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Short communication

Spin effects in oxygen electrocatalysis: A discussion

Renat R. Nazmutdinov [a],*, Elizabeth Santos [b,c], Wolfgang Schmickler [b]

[a] Kazan National Research Technological University, K. Marx Str., 68, 420015 Kazan, Republic of Tatarstan, Russian Federation
[b] Institute of Theoretical Chemistry, University of Ulm, 89069 Ulm, Germany
[c] Instituto de Fisica Enrique Gaviola (IFEG-CONICET-FaMAF), Universidad National de Córdoba, Argentina

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The reduction of molecular oxygen in triplet and singlet spin states at metal electrodes is analyzed in the framework of quantum mechanical theory of charge transfer. Both outer- and inner-sphere mechanism is considered. Singlet oxygen is argued to be considerably more active in electron transfer processes. It is demonstrated that spin polarization may play a catalytic role, parallel with the effect of overlap of reactant orbitals with the d-band of a metal electrode. Our model is based on two main assumptions: (i) some metal surfaces favor the existence of singlet molecular oxygen in adsorbed state; and (ii) short-living singlet O_2 molecules may appear as intermediates at some reduction steps. These two reasons are expected to increase the local concentration of active singlet molecular oxygen in reaction layer.

The ground state of molecular oxygen is known to be triplet ($^3\sum_g^-$), where two unpaired electrons occupy antibonding — molecular orbitals forming a paramagnetic molecule [1,2]. At the same time in its lowest exited state (singlet, $^1\Delta_g$) a diamagnetic O_2 molecule appears as well. A singlet oxygen molecule is chemically more active and plays a very important role in a variety on biochemical processes (see reviews [2,3]); for example, an O_2 molecule becomes singlet being bound to the heme center of hemoglobin. Singlet molecular oxygen can be produced by photoexcitation of a suitable dye, which subsequently transfers its energy to a triplet oxygen and converts it into a singlet. The latter is not only more reactive because its energy is higher, but also because it removes spin conservation difficulties in certain reactions. In addition, singlet oxygen is expected to appear at metal surfaces. Experimental data by means of the UPS, ELS, LEED and work function measurements on the adsorption of molecular oxygen at Cu(100) and Cu(110) surface [4] were interpreted in terms of a chemisorbed singlet. The same conclusion was made in the work [5], where oxygen adsorption was studied at polycrystalline Ag and Cu surfaces (in the presence of adsorbed chlorine atoms) using X-ray and UV photoelectron spectroscopy. Some additional evidence can be also gained from periodical Density Functional Theory (DFT) calculations [6–8]. It has been predicted that a diamagnetic O_2 molecule (nearly neutral) exists in a stable adsorbed state on the Pt(111) surface (fcc hollow position); a difference in the adsorption energies between this surface place and the most preferable bridge position (for the triplet molecule) is small and amounts to 0.12 eV [6]. The authors of Ref. [7] have argued about the formation of a singlet O_2 molecule at Ag(100) surface at short metal–O atom distances. In work [8] a diamagnetic state has been found for molecular oxygen strongly adsorbed at Ru(0001) surface.

Nowadays the oxygen reduction belongs to one of the most important and challenging research fields in electrocatalysis science, first of all because of its role in fuel cells [9]. In this communication an attempt is made to attract attention to some effect of spin nature which might play a role in this complicated multi-step electrode process. Let us consider the first electron transfer step for molecular oxygen in two different spin states:

$$O_2(\text{triplet}) + e = O_2^- \text{ and } O_2(\text{singlet}) + e = O_2^- . \tag{1}$$

This simple electron transfer is usually the first and rate-determining step in alkaline solutions (see e.g. Ref. [10]). On many substrates it seems to take place in an outer-sphere or near outer-sphere mode [11]. For the sake of simplicity, we consider first the normal outer-sphere mechanism. For further analysis it is convenient to write the rate constant (k) in terms of the Marcus theory:

$$k = \nu_{eff}\gamma \exp(-\sigma) \exp\left(-(\lambda - F\eta)^2/4\lambda k_B T\right), \tag{2}$$

where λ is the solvent reorganization energy; η is the overpotential with respect to the equilibrium potential; ν_{eff} is effective frequency factor; γ and $\exp(-\sigma)$ are additional pre-exponential factor which will be discussed below.

