

The chemistry of singlet molecular oxygen

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The most important but the least understood part of the oxygen cycle is the nature and interaction of oxygen with many chemical and biological systems in nature. Therefore, there is a need to understand the mechanism of oxygen involvement in such systems. Present review describes the various aspects of singlet oxygen, a high energy state of ground state oxygen. These aspects include electronic structure, generation, detection, quenching, various reactions etc.

For every atom and molecule known to us in the ground state, there are likely to be one or more excited states. Since these states possess different electronic structures and higher energies than their parents, their chemistry is almost inevitably distinct from that of the ground state species. Excited forms of molecular oxygen of high chemical activity were discovered as two singlet forms $^1\Delta_g$ and $^1\Sigma_g^+$. The field of singlet oxygen chemistry has developed dramatically during the past three decades. This period has witnessed an enormous increase in the interest in the role of singlet oxygen in physical, chemical and biological system and as a specific oxidative reagent.

Discovery

Faraday discovered that oxygen is paramagnetic having two outer electrons with parallel spins¹. This uncoupled electron pair classified oxygen as a triplet in its lowest energy state, $^3\Sigma_g^-$. A few years later, two higher energy states of oxygen ($^1\Sigma_g^+$ and $^1\Delta_g$) were observed spectroscopically by Childe and Mecke² and Herzberg³, respectively. These were classified as spectroscopic singlets and this classification was interpreted as being the result of their outer electron pair having antiparallel spins. These three forms of oxygen molecule attracted the attention of Kautsky. It was observed that red fluorescence from chlorophyll is suppressed in presence of oxygen⁴. Kautsky *et al.*⁵ also reported an experimental evidence for a 'metastable reactive state of the oxygen molecule' by photochemical oxidation of leucomalachite green supported on dry silica gel. The photosensitized generation of 1O_2 in solution containing dye was also suggested by Kautsky. Although the result obtained by Kautsky was basically correct even then this work remained almost unrecognized for more than two decades. Meanwhile the atomic oxygen and ozone were regarded as the oxidants in photochemical reactions⁶. The role of singlet oxygen in air pollu-

tion has also been discussed by Lighten⁷. It was the work of Foote and Wexler⁸ and Corey and Taylor⁹, which rediscovered singlet oxygen and rejuvenate interest in photo-oxidation reactions.

Nature¹⁰

The electronic state of molecular oxygen has been explained by molecular orbital theory. The last two valence electrons enter one each into degenerate $\pi^* 2p_x$ and $\pi^* 2p_y$ pair of orbitals with parallel spins giving triplet ground state $^3\Sigma_g^-$. Pairing of the electrons in one molecular orbital results in the $^1\Delta_g$ state, and spin pairing in different orbitals results in $^1\Sigma_g^+$ state. The potential energy diagram for the three low lying electronic states of molecular oxygen is shown in Fig. 1. The energy difference between $^3\Sigma_g^- - ^1\Delta_g$ and $^3\Sigma_g^- - ^1\Sigma_g^+$ are 94.5 and 156.9 kJ mol⁻¹, respectively.

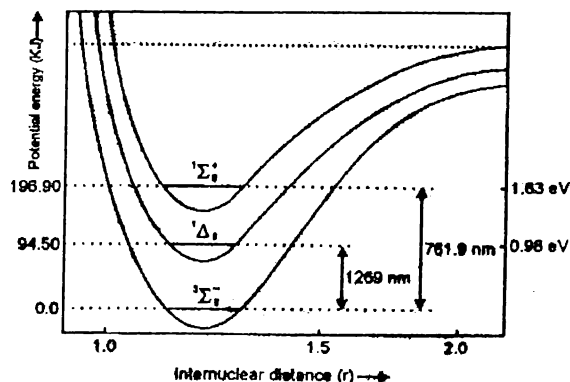


Fig. 1

$^1\Delta_g$ is decidedly electrophilic in nature whereas $^3\Sigma_g^-$ participates in reaction as a radical and $^1\Sigma_g^+$ possesses intermediate properties of $^1\Delta_g$ and $^3\Sigma_g^-$. The properties of singlet and triplet states of molecular oxygen have been summarized in Table 1.

Table 1. Electronic states and properties of molecular oxygen¹⁻¹⁴

Sl. no.	Properties	Electronic state		
		³ Σ _g ⁻	¹ Δ _g	¹ Σ _g ⁺
1.	Configuration of electrons in highest occupied molecular orbital	↑↑	↑↓	↑↓
2.	Relative energy (kJ mol ⁻¹)	0.0	94.5	156.9
3.	Gas phase life time at zero atmospheric pressure	∞	2700 s	7
4.	Liquid phase life-time	∞	10 ⁻³ s	10 ⁻⁹
5.	Light emission band (nm)	-	1269	761.9
6.	Half-life at one atmosphere	-	5.0 × 10 ⁻²	-
7.	Gas collision survival	-	10 ⁸	10-100

When the excited energy of a sensitizer molecule exceeds 94.50 kJ mol⁻¹, singlet oxygen ¹O₂ (¹Δ_g) may be formed. For the formation of singlet oxygen ¹O₂ (¹Σ_g⁺) the excited energy of the sensitizer molecule should exceed 157 kJ mol⁻¹. A schematic diagram for the energy transfer in dye-photosensitized reactions, in which singlet oxygen ¹O₂ (¹Δ_g and ¹Σ_g⁺) may be formed, is given in Fig. 2.

