Oxygen in Organic Photochemistry

a common statement:

The reaction is quenched by oxygen,

thus,

it must be a triplet reaction

true or false?

Electronic structure

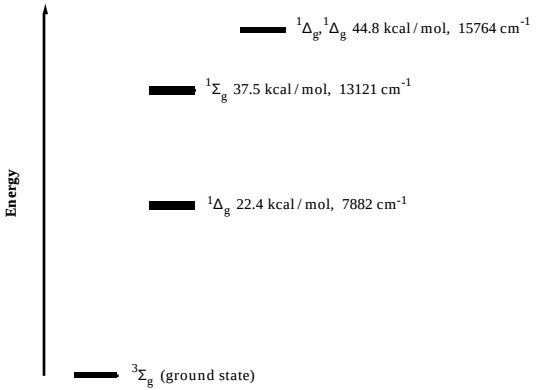
The basic electronic structure of the oxygen molecule in the ground state can be written as:

$$O_2 \quad (1\sigma_g)^2\,(1\sigma_\mu)^2\,(2\sigma_g)^2\,(2\sigma_\mu)^2\,(3\sigma_g)^2\,(1\pi_\mu)^4\,(1\pi_g)^2$$

or

$$O_2 \quad (1\sigma)^2\,(1\sigma\ )^2\,(2\sigma)^2\,(2\sigma\ )^2\,(3\sigma)^2\,(1\pi)^4\,(1\pi^*)^2$$

Energy levels for molecular oxygen



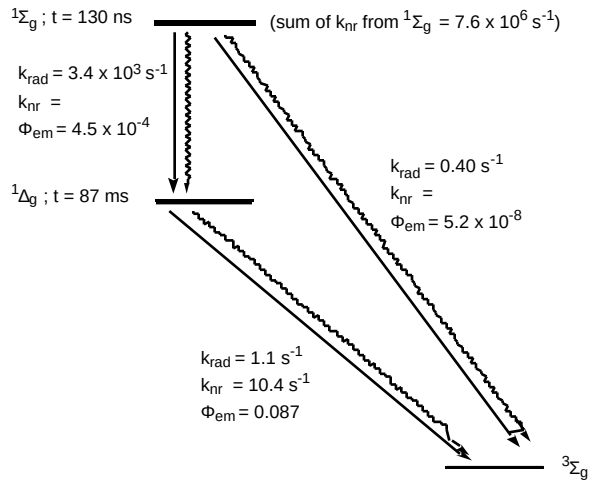
Energy levels for molecular oxygen. Excited triplet states have not been included because they are much higher in energy. The $^1\Delta_g$ state is the one normally refereed to as singlet oxygen.

Dimol emissions

Oxygen shows several "*dimeric*" emissions, the best known of which is the dimol emission at ~635 nm. No dimer is formed under normal laboratory conditions. Kasha has pointed out that the simultaneous transition for a pair of emitting species does not require an actual complex to exist, although the two molecules must be within contact distance; i.e. close enough for electron exchange to be possible. The process has also been described as *energy pooling* and is reminiscent of triplet-triplet annihilation processes

$$O_2\left(^1\Delta_g\right) + O_2\left(^1\Delta_g\right) \rightarrow O_2\left(^3\Sigma_g\right) + O_2\left(^3\Sigma_g\right) + h\nu$$

Jablonski diagram for the excited states of molecular oxygen



CCl_4

Singlet oxygen spectroscopy

Solvent	Φ_{em}	τ_o^{Δ} (μs)	k_{rad} (s^{-1})
C_6H_6	4.7 x 10^{-5}	31	
CH_3CN	7.1 x 10^{-5}	75	
$CHCl_3$	3.6 x 10^{-4}	207	
CS_2	0.040	34000	
CCl_4	0.087	87000	
Freon-113	0.15	99000	
H_2O		~5	
CH_3OH		10.4	

Sources: (Schmidt, 1989),

Singlet oxygen ($1\Delta g$) lifetimes, emission quantum yields and radiative decay rate constants (krad) in various solvents at room temperature

