Physical Mechanisms of Generation and Deactivation of Singlet Oxygen

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Received September 6, 2002

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I. Introduction

For more than 70 years, researchers in several areas of science have been intrigued by the physical and chemical properties of the lowest excited states of molecular oxygen. With two singlet states lying close above its triplet ground state, the O2 molecule possesses a very unique configuration, which gives rise to a very rich and easily accessible chemistry, and also to a number of important photophysical interactions. In particular, photosensitized reactions of the first excited state, O2(1Aγ), play a key role in many natural photochemical and photobiological processes, such as photodegradation and aging processes including even photocarcinogenesis. Reactions of O2(1Aγ) are associated with significant applications in several fields, including organic synthesis, bleaching processes, and, most importantly, the photodynamic therapy of cancer, which has now obtained regulatory approval in most countries for the treatment of several types of tumors. The development of both applications and novel observation techniques has strongly accelerated during the past few years. Significant recent advances include, for example, the development of novel luminescent singlet oxygen probes,1−4 the time-resolved detection of O2(1Aγ) in a transmission microscope,5 the first time-resolved measurements of singlet oxygen luminescence in vivo,6 and the observation of oxygen quenching of triplet-excited single molecules.7

Experimental and theoretical studies on the mechanisms of photosensitized formation of excited O2 states and of their deactivation have been performed for almost 40 years. While most early liquid-phase studies were exclusively concerned with O2(1Aγ), recent technological advances also made possible time-resolved investigations of the second excited state, O2(1Σg+), which can be formed in competition with O2(1Aγ) in many cases. A significant number of
Our review will conclude with a short presentation of the most recent advances in the field of singlet oxygen detection, and with a guide to the utilization of the mechanistic knowledge presented here, showing, for example, how to evaluate the contribution of individual physical and/or chemical mechanisms to the generation or deactivation of $\text{O}_2(\Sigma_g^+)$ and $\text{O}_2(\Lambda_g)$ in a given situation, or how to design molecules in order to maximize or minimize their $\text{O}_2(\Sigma_g^+)$ and/or $\text{O}_2(\Lambda_g)$ photosensitization ability in a given medium.

The review is strictly limited to physical mechanisms of generation and deactivation of singlet oxygen. Chemical processes are discussed only in those cases where they compete with the physical processes and/or proceed via common intermediates. It should be noted that most chemical reactions of singlet oxygen are well understood, and only a few fundamentally new aspects have been revealed since the publication of previous reviews.8–11 The only significant exception seems to be the antibody-catalyzed singlet oxygenation of water, which was suggested in 2001.12,13 An introduction to applications of photosensitized reactions of singlet oxygen was also published very recently.14

The solvent dependence of singlet oxygen formation and deactivation parameters is discussed to the extent to which it provides relevant mechanistic information; a more detailed review of the solvent dependence of singlet oxygen deactivation can be found elsewhere.15 Also, extensive data collections of quantum yields of $\text{O}_2(\Lambda_g)$ generation16 and of rate constants for its deactivation17 were published in 1993 and 1995, respectively, and are freely accessible on the Internet.18 A recent (1999) update of singlet oxygen yields from biologically relevant molecules is also available.19 The present review considers the literature published through the end of November 2002.

Electronic-to-vibrational, charge transfer, and electronic energy-transfer processes, which all may compete in a given chemical system. We also cover the physical mechanisms of generation of $\text{O}_2(\Sigma_g^+)$ and $\text{O}_2(\Lambda_g)$, focusing mainly on the quenching of excited singlet and triplet states by $\text{O}_2(\Sigma_g^-)$. Both processes can proceed via energy-transfer and charge-transfer pathways, and we explain here how the physical properties of the quencher and of the medium influence the mechanisms, rate constants, efficiencies, and products of the individual deactivation processes.

Studies have been carried out during the past 10 years, and it has become clear that a full discussion of all photophysical processes involving $\text{O}_2(\Sigma_g^+)$, $\text{O}_2(\Lambda_g)$, and ground-state oxygen, $\text{O}_2(\Sigma_g^-)$, is required to achieve a complete understanding of photosensitized reactions of molecular oxygen.

Starting with a short presentation of the most important features of the $\text{O}_2(\Sigma_g^+)$, $\text{O}_2(\Lambda_g)$, and $\text{O}_2(\Sigma_g^-)$ states, we propose here an overview of experimental and theoretical studies on the mechanisms of physical deactivation of $\text{O}_2(\Sigma_g^+)$ and $\text{O}_2(\Lambda_g)$ to $\text{O}_2(\Lambda_g)$ and/or $\text{O}_2(\Sigma_g^-)$ in the gas and liquid phases, and in the absence and presence of physical and/or chemical quenchers. This includes radiative,