A value of −0.33 V was found experimentally for the standard electrode potential of the process $O_2 + e \rightleftarrows O_2^-$ [12] for the triplet on the

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* Corresponding author. Tel.: +7 8432318983.
E-mail address: nazmutdi@mail.ru (R.R. Nazmutdinov).

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SHE scale. On the other hand, the energy of the molecular oxygen $^1\Delta_g$ state is 0.98 eV higher than the $^3\sum_g^-$ ground state [1]. The E_0 value for singlet oxygen can be readily estimated as $0.98 - 0.33 = 0.65$ V (see Table 1). The striking difference between the two E_0 values can be discussed in terms of the energy of Coulomb repulsion of electrons on the reactant orbital (U); this parameter plays an important role when constructing reaction free energy surfaces on the basis of the Newns–Anderson Hamiltonian [13]. In the case of the triplet oxygen an electron is transferred from a metal electrode to a half-occupied antibonding π-orbital ($U > 0$), while at the reduction of singlet oxygen an electron is transferred to an empty molecular orbital ($U = 0$). Therefore, the reduction of singlet molecular oxygen starts at significantly more positive electrode potentials. Assuming comparable work terms for the both oxygen forms (which is reasonable for the outer-sphere mechanism) a higher reactivity of singlet O_2 molecules becomes evident.

So, in the outer sphere mode there is a potential range of about 1 V in which the reactive singlet can be reduced to the superoxide ion, and the triplet state cannot. In aqueous solutions the lifetime of the singlet is short, of the order of pico- to at most a few milliseconds, which makes it difficult, though not impossible, to study electron transfer to a singlet oxygen in the outer sphere mode. In some organic solvents the lifetime of singlet oxygen is of the order of several ms, long enough for its detection. As shown in Ref. [14] singlet oxygen can be produced by a strong electric field in the gas phase, and can subsequently react in a suitable solvent. Obviously, the standard electrode potentials would be different in a non-aqueous solvent, but the difference between the potentials for the two oxygen species should remain the same.

However, the situation in the inner sphere mode is quite different. As a triplet oxygen molecule approaches a metal electrode surface, the Coulomb repulsion U decreases, because it is shielded by the *s*- and *p*-electrons of the metal. This entails a spin depolarization, the extent of which depends on the metal. Thus, on Cu(100) and Cu(110) the adsorbed state molecular oxygen is singlet [4,5], on Ag(100) [7] and Pt(111) [6] there can be two adsorbed states: a singlet and a paramagnetic state with a spin polarization of about 1, the latter on Pt(111) being slightly more favorable energetically (by about 0.12 eV).

There is no evidence for a stable, adsorbed, fully charged superoxide ion O_2^-; earlier suggestion for its existence on Pt(111) proved to be unfounded. Sizable negative excess charges are known for the adsorption of halides on mercury, but even in this case, the magnitude of the electrosorption valence is notably less than one. Reaction (1) usually proceeds with a transfer coefficient of about 1/2, and the reaction order with respect to oxygen is unity. This is in line with the near outer-sphere mechanism, which we recently theoretically predicted on Au(100) electrode. In this case the reaction takes place close to the metal surface, but neither the reactant nor the product is chemisorbed [11]. We have suggested that the produced O_2^- ion reacts rapidly, which explains why reaction (1) is rate determining.

Thus the electron transfer happens in the region close to the metal surface, where the spin polarization decreases. It is worthwhile to study the two limiting cases of a triplet and singlet oxygen and compare some of their reactivity properties. The energy of reorganization should be nearly the same for both states. The tunneling factor $\exp(-\sigma)$ in Eq. (2) results from the fact that the equilibrium O–O distance differs for the reduced (f) and oxidized (i) states, and the vibration frequencies fall in quantum region, $\hbar\omega_{i(f)} >> k_BT$. Assuming the linear response theory the parameter σ can be calculated as follows [13]:

$$\sigma = \frac{m\left(r_f - r_i\right)^2}{\hbar} \frac{\omega_i \omega_f}{\left(\omega_i + \omega_f\right)}, \tag{3}$$

where $r_{i(f)}$ are the O – O bond length in oxidized and reduced states and m is the effective oscillator mass.

