Singlet Oxygen $O_2(^1\Delta_g)$ Bimolecular Processes. Solvent and Compartmentalization Effects

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Contents

I. Introduction

Singlet oxygen ($O_2(^1\Delta_g)$) processes are a matter of current interest, mainly due to the role that these reactions play in biological processes.[1-7] Regarding photoinduced processes, $O_2(^1\Delta_g)$ is believed to be involved in the photosensitivity of patients with erythropoietic protoporphyria[8] and drug phototoxicity,[9-11] and its formation has been extensively employed therapeutically.[12-16] The reactions of $O_2(^1\Delta_g)$ are generally non-diffusion-controlled processes, and the extent of reaction in a complex biological system toward a given target is determined by the $O_2(^1\Delta_g)$ steady-state concentration at the reaction locus and by the bimolecular rate constant (expressed in terms of local concentrations). The first factor is determined by the rate and locus of $O_2(^1\Delta_g)$ generation, its diffusion rate, its partition between different microenvironments, and its lifetime (τ_Δ). In microheterogeneous systems, τ_Δ is determined, in each differential volume (dV) of the system, by the solvent-dependent radiationless decay constant (k_d) and a term comprising all bimolecular processes:

$$\tau_\Delta^\circ = (k_d)^{-1} + (\sum k_i[i])^{-1} \quad (1)$$

k_d values in a variety of solvents have been reported,[17-22] and efforts have been made to establish the partition of $O_2(^1\Delta_g)$ in different micromedia.[23-26] The reactivity of $O_2(^1\Delta_g)$ with a large number of substrates has been measured, and several comprehensive data compilations are presently available.[27-29] In contrast, an important factor such as the effect of the medium upon the bimolecular rate constant has received considerably less attention, in spite of the effect that this factor can have both upon τ_Δ and upon the extent of reaction of $O_2(^1\Delta_g)$ with a given substrate. This information is particularly relevant since a substrate incorporated into a particular structure (such as a membrane) can be located in a variety of media that could be widely different with regard to k_i values. The present paper attempts to cover this field with emphasis on the effect of the medium upon k_i both in homogeneous and in microheterogeneous systems.

Most of the bimolecular rate constants measured before 1980 have been compiled by Wilkinson and Brummer,[28] and the knowledge on $O_2(^1\Delta_g)$ processes up to the late 1970s has been thoroughly reviewed.[1,29-32] The data compiled by Wilkinson and Brummer[28] indicate that the solvent plays apparently only a minor role in $O_2(^1\Delta_g)$ processes. Actually, even after considering that several $O_2(^1\Delta_g)$ processes involve a charge-transfer interaction, as evidenced in the *N,N*-dimethylanilines by the slope of Hammett-type plots,[33] Wilkinson and Brummer[28] stated that it is interesting to note that the efficiency of quenching by the amines in the gas phase is similar to that observed in solution.[34-36] This result would be consistent with a lack of a major difference among the solvents considered. Most of the early works tend to support the statement that $O_2(^1\Delta_g)$ reactions are almost solvent independent. However, later studies comprising a wider range of solvents have revealed a large dependence of k_i on the solvent in some systems.[37-40] This could modify the relative reactivity of substrates located in different locations in microheterogeneous systems. This type of information may be relevant when one attempts to extrapolate data obtained in homogeneous solutions to complex biological systems.[41-43]

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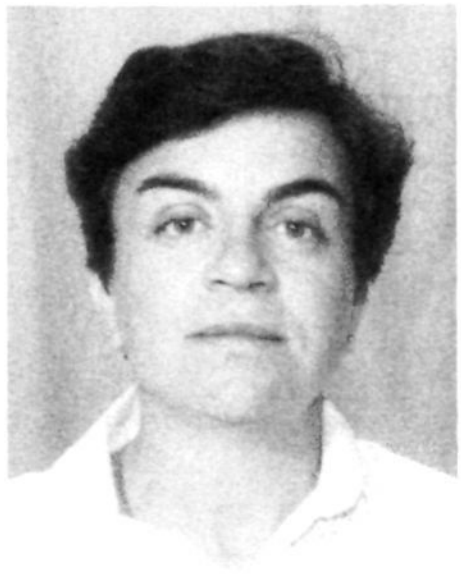