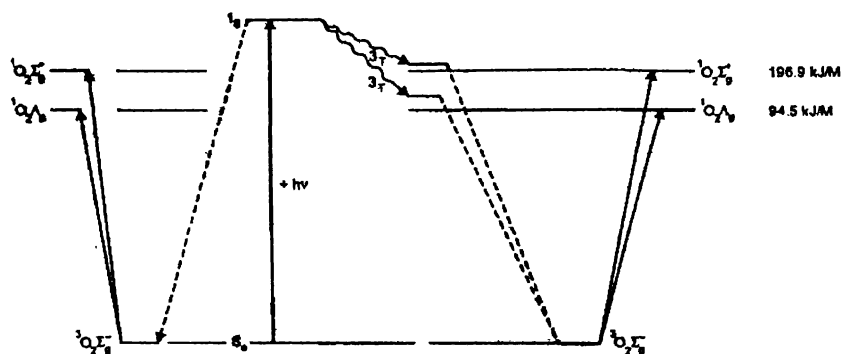
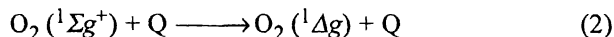
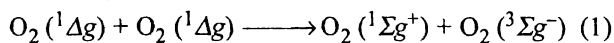
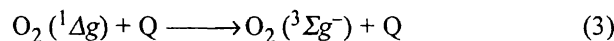


Fig. 2. Diagram of energy transfer from the excited singlet (¹Σ) or triplet (³T) of a sensitizer to molecular oxygen (³O₂) forming singlet oxygen ¹O₂ (¹Δ_g) or (¹Σ_g⁺).

In gas phase, both the ¹O₂ (¹Δ_g) and ¹O₂ (¹Σ_g⁺) states are important because of their inter-convertibility through the following reactions¹⁴,



where Q is any quenching species present in the system. Reaction (2), which is not 'spin-forbidden' but a 'spin-allowed process' and liberates 62.4 kJ of electronic energy, while removal of the singlet delta state by a quencher Q, which can be written as



is a 'spin-forbidden' process unless Q has a multiplicity greater than one and furthermore liberates 94.50 kJ, which must be accommodated in the products of reaction (3). These

two factors combine to make most molecules quench O₂ (¹Σ_g⁺) about 105 times more rapidly than O₂ (¹Δ_g). The various sensitizers like anthracene, fluorescence, rose bengal etc. possess triplet energies more than 156.90 kJ. The triplet energies of such sensitizers are enough for the transfer forming the singlet oxygen ¹O₂ (¹Σ_g⁺). The sigma singlet oxygen is rapidly quenched in solution indicating that ¹O₂ (¹Σ_g⁺) is not important as an oxidant in these reactions. Singlet oxygen ¹O₂ (¹Δ_g) is presumably responsible for the initiation of oxidation.

Life-time

The life-time of singlet oxygen varies considerably depending on the solvent, and a selection of literature values are given in Table 2. It has been shown^{15,16} that there is a correlation between the life-time of singlet oxygen and infrared spectral properties of the solvent. The greater the absorption near 8000 cm⁻¹ the shorter is the life-time of singlet oxygen, which suggests that direct conversion of the

electronic energy from singlet oxygen (¹Δ_g) into vibrational energy of the solvent is predominant in determining the decay of singlet oxygen.

Table 2. Life-time of singlet oxygen in fluid solvents

Solvent	Life-time μs	Ref.	Solvent	Life-time μs	Ref.
H ₂ O	2.0	16	CH ₃ COCH ₃	26.0	16
Glycol	6.1	17	CH ₃ COCN	30.0	16
CH ₃ OH	8.5	18	Dioxane	32 ± 10	19
C ₂ H ₅ OH	12.0	16	C ₆ H ₅ COOCH ₃	40 ± 16	17
C ₆ H ₆	24.0	16	CH ₃ COOC ₂ H ₅	47 ± 15	17
CS ₂	200 ± 60	20	CHCl ₃	60	16
Freon-11	1000 ± 200	20	C ₂ H ₅ Br	75 ± 30	17
CCl ₄	700	17	CH ₂ Cl ₂	140	17

Properties of singlet molecular oxygen in binary solvent mixtures of different polarity and proticity have also been studied²¹. Kinetics of decay of singlet molecular oxygen in a solution containing dimeric metalloporphyrin has been reported²².

