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Unusual Role of Oxygen in Electron-Transfer Processes

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Efficient mimicking of photosynthesis has been a long-standing goal of research in the field of photoinduced electron transfer. Optimization of the latter requires that the light-induced charge separation effectively competes with undesired relaxation via energy transfer and back electron transfer. Numerous studies have demonstrated the importance of the redox properties of the donor and acceptor moieties, the separation distance in the donor−acceptor pair, and the reorganization energy of species involved.[1−5] Slow recombination, which can be achieved in distant ion radical pairs, provides favorable conditions for further chemical utilization of separated charges.

We report herein that a simple molecule, such as oxygen, can be employed either as a catalyst or an **inhibitor** of the back electron transfer reaction from a fullerene radical anion to a porphyrin-like cation within photolytically generated radical ion pair states. This is the first example in which O_2, the most important biological oxidant, acts as an inhibitor rather than an active participant (oxidant) or a catalyst of back electron transfer.

Oxygen is usually considered an undesired participant in photoconversion processes except for the cases where its own products in a form of either excited singlet oxygen or superoxide ion were sought.[8] The effects that we are presenting here relate exclusively to paramagnetic properties of oxygen and, as we show, can be extended to other paramagnetic species. Unique involvement of molecular oxygen in electron-transfer phenomena arises from the different roles it can play. On one hand, molecular oxygen is a fairly good electron acceptor and can oxidize excited-state molecules.[6] On the other hand, due to its paramagnetic ($^3\Sigma_g^-$) ground state, it can also induce intersystem crossing between the singlet and triplet states of the molecule.[7]

The mechanisms of interaction of the electronically excited states of molecules with oxygen have been a classic problem in photochemistry and a field of intensive research for decades.[6,7] Oxygen-induced relaxation of excited singlet states $^1M^*$ proceeds primarily via intersystem crossing[7] to excited triplets, $^3M^*$, which also can react with oxygen. All these reactions are believed to proceed via a transient charge-transfer state, $M^+\cdots O_2^-$, where oxygen serves as an electron-accepting species.[6−8]

In our previous studies we have characterized the two series of dyads between the fullerene C_{60} and either porphyrin- or chlorin-linked molecules (ZnP−C_{60}, P−C_{60}, ZnChl−C_{60}, and Chl−C_{60}) by means of the transient displacement current technique.[9,10] In this technique, the signal is formed by reorientation of newly formed dipoles (CT states) in the applied electric field; it results in the appearance of transient displacement current in the dipole cell. The details of the setup can be found elsewhere.[10,11] We found that in all four dyads, upon photoexcitation of porphyrin (or chlorin), their fluorescence is 100% quenched and a CT state is formed within our time resolution.

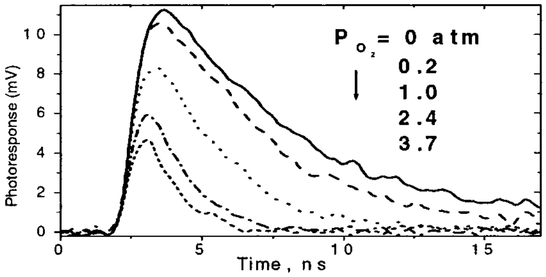
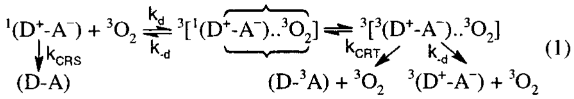


Figure 1. Dipole signals for ZnPor−C_{60} dyad in toluene with varying [O_2].

Figure 1 represents a series of dipole signals induced by laser excitation of ZnPor−C_{60} in toluene and with different oxygen concentrations. When no oxygen is present, the signal decays with the rate constant k_{CRS} due to charge recombination of the singlet CT state; however, that rate increases due to oxygen quenching—a process usually expected of oxygen in photoinduced electron transfer.[6−8] The same effect is observed for two other dyads, Por−C_{60} and Chl−C_{60}. The quenching rate constants are almost identical for all three dyads and are equal to the diffusion control rate constant, $k_d = 2.2 \times 10^{10}$ M^{-1} s^{-1}. Figure 2 illustrates that addition of oxygen to a toluene solution of ZnChl−C_{60} causes the opposite effect—a long-lived component is produced instead. Upon further oxygen concentration increase, the amplitude of the long-lived component increases, but its lifetime gradually shortens (compare the 2.4 and 1 atm curves in Figure 2, for example). Despite these seeming contradictions, all these phenomena are consistent and can be explained by oxygen-induced intersystem crossing depicted by reactions (1−2).