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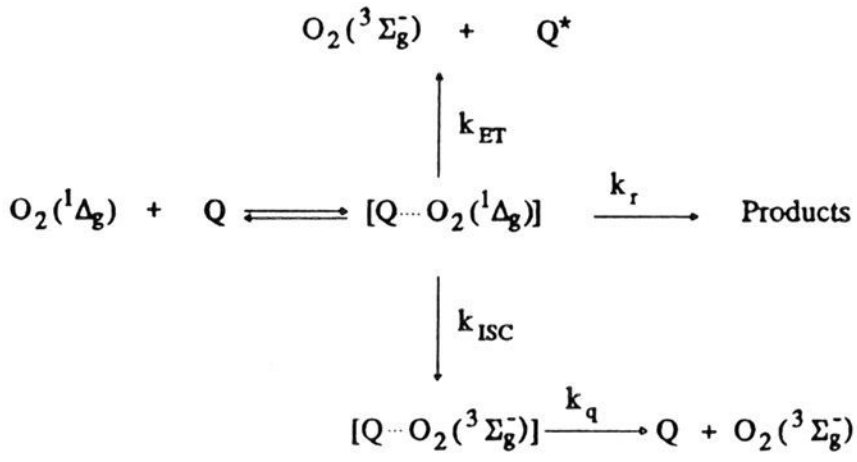
$O_2(^1\Delta_g)$ reactions comprise physical quenching (k_q) (e.g., with azide), chemical processes (k_r) dominated by a single reaction (e.g., anthracene, diphenylisobenzofuran) or involving several competitive pathways (e.g., in polyolefins), and mixed processes where chemical reactions and physical quenching are competitive processes (e.g., amines, sulfides, and phenols). When more than one process contributes to the total rate (k_t), changing the solvent can produce changes not only in the total rate but also in the relative importance of the different reaction channels. In the present review, this last point will be considered only for those systems in which the solvent modifies the relative rates of processes going through different reaction paths and/or alters the behavior of transient intermediates. Reactions of the solvent with the primary products, leading to differences in the final product distribution, will not be considered.

A general mechanism for $O_2(^1\Delta_g)$ processes is depicted in Scheme 1. Scheme 1 involves a complex formed rapidly and reversibly. Depending upon the energy of the excited quencher, Q, and its ionization potential, this complex can be characterized as an exciplex or as a charge-transfer complex. The mechanism implies that different relative rates of energy transfer and physical

Scheme 1



and chemical quenching will result from the competition between exciplex photophysic and exciplex photochemistry.[44] Evidently, the solvent can influence both the total rate of the process and the relative importance of the different reaction pathways. In this context, it is interesting to note that the intersystem crossing rate constant (k_{isc}) will also be influenced by the properties of the complex since the perturbation offered by a ground-state molecule in inducing the forbidden ($O_2(^1\Delta_g) \rightarrow O_2(^3\Sigma_g)$) transition depends on the extent of charge-transfer character in the complex.[45]