Effect of deuteration on singlet oxygen lifetimes

O_2 ($^1\Delta g$) lifetimes in	
CH_3OH	10.4 µs
CH_3OD	37 µs
CD_3OD	227 µs

$$P_r = \frac{k_M[M]}{\tau^{-1} + k_M[M]}$$ **Probability of reaction**

Effect of deuterium on reaction yields

$$P_r = \frac{k_M[M]}{\tau^{-1} + k_M[M]}$$ **Probability of reaction**

There are two extreme situations in which we would NOT expect an effect:

(i) if the reaction does not involve singlet oxygen; and

(ii) if the reaction with singlet oxygen is extremely fast

Simple rules let us anticipate changes in O_2 ($^1\Delta_g$) lifetime as a function of the solvent

- **The longest lifetimes are observed in perhalogenated solvents.**
- **τ_0^Δ decreases on increasing the number of H atoms in the solvent molecule.**
- **The shortest τ_0^Δ values are observed with solvents having O–H groups, notably water.**
- **The presence of heavy atoms reduces τ_0^Δ .**
- **Solvent deuteration invariably increases τ_0^Δ .**

Bond dissociation energies for selected oxygen containing species

Molecule	Bond type	BDE (kcal/mol)
O_2	O = O	119.0
H_2O_2	O – O	51
H – O	H – O	102.2
H_2O	H – O	119.3
H_2O_2	H – O	88.1
HO_2	H – O	
ROH	H – O	105
ROOH	H – O	
R_2O_2	O – O	37
ketone	C = O	
methanol	H – O	104.4

Redox properties

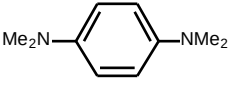
- **Oxygen is a good electron acceptor, but a very poor donor.**
- **Reduction of oxygen can lead to $O_2^{\cdot-}$, $HO_2^{\cdot}$, HO_2^-, H_2O_2 and HO•**
- **It is usually the first electron transfer to O_2 that is the rate limiting step.**
- **The O_2/ $O_2^{\cdot-}$ couple has an immense importance in nature.**
  - **It has an E° of -0.15 V in water and -0.60 in dimethylformamide.**
- **Under many conditions, $O_2^{\cdot-}$ is itself a good reductant.**
- **Superoxide is a poor oxidant, since E° ($O_2^{\cdot-}$/ O_2^{2-}) < -1.7 V**

Redox properties of singlet oxygen

Singlet oxygen is a better oxidant than ground state oxygen.

When the excitation energy of singlet oxygen is taken into consideration the values of E° ($^1O_2$/ $O_2^{\bullet-}$) are 0.34 V in dimethylformamide and 0.79 V in water.

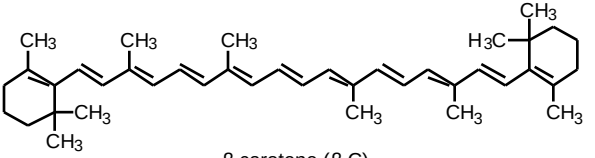
Singlet oxygen oxidizes molecules such as N,N,N',N'-tetramethyl-p-phenylenediamine to its radical cation.



Energy transfer
Singlet oxygen as a donor

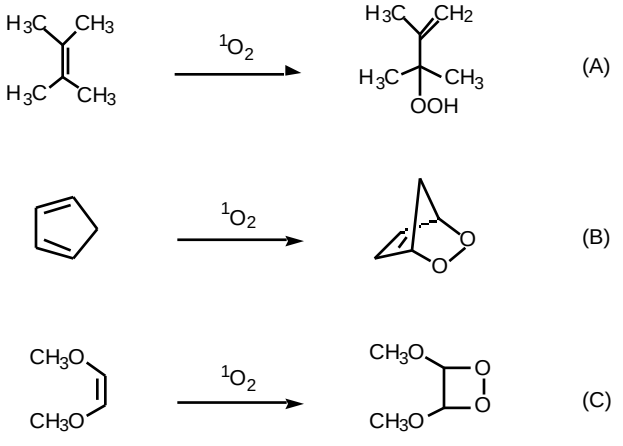
There are not many examples of energy transfer <u>from</u> oxygen, largely because few molecules have such a low excitation energy

$$^1O_2\ ^1\Delta_g + \beta\text{-C} \longrightarrow {}^3O_2\ ^3\Sigma_g + {}^3\beta\text{-C}^*$$

