ s⁻¹. Because the protonation reaction is approximately isogonic, k_2 is close to the zero-driving force rate constant. Having a zero-driving force rate constant ca. 2 orders of magnitude below the diffusion limit is not surprising in view of the substantial solvent and internal reorganization required to pass from $O_2^{\bullet-} + NH_4^+$ to $HO_2^{\bullet} + NH_3$.¹⁷

In the conditions of the experiments in ref 5 ($[NH_4^+] \leq 4$ mM, $[C_{60}] = 1$ mM)

$$k_2[NH_4^+] \leq 2 \times 10^4 \text{ s}^{-1}, \quad k_{-1}[C_{60}] = 10^6 \text{ s}^{-1}$$

and therefore

$$k_2[NH_4^+]/k_{-1}[C_{60}] \leq 0.02$$

It follows that the second term in the denominator of eq 2 is negligible as compared to the first, leading to a situation where the observed rate constant is indeed proportional to $[NH_4^+]$ within experimental uncertainty. Then

$$-\frac{d[C_{60}^{\bullet-}]}{dt} = k_{ap}[NH_4^+][C_{60}^{\bullet-}]$$

with

$$k_{ap} = 2 \frac{k_1 k_2 [O_2]}{k_{-1} [C_{60}]} \quad (3)$$

We also note that, because the C_{60} concentration is 1 mM and the maximal $C_{60}^{\bullet-}$ concentration is 0.05 mM, $[C_{60}]$ is constant with a very good precision. The reaction is thus predicted to be first-order in $C_{60}^{\bullet-}$, as observed experimentally.

From experiment⁵ $k_{ap} = 130$ M⁻¹ s⁻¹, and from eq 3, $k_{ap} = 110$ M⁻¹ s⁻¹. This excellent agreement confirms the validity of the stepwise mechanism.

In summary, (i) contrary to previous assertion,⁵ the linear acceleration of the homogeneous reduction of dioxygen by NH_4^+ ions cannot be interpreted as resulting from the driving force of the reaction depending on NH_4^+ concentration simply because, from first principles, driving forces do not depend on the concentrations of reactants. (ii) NH_4^+ ions may a priori exert their influence in the framework of either a concerted pathway or of an electron-first, proton-second stepwise pathway. Analysis of the experimental data showed that the stepwise mechanism is followed in both the homogeneous reduction and the electrochemical reaction at an inert electrode. Analysis of the electrochemical reaction by means of cyclic voltammetry on a glassy carbon electrode served not only the purpose of comparison with the homogeneous reaction but also the determination of key thermodynamic and kinetic parameters. (iii) In the homogeneous reduction of dioxygen by $C_{60}^{\bullet-}$ in 1:1 DMSO/PhCl, with addition of NH_4^+ ions, the strongly uphill initial electron transfer serves as pre-equilibrium to the rate-determining protonation of superoxide ion by NH_4^+ . (iv) In all cases, a second electron transfer, which requires less energy than the first, leads after protonation by NH_4^+ to hydrogen peroxide.

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