II. Deactivation Dominated by Energy-Transfer Interactions

Energy-transfer processes such as

$$O_2(^1\Delta_g) + Q(S_0) \rightarrow O_2(^3\Sigma_g) + Q(T_1) \quad (2)$$

$$O_2(^1\Delta_g) + Q(T_1) \rightarrow O_2(^3\Sigma_g) + Q(S_1) \quad (3)$$

are spin allowed by the exchange mechanism. In this review, reactions between $O_2(^1\Delta_g)$ and quenchers in the triplet state will not be considered. Energy transfer to a ground-state molecule to produce the first excited triplet of the quencher (reaction 2) will take place efficiently only with compounds whose triplet energy is smaller than or equal to the energy of the $O_2(^1\Delta_g)$ (22.5 kcal mol^{-1}). $O_2(^1\Delta_g)$ deactivation taking place predominantly by this mechanism has been invoked for iodine,[46] metal complexes,[47-51] phthalocyanines,[52] naphthalocyanines,[52-54] and polyolefins such as carotenoids.[55-64] Solvent effects in the rate of these reactions can be due to solvent-induced changes in the relative energies of $O_2(^1\Delta_g)$ and the triplet of the quencher and/or the effect of the solvent viscosity if the rate of the process is near the diffusion-controlled limit. The first effect has been invoked to explain the dependence of photooxidation rate of bacteriochlorophyll *a* with the solvent.[65] In this system, the rate of the process, relative to that of rubrene, varies from 1.12 (in dichloromethane) to 0.015 (in THF). Since the rate of addition to rubrene is only moderately solvent dependent,[66] the data indicate a strong solvent dependence in the reaction of bacteriochlorophyll *a*. This difference has been related to differences in the energy content of bacteriochlorophyll in pentacoordinating (tetrahydrofuran) and hexacoordinating (dichloromethane) solvents.[66] However, from the comparison of the experimentally determined rate constant for bacteriochlorophyll *a* in chloroform (1×10^9 M^{-1} s^{-1}) with the value expected from the energy gap between the bacteriochlorophyll triplet and $O_2(^1\Delta_g)$ and the Sandros equation,[67] Krasnovsky et al.[52] concluded that, at least in this solvent, the quenching must be explained through a mechanism involving charge-transfer complex formation.

Nickelocene, contrary to paramagnetic Ni(II) complexes in general, is an efficient quencher of $O_2(^1\Delta_g)$ ($k_t = 2.8\text{–}6.8 \times 10^9$ M^{-1} s^{-1}). The data obtained in different solvents, ranging from cyclohexane to methanol, do not show a clear trend with solvent viscosity and/or polarizability.[48] The results can be interpreted according to Scheme 1 with decay channels involving competitive energy-transfer and charge-transfer paths, followed by back electron transfer.

Energy-transfer-mediated quenching was also proposed for several metal porphyrins[49,50] in carbon tetrachloride, although the reported values (ca. 1×10^9 M^{-1} s^{-1}) are considerably smaller than the diffusion-controlled limit. These results can be explained in terms of the reversibility of the process, as proposed by different phthalocyanines[52] and naphthalocyanines.[52-54]

Early work by Farmilo and Wilkinson,[68] employing laser flash techniques, showed that the quenching mechanism by β-carotene involves electronic energy transfer to produce the triplet carotene with a rate constant close to the diffusion-controlled limit (1.32×10^{10} M^{-1} s^{-1}) in benzene. An efficient energy transfer was also reported for other polyolefins.[57] The values obtained in different solvents for β-carotene and closely related polyolefins are listed in Table 1. The diffusion control of the process leads to enhanced reaction rates when the $O_2(^1\Delta_g)$ is generated close to the target, as in the work by Neckers and Paczkowski[74] in which the sensitizers are covalently bound to β-cyclodextrin cavities that concentrate the β-carotene molecules.

The data reported by Conn et al.[63] in benzene and toluene and by Devasagayam et al.[64] in chloroform for a series of carotenoids confirm previous studies[55,56,71] indicating that the deactivation efficiency slightly increases with the number of conjugated double bonds, a result that can be interpreted in terms of the lower triplet energy of the acceptor (that pushes the system toward the diffusion-controlled limit) and the larger size of the conjugated double-bond system (that would increase the diameter of the target in the diffusion limit[75,76]).

The quenching of $O_2(^1\Delta_g)$ by β-carotene in toluene has been further analyzed by measuring the quenching rate from −90 to 90 °C.[44] A change in slope observed at −10 °C was attributed to a change from the diffusion limit to the pre-equilibrium limit. The data of Conn et al.[63] show that the rate of the process is slightly dependent on the solvent viscosity, a result also compatible with a partially diffusion-controlled process. Under these conditions subtle changes in the relative energies of $O_2(^1\Delta_g)$ and the quencher triplet could produce significant changes in the overall rate constant, due to both changes in the rate of the process and the contribution of the back reaction.