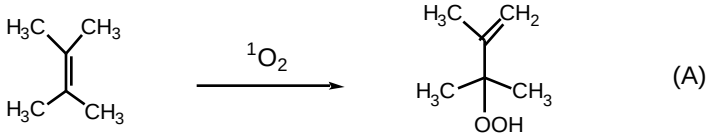


β-carotene (β-C)

Singlet oxygen: chemical quenching

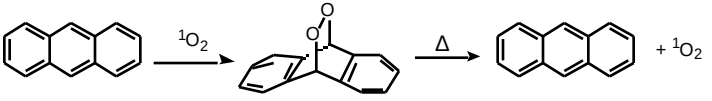


The Schenck or *ene* reaction



Singlet oxygen: reversible addition

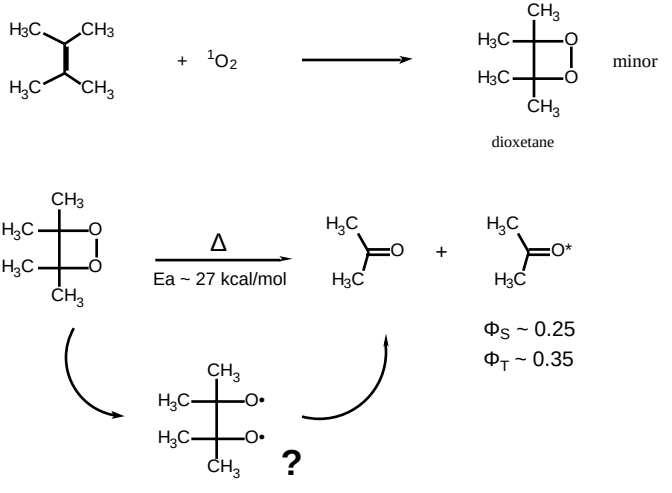
Addition to a conjugated system can be reversed thermally with regeneration of singlet oxygen



endoperoxide

Provides a chemical mechanism for 'storing' singlet oxygen

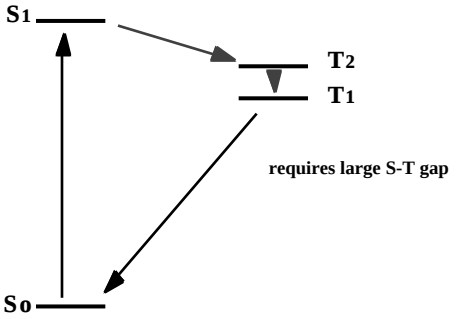
Dioxetane formation is not reversible



Interaction of oxygen with excited singlet states

Possible but unlikely

$$ {}^1X^* + {}^3O_2 \rightarrow {}^3X^* + O_2\left({}^1\Delta_g\right) $$



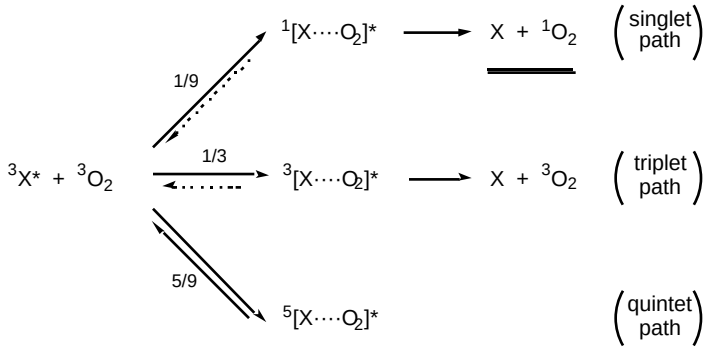
requires large S-T gap

Common

Assisted intersystem crossing

$$ {}^1X^* + {}^3O_2 \rightarrow {}^3X^* + {}^3O_2 $$

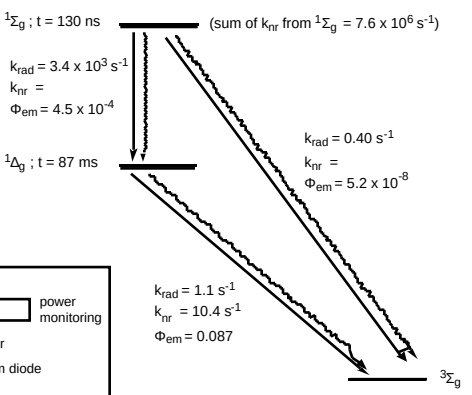
Energy transfer processes
Quenching by oxygen of excited triplet states