$$^1(D^+\text{-}A^-) + {}^3O_2 \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} {}^3[{}^1(D^+\text{-}A^-)..{}^3O_2] \rightleftharpoons {}^3[{}^3(D^+\text{-}A^-)..{}^3O_2] \qquad (1)$$

$$^1(D^+\text{-}A^-) \xrightarrow{k_{CRS}} (D\text{-}A)$$

$$^3[{}^3(D^+\text{-}A^-)..{}^3O_2] \xrightarrow{k_{CRT}} (D\text{-}{}^3A) + {}^3O_2 \qquad {}^3[{}^3(D^+\text{-}A^-)..{}^3O_2] \xrightarrow{k_{-d}} {}^3(D^+\text{-}A^-) + {}^3O_2$$

Oxygen, as a paramagnetic species in the ground state, can induce intersystem crossing without participation in actual electron transfer. Such a process can take place without changing the total spin and its projection in the pair dyad/oxygen. There are only two possible configurations that can be produced upon collision of the dyad and oxygen, both with equal probability. They are shown in reaction 1 and involve singlet, $^1(D^+-A^-)$, and triplet, $^3(D^+-A^-)$, CT states of the dyad. If the energy of the CT state lies above that of the locally excited triplet states of a porphyrin and C_{60} (E_T = 1.50 eV), then charge recombination from the triplet state of a dyad,

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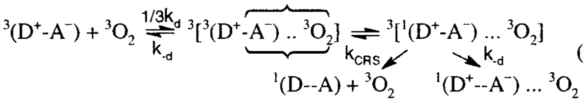
$^3(D^+{-}{-}A^-)$, to the locally excited triplet state, with the rate constant k_{CRT}, will deplete the CT state. Such a situation is realized in toluene for all but one of the dyads studied, namely the ZnChl−C_{60}. Energy of its CT state (E_{CT}) in toluene is estimated to be $E_{CT} = 1.32$ eV above the ground state, as opposed to $E_{CT} > 1.5$ eV for other dyads. The rate constant of the oxygen-induced charge recombination in the three dyads with high E_{CT} is the same and equal to the rate constant of diffusional collisions ($k_d = 2.2 \times 10^{10}$ M^{-1} s^{-1}). In case of ZnChl−C_{60}, where $E_{CT} < E_T$, collisions with oxygen "scramble" spins of separated charges in the CT state designated as equilibrium in reaction 1 and thus induces in half the cases intersystem crossing to the triplet CT state. Thus, the rate of oxygen-induced intersystem crossing from $^1(D^+{-}A^-)$ into $^3(D^+{-}A^-)$ for of ZnChl−C_{60} equals half the diffusion-controlled rate, in remarkable agreement with the experimental constant $k_{isc} = 1.1 \times 10^{10}$ M^{-1} s^{-1}.

Moreover, in more polar THF solutions, where enhanced solvation of CT states causes them to move lower in energy than that of $^3C_{60}$ even for Por−C_{60} (where we estimated $E_{CT} = 1.25$ eV), charge recombination into $^3C_{60}$ also becomes insignificant, and collisions with oxygen produce long-lived triplet CT, $^3(D^+{-}A^-)$, instead of quenching.

Oxygen is a ubiquitous paramagnetic species and a key player in photosynthesis, which makes the investigation of its role in impeding charge recombination for other systems even more interesting. However, other paramagnetic species should perform the same task of enhancing the intersystem crossing as does oxygen. Indeed, a stable radical TEMPO produces the same discrimination in reacting with the dyads: Chl−C_{60}, Por−C_{60}, and ZnPor−C_{60} suffer shortening of their CT lifetimes with an almost identical rate constant in toluene, $k_S = 1.0 \times 10^{10}$ M^{-1} s^{-1}, while ZnChl−C_{60} experiences intersystem crossing to the long-lived triplet CT with a rate constant half the size, $k_{isc} = 5.0 \times 10^9$ M^{-1} s^{-1}.

The triplet CT of the dyad is also vulnerable to oxygen-quenching; its lifetime gradually shortens while intensity increases. The appropriate mechanism of such quenching involves reverse intersystem crossing (reaction 2):



$$^3(D^+\text{-}A^-) + {}^3O_2 \underset{k_{-d}}{\overset{1/3k_d}{\rightleftharpoons}} {}^3[\underbrace{\overbrace{^3(D^+\text{-}A^-) \,..\, {}^3O_2}}] \rightleftharpoons {}^3[^1(D^+\text{-}A^-) \ldots {}^3O_2] \qquad \xrightarrow{k_{CRS}} {}^1(D\text{--}A) + {}^3O_2 \qquad \xrightarrow{k_{-d}} {}^1(D^+\text{--}A^-) \ldots {}^3O_2 \tag{2}$$

which can be induced by oxygen in the opposite direction, from the triplet to the singlet CT. Note that the process again takes place without changing the total spin and projection; thus, only one-third of diffusionally encountered complexes, $[^3(D^+{-}A^-)\cdots{}^3O_2]$ are in the appropriate total triplet spin state. As in the case of oxygen interaction with singlet CT, the intersystem crossing process can proceed without transient formation of superoxide ion, O_2^-, and without changing the total spin and the spin projection for the $[^3(D^+{-}A^-)\cdots{}^3O_2]$ complex. Inverse intersystem crossing rate constant, k_{-isc}, for the triplets in reaction 2 should vary between $k_d/3$ and $k_d/6$, depending on the relation between the rate constants of charge recombination in the singlet CT state, k_{CRS}, and (spin-independent) dissociation of the complex, k_{-d}. When only reactions 1−2 were used for describing the dipole signal time evolution, a reasonably good fit was obtained for rates corresponding to $k_{-isc} = 6 \times 10^9$ M^{-1} s^{-1}, that is approximately $k_d/3.7$.