Quenching by β-carotene, at least in nonpolar solvents, is dominated by the physical pathway, a result that can explain the protection toward photodamage afforded by these compounds even in vivo.[77] Manitto et al.[60] have measured the physical and chemical quenching rate constants of $O_2(^1\Delta_g)$ by crocetin in water, dimethylformamide, and dimethyl sulfoxide (Table 1). The most relevant result is the marked decrease in k_r (about 2 orders of magnitude) found on going from water to solvents of lower dielectric constant, as expected from Scheme 1 if product formation occurs via an electron-transfer process. A significant contribution of the reactive channel in aqueous solution has also been reported for a number of 6,6′-diapocarotenoids (bixinoids),[73] suggesting that polyenes having a large number of conjugated double bonds, in spite of the exothermicity of the energy-transfer process, can be involved in chemical reactions, at least in very polar solvents. This chemical pathway could partly account for the reported bleaching of β-carotene and similar carotenoids in vivo.[78]

III. Dyes and Sensitizers

$O_2(^1\Delta_g)$ interaction with sensitizers is frequently a perturbing factor in dye-sensitized photooxidations[79-85] and can lead to significant photobleaching.[50,72,79,86-90] However, in some systems, as in the self-sensitized photooxidation of bilirubin[91] or in the photodynamic treatment of malignant tumors,[92] this interaction can play a beneficial role.[92] To evaluate the relevance of the process and the range of dye concentrations over which the process can be disregarded, rate constants for several sensitizers have been measured.[50,72,79,80,82,86,89,93] However, data bearing on the solvent effect on these processes are scarce. The available data are collected

Table 1. Bimolecular Rate Constants for the Total (k_t) and Reactive (k_r) Quenching of O_2 ($^1\Delta_g$) by Carotenoid Compounds

compound	solvent	$k_t \times 10^{-9}$, M^{-1} s^{-1}	$k_r \times 10^{-7}$, M^{-1} s^{-1}	ref[a]
β-carotene	freon 113	9.5		69[d]
	hexane	14		63[d]
	benzene	13.8, 13, 13.2, 21.3		70,[c] 63,[d] 68,[c] 71[d]
	toluene	14, 11		63,[d] 44[d]
	CCl_4	5.9, 10, 7		59[b], 63[d], 72[a]
	dichloromethane	13		69[d]
	chloroform	11		63[d]
	ethanol/chloroform/H_2O (50:50:1)	12, 14.5		63[d], 61[b]
crocetin	dimethylformamide	7	<0.5	60[a]
	dimethyl sulfoxide	2	<0.5	60[a]
	D_2O (pD 8.4)	2.5	40	58[a]
	H_2O (pH 7.8)	5.5	25	60[a]
bixin	chloroform	9.2		63[d]
	dimethylformamide	23	0.16	73[a]
	dimethyl sulfoxide	21	0.14	73[a]
	ethanol/chloroform/H_2O (50:50:1)	14		61[b]
	H_2O (pH 7.8)	18	9	73[a]
norbixin	dimethylformamide	12	0.17	73[a]
	dimethyl sulfoxide	17	0.19	73[a]
	H_2O (pH 7.8)	23	15	73[a]
canthaxanthin	benzene	17.8, 14.5		57,[c] 70[c]
	toluene	13		63[d]
	CCl_4	10		59[b]
	CD_3OD	12		59[b]
lycopene	cyclohexane	19		63[d]
	benzene	17		63[d]
	toluene	18		63[d]
	CCl_4	14		63[d]
	chloroform	19		63[d]
	ethanol/chloroform/H_2O (50:50:1)	17.5		63[d]

[a] Superscripts a–d refer to the $O_2(^1\Delta_g)$ generation and rate constant determination methods: a, steady-state ilumination and indirect detection of $O_2(^1\Delta_g)$; b, steady-state ilumination and direct determination of $O_2(^1\Delta_g)$; c, flash photolysis generation of $O_2(^1\Delta_g)$ and indirect detection; d, flash photolysis generation of $O_2(^1\Delta_g)$ and direct determination of its decay.