Generation

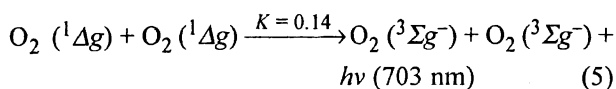
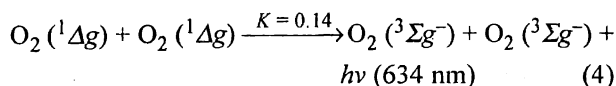
The most universal and probably the most important mechanism by which singlet oxygen is formed in the earth's biosphere is in the following way. The absorption of visible and ultraviolet light (from the sun) usually leads to the electronic excitation of the molecules. Since oxygen permeates most organic matter, O₂ is a common quencher of this electronic excitation. In this process, singlet molecular oxygen is formed.

Methods of generating singlet oxygen can be grouped under two categories, namely, physical and chemical methods.

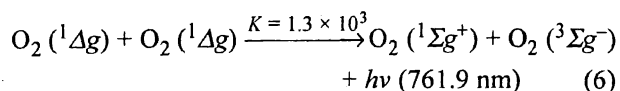
Physical methods :

Electric discharge through oxygen : The products of an electric discharge through molecular oxygen contain appreciable quantities of singlet oxygen as indicated by calorimetric and spectrometric studies²³.

*Energy pooling process*¹⁰ : At an O₂ (¹Δg) concentration of 2 × 10⁻³ M emission from the following processes assume the same intensity,



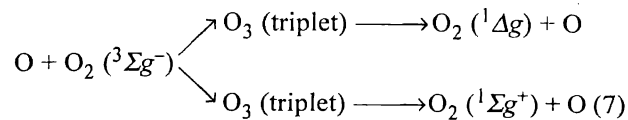
Under the same reaction, the 'disproportionation' reaction occurs,



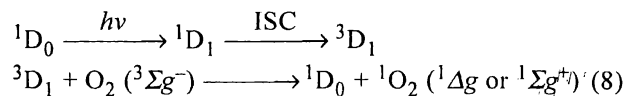
The infrared emission at 761.9 nm can be much more intense than the red emission (634 and 703 nm), so O₂ (¹Σg⁺) concentration is established within a few cm of the discharge.

*Ozone reaction*²³ : The ground state atomic oxygen produced in discharge or thermal reactions can react with ozone to produce singlet molecular oxygen ¹Σg⁺.

Energy transfer : De More and Raper²⁴ suggested the production of ¹O₂ by energy transfer mechanism, in which an excited triplet ozone molecule is formed as



Dye-sensitization : A wide variety of methods for generation of singlet oxygen have been developed but this method is still most widely used in the laboratory, i.e. dye-sensitized excitation of oxygen²⁵,



This method has the disadvantage that (i) dye is present throughout the reaction, (ii) most of the dyes are not readily soluble in organic solvents and (iii) dye can bleach depending upon solvent, temperature and concentration etc. Due to these disadvantages, a method using polymers for heterogeneous photosensitization of oxygen has been reported²⁶.

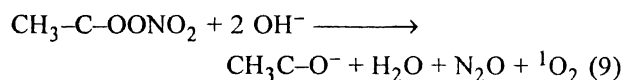
Miscellaneous excitation process : Khan *et al.*²⁶ suggested that any organic compound that absorbs radiation at a wavelength greater than the atmospheric cut off at 300 nm could act as donors (D) in an energy transfer mechanism. Pitts *et al.*²⁷ suggested that the reaction of ozone with a number of other atmospheric contaminants (particularly sulfides) could also yield singlet oxygen as a product. Recently, parametric study of a twisted aerosol type singlet oxygen generator has also been reported²⁸. Performance characteristics of jet type generator of singlet oxygen has also been studied²⁹.

Chemical methods :

Decomposition of H₂O₂ : Mckeown and Waters³⁰ suggested generation of ¹O₂ by the decomposition of alkaline H₂O₂ with bromine. Reaction of hydrogen peroxide and hypochlorite also generates singlet oxygen.

Self-reaction of sec-butylperoxy radicals : Russell³¹ proposed that *sec*-peroxy radicals could undergo a self-reaction involving a cyclic transition state with the formation of singlet oxygen.

Base-induced decomposition of peroxyacetyl nitrate : Steer *et al.*³² observed the decomposition of peroxy acetyl nitrate in presence of base leading to the production of singlet oxygen.



Decomposition of superoxide ion : Khan³³ reported that potassium superoxide evolves singlet oxygen in dimethyl sulfoxide solution.