Both intersystem crossing processes discussed here, forward and reverse, can be explained as happening with conservation of the total spin and its projection within the dyad/radical "complex". Thus, no effect of external magnetic field should be observed on either of them, opposite to the radical pair mechanism of intersystem crossing.[12] Indeed, application of an external field of 0.15 T made no difference. The dyad/oxygen "complex" shows no specific binding, since effects are identical for free base and Zn forms of the dyads, opposite to what was thought.[8] The "complex" lifetime is limited by diffusion, and the outcome of the encounter is caused exclusively by energetics.

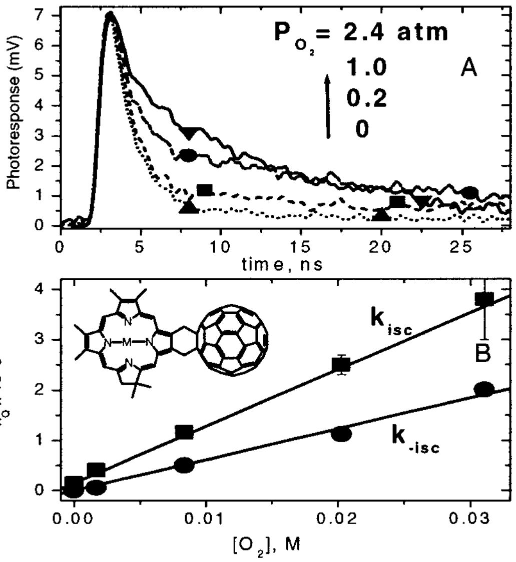


Figure 2. (A) Dipole signals for ZnChl−C_{60} dyad in toluene with varying oxygen concentrations. (B) Quenching rates of forward and reverse ISC obtained from fitting the signals in A. (Inset) Chl−C_{60}.

Thus, we have shown that oxygen can play an unusual role in photoinduced electron-transfer processes, namely it can impede charge recombination. Due to its paramagnetism, oxygen induces intersystem crossing into the triplet CT state, which, depending on relative energies of the CT state with respect to locally excited triplet state(s), may result in formation of the long-lived triplet CT state. The same effect can be induced by other paramagnetic species. The resulting triplet CT state is also affected by oxygen through the process of reverse intersystem crossing. Such a mechanism most likely plays a role in naturally occurring photoinduced electron-transfer reactions where oxygen or other paramagnetic species are involved. It can also be applied in manipulating outcomes in artificial photoinduced electron-transfer processes.

References

(1) Gust, D.; Moore, T. A. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic: San Diego, CA, 2000; Vol. 8, p 153.
(2) Wasielewski, M. R. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part A, p 161.
(3) Jordan, K. D.; Paddon-Row: M. N. *Chem. Rev.* **1992**, *92*, 395.
(4) Fukuzumi, S.; Itoh, S. In *Advances in Photochemistry*; Neckers, D. C., Volman, D. H., von Bünau, G., Eds.; Wiley: New York, 1998; Vol. 25, p 107.
(5) Warman, J. M.; De Haas, M. P.; Verhoeven, J. W.; Paddon-Row, M. N. *Adv. Chem. Phys.* **1999**, *106*, 571−601.
(6) *Singlet Oxygen*; Frimer, A. A., Ed.; CRC: Boca Raton, FL, 1985; Vols. I−IV
(7) Wilkinson, F.; McGarvey, D. J.; Olea, A. F. *J. Am. Chem. Soc.* **1993**, *115*, 12144−12151.
(8) Fukuzumi, S.; Imahori, H.; Yamada, H.; El-Khouly, M.; Fujitsuka, M.; Ito, O.; Guldi, D. *J. Am. Chem. Soc.* **2001**, *123*, 2571−2575
(9) Kutzki, O.; Wedel, M.; Montforts, F.-P.; Smirnov, S.; Cosnier, S.; Walter, A. *Proc. Electrochem. Soc.* **2000**, *8*, 172−181
(10) Montforts, F.-P.; Vlassiouk, I.; Smirnov, S.; Wedel, M., Kutzki, O. *J. Phys. Chem.* **2002**. In press
(11) Smirnov, S.; Braun, C. *Rev. Sci. Instrum.* **1998**, *69*, 2875−2887.
(12) Kuciauskas, D.; Liddell, P.; Moore, A.; Moore, T.; Gust, D. *J. Am. Chem. Soc.* **1998**, *120*, 10880−10886.

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