Table 2. Total (k_t) and Reactive (k_r) Rate Constants for the Quenching of $O_2(^1\Delta_g)$ by Dye Molecules

compound	solvent	$k_t \times 10^{-8}$, M^{-1} s^{-1}	$k_r \times 10^{-8}$, M^{-1} s^{-1}	ref[a]
bilirubin	freon 113		1.0	94[a]
	CCl_4	23	1.7	95[a]
	chloroform	22	2.1	86[a]
	chloroform/methanol (9:1)	13	4.3	86[a]
	D_2O (pD 8.4)	13	3.5	96[a]
mesoporphyrin IX dimethyl ester	CCl_4	0.026		72[c]
	acetone	0.38		97[d]
	acetonitrile	0.25		97[d]
rose bengal	acetonitrile	0.5		80[a]
	methanol	0.2		80[a]
eosin	acetonitrile	0.72		80[a]
	methanol	0.24		80[a]
tellurapyrylium	methanol	0.09		98[c]
	methanol/H_2O (1:1)	0.18		98[c]
	H_2O	8		98[c]
bacteriochlorophylls *a*	CCl_4	9		99
	ether	2.2		99
	pyridine	5.9		99
bacteriochlorophylls *b*	CCl_4	15		99
	ether	5.8		99
	pyridine	13		99
bacteriopheophytins *a*	CCl_4	0.12		99
	ether	0.3		99
bacteriopheophytins *b*	CCl_4	2		99
	ether	1.9		99
	pyridine	2.8		99
chlorophyll *a*	CCl_4	7		99
	ether	1		99
	deuteriopyridine	0.9		99

[a] Method as described in Table 1.

in Table 2, where aromatic compounds (such as rubrene or anthracene derivatives) are excluded since they will be discussed in section VII.5. The values of k_t for bilirubin are near the diffusion control in all of the solvents considered. On the other hand, k_r values are nearly an order of magnitude smaller and, albeit taken from a different source, tend to show a small increase with solvent polarity. However, the difference is only

ca. 3.5 for solvents ranging from freon 113 to water. The results reported for rose bengal and eosin indicate that, similar to other nitrogen-bearing compounds, the total quenching process in protic solvents is slower than that measured in nonprotic solvents of similar polarity.

Ogilby and Foote[97] measured the rate constants for the quenching of $O_2(^1\Delta_g)$ by mesoporphyrin IX dimethyl ester in acetonitrile and acetone, and the reported values are an order of magnitude higher than those previously reported in carbon tetrachloride.[72] However, this difference probably does not reflect a true solvent effect but arises from secondary processes resulting from the high intensities employed.[97] The quenching of $O_2(^1\Delta_g)$ by protoporphyrin IX dimethyl ester in dichloromethane solution takes place with $k_t = 8.5 \times 10^5$ M^{-1} s^{-1}, mainly by a physical pathway.[89] Several products (hydroxyaldehydes, monoformylmonovinylporphyrins, and diformylporphyrin) are produced with low limiting quantum yield. Both the total product yield and the product distribution were found to slightly depend on the solvent employed.[89]

A comprehensive study of the physical and chemical reactions of $O_2(^1\Delta_g)$ with several azo dyes has been reported by Bortolus et al.[100] However, reaction rate constants were measured only in dichloromethane, and the effect of the solvent was only considered with regard to changes in product distribution. The proposed mechanism considers a charge-transfer intermediate that in aprotic solvents decays by competitive pathways, while in protic solvents only leads to a peroxidized zwitterion. In all solvents the chemical pathway represents only a minor contribution to k_t.

Extensive data for the interaction of several pigments with $O_2(^1\Delta_g)$ have been reported by Krasnovsky et al.[49,50,72,101-104] Depending on the triplet energy of the dye, the mechanism is dominated by energy-transfer (for compounds of low triplet energy, e.g., siloxysilicon naphthocyanine) or by charge-transfer interactions (for compounds of high triplet energy, e.g., bacteriochlorophyll). For compounds of intermediate energies, both mechanisms should contribute to the total quenching rate.[52] Egorov et al.[99] have measured the total quenching rate of $O_2(^1\Delta_g)$ by bacteriochlorophylls and bacteriopheophytins in different solvents (Table 2), and Krasnovsky et al.[50,93] reported k_t and k_r values for bacteriochlorophyll *a* and bacteriochlorophyll *b* substantially larger than those for other chlorophylls and pheophytins. With regard to the effect of the solvent, these authors reported that, while similar k_t and k_r values are obtained in acetone and carbon tetrachloride, the rates of both processes are considerably slower in diethyl ether.[93,99]