Miscellaneous methods : Generation of $^1\text{O}_2$ by 2,2' : 5,2''-terthiophene and some of its derivatives³⁴ and aromatic ketones as standards for $^1\text{O}_2$ ($^1\Delta_g$) photosensitization³⁵ have been reported. Investigation of $^1\text{O}_2$ generation by water-soluble diimine complexes of platinum(II) and palladium(II) with 3,4-dihydroxybenzoic acid as photosensitizers³⁶, production of $^1\text{O}_2$ ($^1\Delta_g$) by 9,10-dicyanoanthracene and acridine, quantum yields in acetonitrile³⁷ and $^1\text{O}_2$ production has been studied by Kanofsky *et al.*³⁸. Recently, alloxazine and isoalloxazine have been proved as efficient singlet oxygen generators³⁹. From triplet states of singlet nitrophenyl ethers, generation of singlet oxygen has been suggested⁴⁰. Polymers derivatized with hexanuclear molybdenum clusters were suggested as efficient singlet oxygen generator⁴¹. A kinetic study on singlet molecular oxygen generation and quenching by dihydroxynaphthalenes was carried out by Luiz *et al.*⁴². Singlet oxygen production by hypericin in various solvents was studied by Darmanyan *et al.*⁴³. The role of heterogeneous molybdate catalysts for the generation of singlet molecular oxygen was investigated by Van Laar *et al.*⁴⁴. Recently some newer methods for the generation of singlet oxygen and related work have also been reported⁴⁵⁻⁴⁸.

Detection

Various techniques are used for detecting the presence of singlet molecular oxygen.

Electron paramagnetic resonance : Folik *et al.*⁴⁹ analysed the EPR spectrum of singlet oxygen in discharge of oxygen and proved that $^1\text{O}_2$ concentration is about 10% of the total oxygen concentration.

Photoionization method : Cairns and Samson⁵⁰ were the first to use photo-ionization technique for detection of $^1\text{O}_2$.

Chromatographic method : Recently, in photo-oxidation of 3-substituted-pyrroles, a post-column reaction detection system for singlet molecular oxygen in HPLC was studied by Danham and Milofsky⁵¹.

Chemical method : Limonene(+)⁵² and cholesterol⁵³ are used as probe for detecting singlet oxygen. Winer and Bayes⁵⁴ described a reaction of $^1\text{O}_2$ ($^1\Delta_g$) with the olefin 2,3-dimethylbutene-2 (tetramethylethylene, TME) to form a peroxide. Another method for detection of singlet oxygen utilizes the bright chemiluminescence on addition of molecular iodine in a flow discharge of oxygen⁵⁵.

Quenching

Quenching means deactivation of the excited singlet state of the oxygen molecule. The two singlet oxygen species $^1\text{O}_2$ ($^1\Delta_g$) and $^1\text{O}_2$ ($^1\Sigma_g^+$) differ markedly in the ease with which these are deactivated.

$^1\text{O}_2$ ($^1\Sigma_g^+$)¹⁰ : Quenching rate constants for singlet sigma oxygen have been determined at 25° by a number of workers and the results have been summarized for diatomic molecules like H_2 , HD, D_2 , NO, HCl, HBr, CO, N_2O_2 , and polyatomic molecules as H_2O , NH_3 , amines, alcohols, halides etc. Although our primary interest lies in O_2 ($^1\Delta_g$) in which 62.4 kJ mol⁻¹ (5238.5 cm⁻¹) of electronic energy must be transformed into nuclear motion in O_2 ($^1\Delta_g$) and the quencher.

$^1\text{O}_2$ ($^1\Delta_g$)¹⁰ : Species such as H_2 , H_2O , CO_2 , C_3H_8 , C_2H_4 , NH_3 and a few others (named as 'normal quenchers') have O_2 ($^1\Delta_g$) quenching constants which are about 3–5 orders of magnitude smaller than the corresponding values for O_2 ($^1\Sigma_g^+$). O_2 ($^1\Delta_g$) quenching rates can be considered to be reduced 2 or 3 orders of magnitude relative to the O_2 ($^1\Sigma_g^+$) rates because of spin conservation requirements and an additional 2 or 3 orders of magnitude due to the extra 32.10 kJ of electronic energy, which must be accommodated in the products.

Mechanism of quenching of singlet oxygen¹⁵ :

A number of different mechanisms have been postulated for the quenching of singlet oxygen $^1\text{O}_2$ ($^1\Delta_g$), including energy transfer to vibrational energy (solvents), charge-transfer quenching, electronic energy transfer and quenching by excited triplet state molecules and dimol interactions.

Kearns *et al.*⁵⁶ developed a relation between optical density and the quenching rate constants and gave a theory of decay in solution that is based on the transfer of the electronic energy of singlet oxygen into the vibrational modes of the solvent molecule,

$$K_d \times 10^{-6} \times 0.5 (\text{O.D.}_{7780 \text{ cm}^{-1}}) + 0.05 (\text{O.D.}_{6280 \text{ cm}^{-1}})$$

Different compounds have been suggested to quench singlet oxygen by a charge-transfer mechanism, including amines⁵⁷, azides⁵⁸, super oxides⁵⁹, iodides⁶⁰, metal complexes⁶¹, DABCO⁶², electron-rich compounds⁶³ and bilirubin⁶⁴. A number of different compounds have been reported as effective quenchers of singlet oxygen in solution via an energy transfer mechanism. One of the most effective of these is β -carotene⁶⁵ and others include the transition metal chelates¹⁵, iodine atom⁶⁶ etc. The quenching by energy transfer is the reverse of reaction by which $^1\text{O}_2$ is formed.