For the reduced oxygen form (O_2^-) the ground state is $^2\Pi_g$, where $r_f = 1.348$ Å and $\omega_f = 1108$ cm^{-1} [15,16]. As can be seen from Table 1, the tunneling factor for the singlet oxygen is only 15% higher as compared with that for the triplet form. These simple estimations were made for gas phase. In a strongly adsorbed state the O – O bond length and vibration frequency of singlet oxygen can differ from those for gas phase; for example, $r_i = 1.39$ Å; $\omega_i = 826$ cm^{-1} (Pt) [6] and $r_i = 1.42$ Å; $\omega_i = 750$ cm^{-1} (Ru) [8]. However the qualitative conclusion is expected to remain the same.

Table 1
Standard electrode potential E_0, pre-exponential factor γ, bond length, vibration frequency (ω_i), tunneling factor $\exp(-\sigma)$ calculated for a molecular oxygen in two different spin states.

Spin state	E_0(SHE), V	γ	r_{O-O}, Å [1]	ω_i, cm^{-1} [1]	$\exp(-\sigma)$
Triplet	−0.33 [11]	2/3	1.208	1580	0.23
Singlet	+0.65	1	1.2155	1509	0.27

In general, an additional pre-exponential factor (γ) should be addressed in Eq. (2) as well, when considering reaction (1). The physical meaning of this factor is the probability of the event that a transferred electron can occupy the acceptor π-orbital of molecular oxygen in accordance with the Pauli principle. The probability that the transferred electron has a certain spin projection is 1/2. For a singlet O_2 molecule it can occupy an empty acceptor orbital with probability 1. In turn, there are three different states for a triplet oxygen molecule: $\alpha(1)\alpha(2)$ ($M_s = 1$), $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$ ($M_s = 0$) and $\beta(1)\beta(2)$ ($M_s = -1$), where α and β are spin functions and M_s notes projections of the total spin (1). As only two states can be occupied by an electron taken from an electrode, the corresponding probability is, therefore, $1/2 * 2/3 = 1/3$. As the same situation takes place for the opposite spin projection, the resulting probability is $1/3 + 1/3 = 2/3$ (see Table 1).

The results compiled in Table 1 clearly demonstrate that singlet molecular oxygen is considerably more active in electroreduction as compared with its usual triplet form. For adiabatic electron transfer reactions the orbital overlap effect can noticeably smooth and reduce the activation barrier [13]. This effect is practically the same for both the singlet and triplet forms, because of the identical final electronic state, O_2^-.

On some electrode surfaces reaction (1) may proceed according to an inner-sphere mechanism with bond breaking:

$$O_2\text{ads} + e = O\text{ ads} + O^-\text{ads}. \tag{4}$$

A simple analysis can be done in terms of Savéant's theory [17]. Then the activation barrier (ΔE_a) at zero electrode overvoltage can be recast in the form:

$$\Delta E_a = \frac{\left(\lambda + D + W_f - W_i\right)^2}{4(\lambda + D)}, \tag{5}$$

where D is the dissociation energy of O_2 molecule in gas phase; W_i the adsorption energy of O_2 molecule; W_f is the adsorption energies of O atom and O^- anion.

It is evident that the singlet spin state facilitates the O – O bond breaking and, therefore, decreases the intra-molecular contribution to the activation barrier (Eq. (5)). Catalytically active molecular oxygen in singlet state may also arise in further steps of the oxygen reduction. As an example, we consider the following reaction as a possible second step:

$$O_2^- + H^+ + O_2H_{(ads)} = O_2 + O_2H_{2(ads)}. \tag{6}$$

Since this is a reaction between two radicals, one of the products (O_2) can be both in triplet and singlet state. At the absence of an external