IV. Inorganic Anions

$O_2(^1\Delta_g)$ is quenched by inorganic anions such as azide, nitrite,[105] and iodide.[106,107] Azide ion is often employed as a quencher of $O_2(^1\Delta_g)$ to test its participation in photooxidation processes. Harbour and Issler[108] have proposed that quenching proceeds through a charge-transfer complex that can dissociate, yielding either electron-transfer products or ground-state reactants. The relevance of the electron-transfer deactivation pathway is rather uncertain. After evaluating the formation of an adduct between $N_3^\bullet$ and α-phenyl-*N*-*tert*-butylnitrone, Harbour and Issler[108] concluded that at least 15% of the complex dissociates into free $N_3^\bullet$ and superoxide anion in aqueous medium. On the other hand, Haag and Mill[109] concluded that the electron-transfer channel is ca. 3 orders of magnitude smaller than that leading to physical deactivation. The efficiency of the azide radical formation was estimated from the azide consumption yield under conditions of total trapping of the produced radical by styrene. Bilski et al.[105] proposed that azide and oxygen consumption are mainly due to the occurrence of a reaction between $N_3^\bullet$ and $O_2(^1\Delta_g)$, its relevance being determined by the average $O_2(^1\Delta_g)$ concentration. The azide photooxidation takes place with low quantum yields, producing nitrates as the main reaction product.

Table 3. Total Rate Constant (k_t) for the $O_2(^1\Delta_g)$ Quenching by Azide in Different Solvents

solvent	$k_t \times 10^{-8}$, M^{-1} s^{-1}	ref[a]
ethanol	2.2	111[d]
methanol	2.3	112[d]
methanol/H_2O (8:1)	2.8	113[d]
D_2O	3.0, 4.7, 5.1	111,[d] 114,[d] 115[d]
	6.2, 6.9	116[b]
H_2O	4.7, 5.8, 5	114,[d] 116,[b] 109[a]

[a] Method as described in Table 1.

The effect of the medium on azide reactions has been little studied, and the results do not show a clear dependence on solvent. The data compiled by Wilkinson and Brummer[28] and those reported by Gupta and Rohatgi-Mukherjee[110] seem to indicate that the rate is higher in water than in methanol, but the competitive procedures employed render difficult a quantitative analysis. Most of the data obtained by direct decay measurements are collected in Table 3 and consistently show higher k_t values in aqueous solutions than in methanol or ethanol. Evidence for a small but significant dependence of the quenching rate constant by azide on solvent has also been provided by Miyoshi et al.,[112] who used thermal lensing experiments and reported a faster quenching in methanol/water (40% water) and methanol/ethylene glycol mixtures than in neat methanol. Significant differences were also observed in the activation energy of the process (1.72 kcal/mol in methanol and 4.92 kcal/mol in 60% methanol/water), implying that the higher rate in the mixed solvent is due to a more favorable pre-exponential (entropic) factor.

In aqueous solution, the quenching rate by azide depends both on pH and on the added salt concentration. Haag and Mill[109] data show that k_t values decrease with pH below 5.5 in accordance with the protonation of the azide ion to form hydrazoic acid, whose quenching constant is at least 2 orders of magnitude slower than that of azide ion. Rubio et al.[111] reported a significant increase in quenching rate when the ionic strength of the solution increases. The values obtained were 7.9×10^8 and 7.1×10^8 M^{-1} s^{-1} for ionic strengths of 3 in $N(CH_3)_4Cl$ and NaCl aqueous solutions, respectively. This salt effect was even more noticeable in ethanolic solutions. The effect of "inert" salt addition upon $O_2(^1\Delta_g)$ photoprocesses has been very little addressed and, in particular for the quenching by azide, is rather difficult to interpret, especially taking into account that τ_Δ in the absence of azide depends weakly (and in a rather random way) on the added electrolyte concentration.[111] Bilski et al.[105] discussed the effect of ionic strength on the reaction of $O_2(^1\Delta_g)$ with nitrite