A number of compounds physically quench the singlet oxygen. The important ones include α -tocopherol⁶⁷, cobalt complexes⁶⁸, quenching in silica gel-solvent heterogeneous system⁶⁹ and DABCO, DPBF and some inorganic ions¹¹.

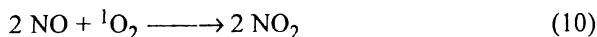
Detty⁷⁰ studied related quenching of singlet oxygen by organometallics. Geometry-dependant quenching of singlet oxygen by dialkyl disulfides has also been reported⁷¹. De-

termination of quenching rate constants of singlet oxygen by derivatized nucleosides in non-aqueous solution has been reported by Prat *et al.*⁷². Virgatic acid from saliva species has been found as singlet oxygen quencher in plants⁷³.

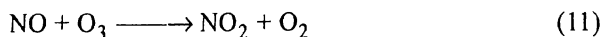
Atmospheric photochemistry

Singlet molecular oxygen is formed by the absorption of visible and ultraviolet light (from sun), which usually leads to the electronic excitation of the molecules and is of interest in connection with atmospheric chemistry with respect to both its mode of excitation and to the consequence of its presence in the upper or lower atmosphere. The sky emits radiation known as the 'air glow', which during day and night contains components resulting from optical transition $^1\Delta_g$ and $^1\Sigma_g^+$.

The pollution of urban atmosphere is becoming a matter of increasing concern as both life and property are endangered by increasing levels of pollutant. In early morning in urban areas such as Los Angeles, there is characteristic build up of nitric oxide and hydrocarbon concentration in atmosphere, which results from an increase in automobile traffic⁷⁴. In polluted urban atmosphere, singlet oxygen may play an essential part in the oxidation of nitric oxide to nitrogen dioxide⁵⁹,



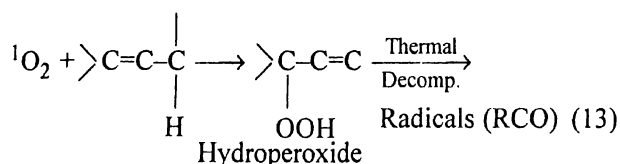
Almost all the nitric oxide has been consumed, which suggests strongly that the major loss process for ozone is⁷⁵



The loss of ozone is balanced by three-body reaction,



In the Los Angeles basin, after sunrise the nitric oxide concentration decreases and nitrogen dioxide appears in its place. Once all the nitric oxide has been consumed, ozone begins to appear⁵⁹. Pitts *et al.*⁵⁹ suggested the involvement of $^1\text{O}_2$ for the formation of hydroperoxide, which participates in the oxidation of nitric oxide via radicals.



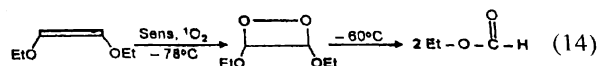
Reactions of singlet molecular oxygen

The reactions are classified into three types : 1,2-cycloaddition reaction, (ii) ene reactions and (iii) 1,2-dioxetanes reaction.

1,2-Cycloaddition reaction :

Footo and Lin⁷⁶ found that photo-oxygenation of enam-

ine produces the carbonyl cleavage products and similar results have been obtained by Wassermann and Terao⁷⁷ for cyclic enamines in methanol. Bartlett *et al.*⁷⁸ were successful in isolating a 1,2-dioxetane from the 1,2-cycloaddition of $^1\text{O}_2$ to an olefin while sensitized photo-oxygenation of *cis*-diethoxyethylene was studied by Wilson and Schaap⁷⁹,



Allenes are relatively unreactive towards singlet oxygen but Greibrokk⁸⁰ observed that upon prolonged photo-oxygenation, tetraphenylallene was converted to benzophenone and CO_2 with the involvement of $^1\text{O}_2$. Oxidation of thiones⁸¹, sulfines⁸², ylides⁸³ etc. have been investigated.

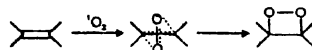
Recently, Adam *et al.*⁸⁴ reported chemiluminescence from the labile 1,2-dioxetanes and epoxides produced in the oxidation of *N*-acetylated dihydro- and tetrahydropyrazines by singlet O_2 and other oxidants. In photodegradation of lignin, 1,2-cycloaddition is proposed⁸⁵.