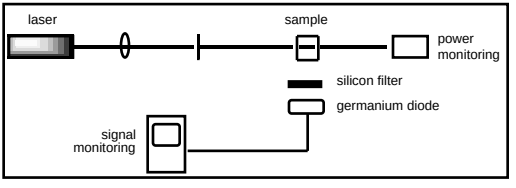


Spin statistics plays a key role indetermining the probabilities of the vatious reaction paths between an excited triplet state and molecular oxygen

Detecting singlet oxygen

The emission at 1270 nm provides a convenient tool to study the chemistry of singlet oxygen in the $^1\Delta g$ state. The next higher electronic state is the $^1\Sigma g$, 37.5 kcal/mol or 13121 cm^{-1} above the ground state. It emits weakly by decay to both the $^1\Delta g$ state and the ground state. Its lifetime of 135 ns in carbon tetrachloride is surprisingly long for an upper electronic state (Kasha's Rule)

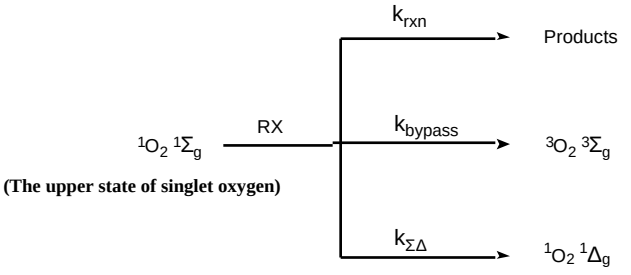




Paradigm for electronic energy transfer from a triplet sensitizer to molecular oxygen

- **It cannot occur if the sensitizer energy is significantly below 22 kcal/mol.**
- **It can only populate the $^1\Delta g$ level of molecular oxygen if the sensitizer energy is between 22 and 37 kcal/mol, since population of the $^1\Sigma g$ level would be energetically unfavorable.**
- **If the sensitizer energy exceeds 38 kcal/mol, excitation of oxygen to either the $^1\Delta g$ or $^1\Sigma g$ levels is possible.**
- **If the energy of the sensitizer is between ~21 and ~25 kcal/mol, it is possible for the process to be reversible, with $^1O_2$ ($^1\Delta g$) also transferring energy back to repopulate the triplet state of the sensitizer.**
- **If the energy of the sensitizer is in the neighborhood of 37-40 kcal/mol – i.e. matching reasonably well the energy of $^1O_2$ ($^1\Sigma g$) – the process is not expected to show reversibility. This is due to the fact that the $^1\Sigma g$ state is too short-lived for reversible transfer to occur with any significant probability at the concentrations of organic solutes frequently used in photochemistry. The process is possible but not probable.**

Reaction paths available in the interaction of *sigma* singlet oxygen with the substrate RX



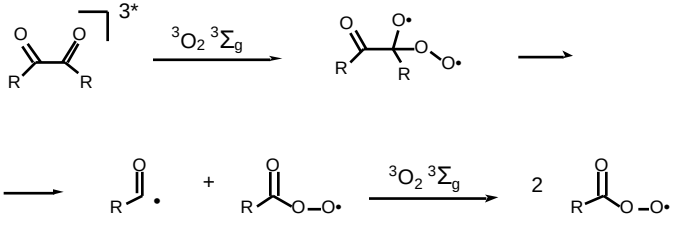
(The upper state of singlet oxygen)

Quenching by oxygen of excited triplet states. Chemical trapping

In the majority of cases, interaction of oxygen with triplet states involves energy transfer.