A number of mechanisms that have been considered are outlined as follows :

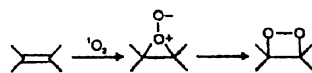
(i) A biradical mechanism⁸⁶ :



(ii) A symmetry-allowed concerted path⁷⁸ :



(iii) Peroxide or peroxirane intermediate⁸⁷ :



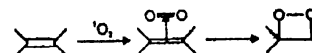
(iv) A zwitterionic mechanism⁸⁸ :



(v) Radical cation and superoxide radical anion pair mechanism⁸⁹ :

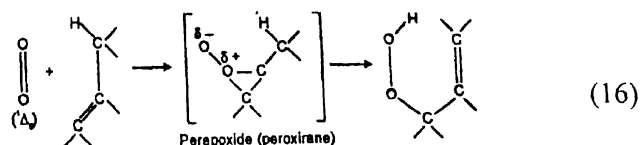


(vi) A charge transfer mechanism⁸⁷ :



Ene reactions :

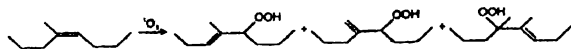
The ene reaction, in which hydroperoxides are formed, is observed with olefins possessing an allylic hydrogen^{73,90}.



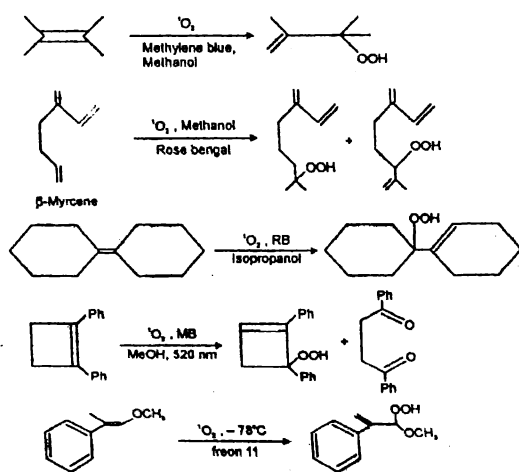
The involvement of peroxide intermediate is in consistent with the observations⁹¹.

Investigation on $^1\text{O}_2$ reactions with olefins have been carried out predominantly in the liquid phase. As a result ene product formation seems to be affected a little by the nature of the solvent but it strongly depends on the stereoelectronic and steric effects exerted by the olefin on the attacking electrophilic singlet oxygen. Ene-reaction of singlet oxygen with respect to the double bond in non-conjugated dienes are regioselective.

Photo-oxygenation of a mixture of *cis*- and *trans*-isomers leads to a mixture of allylic hydroperoxides as¹³



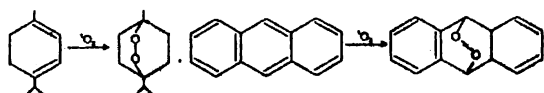
Some ene-reaction of various olefins with singlet oxygen are presented in Scheme 1⁹²⁻⁹⁵.



Scheme 1

Stratakis *et al.*⁹⁶ observed exceptional synselectivity in the ene products during reaction of singlet oxygen and *N*-methyltriazolodiones with β,β -dimethylstyrene. Ene reactions of singlet oxygen with alkenes bearing an electron-withdrawing group at β -position were found to be regioselective⁹⁷. Unusual regioselectivity was reported in the singlet oxygen ene reaction of cyclohexenobuckminsterfullerenes⁹⁸. Recently, regioselectivity in the ene reaction of singlet oxygen with alkenes has been observed⁹⁹.

Diels-Alder reaction : With acceptors such as *cis*-diene or aromatic hydrocarbons, singlet oxygen appears to behave as a good dienophile¹⁰⁰.

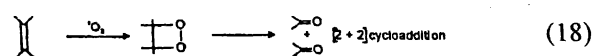
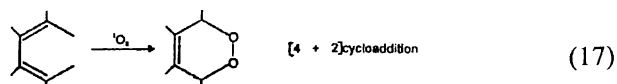


The similarity between these reactions and more familiar Diels-Alder reaction is obvious. The effect of tempera-

ture on the rate of reaction of $^1\text{O}_2$ with a variety of acceptors including a number of dienes has also been studied. It has been found¹⁰¹ that very low amount of activation energy is required ranging from zero to 25.0 kJ mol^{-1} . Recently, Pierlot and Aubry¹⁰² have reported the formation of 5,8-endoperoxide from the oxidation of 1,4-disubstituted-naphthalene by singlet oxygen.

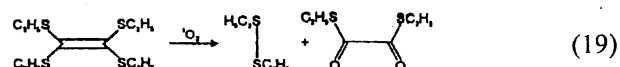
1,2-Dioxetanes :

Singlet oxygen possesses the unique characteristic of being able to undergo both [4 + 2] and [2 + 2] cycloaddition with suitable olefins. In the second case, the resulting dioxetane usually reacts further to give the cleavage products, namely, two carbonyl fragments¹⁰³,

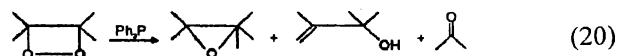


The first dioxetane, trimethyl-1,2-dioxetane was prepared by bromohydroperoxide. Thermal decomposition of trimethyl-1,2-dioxetane forms acetone and acetaldehyde¹⁰³. All the 1,2-dioxetanes luminesce upon thermal decomposition. The most extensively investigated one is TMD (tetramethyl-1,2-dioxetane), a useful tool in determining the nature of the excited acetone from TMD decomposition. A two-step ring cleavage involving the intermediacy of a 1,4-biradical has been proposed to account for the luminescent decomposition of 1,2-dioxetanes¹⁰⁴.

The photo-oxidation of thioethylene leads to products without cleavage of C-C bond¹⁰⁵. For example, the oxidation of tetrakis(ethylthio)ethylene generates dimethylthiooxalate and diethyl disulfide¹⁰⁶.



Reactions of triphenylphosphine with several dioxetane lead to the formation of allylic alcohol, an epoxide and ring cleavage products¹⁰⁷.



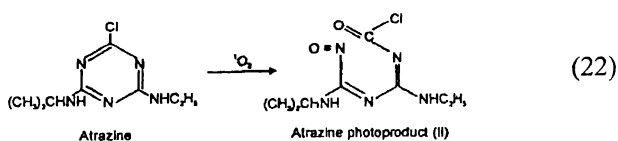
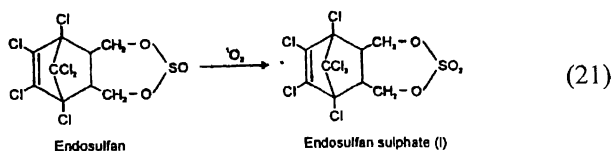
The [4 + 2] cycloaddition of singlet oxygen to aromatic hydrocarbon and thereby an easy method for the determination of oxygen concentration in organic solvents was reported¹⁰⁸. A convenient method for the synthesis of DL-protoquercitol and DL-galaquercitol via ene reaction of singlet oxygen combined with [2 + 4] cycloaddition to cyclohexadiene was proposed¹⁰⁹. [4 + 2] Cycloaddition of singlet oxygen with cyclic 1,3-dienes was carried out in twentyeight solvents by Aubry *et al.*¹¹⁰. Apart from the

above, other studies on cycloaddition reactions of singlet oxygen were also carried out¹¹¹⁻¹¹³.

Photo-oxidation of pesticides

The environmental fate of pesticides is a matter of great interest and concern. Many modern pesticides contain sulfur atoms, which offer reactive sites for environmental degradation process including direct photolysis, photo-oxidation and sensitized photo-oxidations.

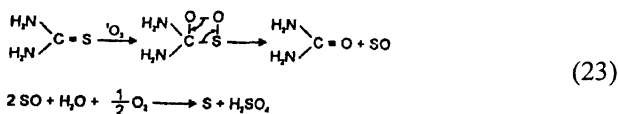
Photodegradation of fluvalinate has been studied by Greenberg¹¹⁴ in grapes, peppers, apples and cotton seeds. Photosensitized oxidation of methylparathion¹¹⁵, endosulfan¹¹⁶, atrazine¹¹⁷ have been reported by singlet oxygen. In case of endosulfan, endosulfan sulfate, while in atrazine, atrazine photoproduct (II) have been reported as a photo-products.



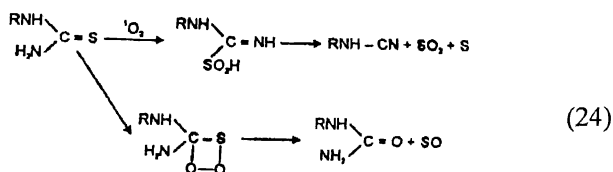
Dye-sensitized photo-oxidation of ethion¹¹⁸ and fenitrothion¹¹⁹, and also of malathion, phenthoate and dimethoate¹²⁰ have been reported.

Photo-oxidation of organosulfur compounds

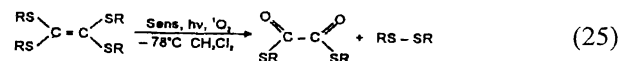
The dye-sensitized photo-oxidation of thiourea in visible region results in the formation of urea¹²¹,



Similar type of mechanisms have been proposed for *o*-tolylthiourea, 1-allyl-3-(2-pyridyl)thiourea, phenyl-3-(2-pyridyl)thiourea and thiosemicarbazide¹²². Crank and Musyidi¹²³ reported that in presence of UV-light, singlet oxygen reacts with thioureas to form cyanamides, ureas, heterocyclic condensation products and sulfur-containing fragment,



Photochemical oxidation of dithizone to form diphenyl-carbazone and thiomalic acid to form dithiodi(malic acid)¹²⁴ as photoproducts was reported. Photosensitized properties of singlet oxygen of bithiophene and terthiophene derivatives have been studied by Boch *et al*¹²⁵. Dye-sensitized photo-oxygenation of thioacetamide was also studied¹²⁶. Harding and Goddard¹²⁷ showed that the photo-oxygenation of tetrathioethylenes gives rise to dithiooxalates and disulfide. The above product was suggested to arise by radical fragmentation of dioxetane, dominated by the low strength of C-S bond compared to C-C bond,



Jensen *et al*^{128,129} reported the revised mechanism for the reaction of singlet oxygen with organic sulfides. Dye-sensitized photo-oxidation of benzthiazide was studied involving ¹O₂ as the active oxidizing species¹³⁰. Sensitized photo-oxygenation of 1,1-dithioalkyl(propyl)ethylene and tetrathioalkylolefins was also investigated¹³¹

Photo-oxidation of organonitrogen compounds

The sensitized photo-oxidation of glucosazone to glucosone in methanol was studied by Vaidya¹³². Singlet oxygen mediated alkaloid tertiary amine oxidation involving single electron transfer has been recently studied¹¹³. The role of singlet molecular oxygen has been suggested in the photochemical ring opening of nitrospiropyrans¹³⁴.