In a few examples, notably diketones, a chemical reaction occurs between the triplet state and O_2: addition to a carbonyl carbon (Schenck mechanism) and subsequent C–C bond cleavage to an acylperoxy and an acyl radical, which itself is scavenged by molecular oxygen to yield a second acylperoxy radical

Schenck mechanism



Efficiency of singlet oxygen, $O_2(^1\Delta g)$, generation:
selecting a good singlet oxygen sensitizer

$$\Phi_\Delta = \Phi_{ISC} \bullet S_\Delta \bullet \frac{k_q [O_2]}{\tau^{-1} + k_q [O_2]}$$

S_Δ is a true indicator of the 'quality' of a triplet sensitizer in the generation of singlet oxygen

Values of S_Δ for some singlet oxygen sensitizers

- The π,π^* triplet states of polynuclear aromatics are generally highly efficient, frequently with $S\Delta \geq 0.8$. Many other π,π^* triplet states are also very efficient.
- The n,π^* triplet states of ketones have low values of S_Δ, for example for benzophenone in the 0.3-0.4 range. There is a modest increase in the value of S_Δ with decreasing triplet energy.

Sensitizer	**Solvent**	S_Δ
naphthalene	cyclohexane	1.0
anthracene	benzene	0.8
benzophenone	benzene	0.3
fluorenone	benzene	0.8
tetraphenylporphyrin	benzene	0.58
$Ru(bipy)_3Cl_2$	methanol	0.92
α-Terthienyl	benzene	0.8
phenazine	benzene	0.83
acridine	acetonitrile	0.82

Parameters to take into consideration in selecting the singlet oxygen sensitizer and conditions

- High value of S_{Δ}.
- Long triplet lifetime in order to maximize triplet quenching.
- High rate constant for triplet quenching by oxygen (true in almost all cases), and low rate constant for triplet quenching by substrate.
- High sensitizer stability toward singlet oxygen. Some good (i.e. high S_{Δ}) sensitizers may also trap singlet oxygen efficiently, thus reducing their own usefulness.
- Good spectral properties making possible the selective excitation of the sensitizer (as opposed to the substrate) with a readily available light source.
- A sensitizer with efficient intersystem crossing under the experimental conditions (that could include oxygen-assisted intersystem crossing).
- A solvent with good solubility for oxygen (e.g. halogenated) and where singlet oxygen has a long lifetime.
- Easy sensitizer removal. For synthetic applications it may be desirable to eliminate the sensitizer at the end of the reaction. Some heterogeneous sensitizers have been developed (e.g. on polymer particles) that can be readily filtered at the end of the oxidation.

Reaction of oxygen with reaction intermediates:
Mechanisms and kinetics

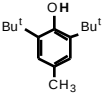
Free radical scavenging by oxygen

Carbon-centered free radicals frequently react with oxygen with rate constants exceeding 10^9 M^{-1} s^{-1} in fluid solution, to yield a peroxyl radical

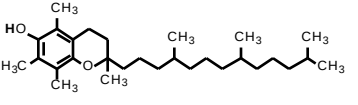
$$R\bullet + O_2 \rightarrow R\text{–}OO\bullet$$

$$ROO\bullet + RH \rightarrow R\bullet + ROOH$$

ANTIOXIDANTS



BHT

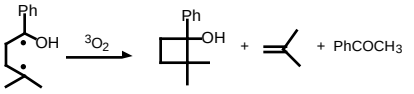


Vitamin E

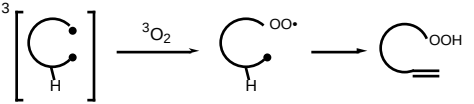
Biradical scavenging by oxygen

A) Assisted intersystem crossing

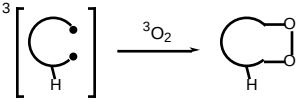
E.g.



B) Hydroperoxide formation



C) Peroxide formation



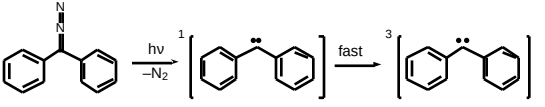
Reactions of carbenes with oxygen

$$\left[{}^{3}(C_6H_5)_2C:\right] + {}^{3}O_2 \xrightarrow{3/4} (C_6H_5)_2COO$$

Carbonyl oxide or Criegee intermediate

Making carbenes:

Diazo precursor of carbene with triplet ground state



Diazirine precursor of carbene with singlet ground state