Photo-oxidation of some heterocyclic compounds

Kinetic study of the singlet molecular oxygen mediated photodegradation of monohydroxylated *N*-heteroaromatic compounds has been reported recently¹³⁵. Ling¹³⁶ reported synthesis of bulky 2,2-diaryl-1,2-dihydro-3*H*-indol-3-ones via singlet oxygenation of 2-arylindoles.

Addition of ¹O₂ to a heterocyclic system usually occurs by three methods : (a) 1,4-addition to the 1,3-diene system : photo-oxidation of pyrrole, oxazoles, etc. involves 1,4-addition, (b) dioxetane formation : photo-oxidation of tetraphenylimidazole, 3,4-benzofurans occurs via dioxetane, and (c) hydroperoxide formation : in typical ene type reaction, 2-methylfuran reacts with singlet oxygen in methanol to yield methoxyhydroperoxide.

Reaction conditions like solvent, dilution, temperature etc. play key role in heterocycle oxidations and significantly affects the nature of the products. Thus, the photo-oxidation of pyrrole in methanol forms maleimide (major) and 5-methoxypyrrolin-2-one (minor) while in aqueous solution forms 5-hydroxypyrrolin-2-one¹³⁷.

Dye-sensitized photo-oxygenation of histidine is of special interest in connection with the photodynamic destruction of the histidine residues in protein¹³⁸. The reaction of histidine shows a pH-dependence; it is faster at higher pH, in the pH range 3–8, thus indicating that protonated imidazole ring is insensitive to the reaction, so a complex mixture of products have been formed. Wasserman *et al.*¹³⁹ reported pyrrole oxygen reactions leading to the α,α -bipyrroles and thereby synthesizing prodigiosin and analogs.

Miscellaneous reactions

Photocyclization of creatine during oxidation by $^1\text{O}_2$ has been reported¹⁴⁰. Photosensitized oxygenation of twisted 1,3-dienes revealed that vinyl hydrogen possesses abnormally higher reactivity towards $^1\text{O}_2$ rather than allylic hydrogen¹⁴¹. Mehta *et al.*¹⁴² studied the effects of remote substituents in singlet oxygen addition to hexacyclo[7.5.1.0(1,6).0(6,13).0(8,12).0(10,14)]pentadeca-2,4-diene system. The role of $^1\text{O}_2$ in various polymer degradation has been investigated^{143–145}. The role of singlet oxygen in the photochemical formation of C_{60} has been suggested by Schuster *et al.*¹⁴⁶. Reaction of singlet oxygen with fullerenes was also reported^{147,148}. Addition of $^1\text{O}_2$ to bisdialine has been reported^{147,148}. Addition of $^1\text{O}_2$ to bisdialine has been reported to occur in *syn* and *anti* manner¹⁴⁹. $^1\text{O}_2$ oxidation of bipyrroles was studied by Wassermann *et al.*¹⁵⁰. Phosphadi-oxirane intermediates in the reaction of $^1\text{O}_2$ with phosphates and phosphines was reported¹⁵¹.

Singlet oxygen in inorganic chemistry

In reaction of singlet oxygen with Ni^{II} and Pd^{II} thiolates, production of sulfur oxygenates was reported¹⁵². Photochemical elimination of singlet oxygen from oxidoperoxomolybdenum(VI) complexes with aromatic *N,N*-chelate was reported¹⁵³. Selective oxyfunctionalization of iron substituted ligands takes place in reaction with $^1\text{O}_2$ (Ref. 154). Reaction of $^1\text{O}_2$ with organometallic complexes was investigated by Selke and Foote¹⁵⁵. Dioxygen insertion in Si–Si σ -bonds was reported in the reaction of singlet oxygen with disiliranes¹⁵⁶. The quenching of $^1\text{O}_2$ by various inorganic ions has been reported¹⁵⁷.

Singlet oxygen has been used as an oxidizing agent to oxidize various organic and inorganic substrates. Such reactions proceed through various intermediates like hydroperoxide, dioxetanes, endoperoxide etc. On the other hand, singlet oxygen is also considered a dreadful species as it is responsible for creating many diseases specially neo-natal jaundice, skin cancer, porphyria etc. It is, therefore, important to know the role of singlet oxygen in various chemical and biological processes.

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