Table 4. Bimolecular Rate Constant for the Total Quenching (k_t) of $O_2(^1\Delta_g)$ by Amines[a]

solvent	piperidine	DEA	TEA	DABCO	strychnine	TMH
gas		8.5×10^4 (125)	2×10^6 (126)[d]			
freon		0.6×10^6 (36)[a]	2.1×10^6 (36)[a]			
n-hexane		4.8×10^6 (39)[a]	4.75×10^7 (39)[a]			
benzene		4.6×10^7 (39)[a]	1.76×10^8 (39)[a]	2.6×10^8 (127)[d]	1×10^9 (127)[d]	1.8×10^8 (128)[d]
toluene				2.1×10^8 (127)[d]	9.3×10^8 (127)[d]	
chloroform	0.58×10^7 (123)[a]	1.15×10^7 (39)[a]	7.4×10^7 (39)[a]	5.2×10^7 (123)[a]		
	0.36×10^7 (129)[d]	1.5×10^7 (123)[a]	6.5×10^7 (123)[a]			
acetone	7.82×10^7 (129)[d]	10.1×10^7 (39)[a]	30.5×10^7 (39)[a]	3.8×10^8 (127)[d]	9.4×10^8 (127)[d]	
acetonitrile	5.61×10^7 (129)[d]	14.8×10^7 (129)[d]	33.3×10^7 (129)[d]	49×10^7 (129)[d]	6.4×10^8 (127)[d]	
		8.6×10^7 (39)[a]	19.5×10^7 (39)[a]	40×10^7 (127)[d]		
2-butanol	0.1×10^7 (129)[d]					
2-propanol	0.09×10^7 (129)[d]	0.38×10^7 (129)[d]	3.64×10^7 (129)[d]	0.36×10^7 (129)[d]		2.14×10^7 (128)[d]
ethanol				5×10^6 (127)[d]	1.1×10^8 (127)[d]	
				6.4×10^6 (130)[a]		
methanol		1.88×10^6 (36)[a]	9.3×10^6 (36)[a]	1.2×10^7 (122)[d]		
		2.2×10^6 (39)[a]	1.3×10^7 (39)[a]			
		3×10^6 (123)[a]	1.5×10^7 (123)[a]			
2,2,2-trifluoroethanol	6.5×10^3 (129)[d]		1.73×10^4 (129)[d]	4.42×10^4 (129)[d]		1.15×10^6 (128)[d]
buffer					2.8×10^8 (130)[a]	

[a] k_t values are given in M^{-1} s^{-1}. Superscripts refer to measurement method as described in Table 1. DEA, diethylamine; TEA, triethylamine; TMH, tetramethylhydrazine.

anion, mainly analyzing oxygen consumption. On the basis of specific anion effects, the authors proposed some sort of anion/$O_2(^1\Delta_g)$ complex. The lack of effect of the added salt on τ_Δ and the influence observed on the bimolecular rate constant are difficult to rationalize in terms of this complex. Nevertheless, the salt effect observed in the inactivation of $O_2(^1\Delta_g)$ by azide,[111] as well as that reported for nitrite[105] and for the chemical reaction of anthracene derivatives,[117] could be important in buffer solutions or for reactions taking place near charged interfaces. This effect could then explain the higher quenching rate constants measured for azide in cationic micelles,[115,118] since the azide anion is located as counterion in a region of high ionic strength.[119]

Nitrite ion is believed to quench $O_2(^1\Delta_g)$ through the formation of a charge-transfer intermediate. The fraction of reactive quenching depends upon the competition between back electron transfer and ion pair separation (or reaction). On the basis of the increase in the fraction of chemical quenching with nitrite concentration, a mechanism involving interaction of the charge-transfer complex with a second nitrite anion has been proposed.[105] The occurrence of this process could explain the observed increase in the fraction of reactive quenching with the ionic strength of the solution. However, this explanation cannot apply to the azide data, where the ionic strength must modify the rate of charge-transfer complex formation or its stability.

Iodide ions deactivate $O_2(^1\Delta_g)$ with partial contribution of a chemical step leading to I_3^- formation.[120,121] Rosenthal and Frimer[120] reported a total quenching rate in bromobenzene/acetone (2:1) of 8.1×10^7 M^{-1} s^{-1} (employing LiI as quencher), while no detectable quenching was observed in a protic (bromobenzene/methanol, 2:1) mixture. Conversely, the data of Gupta and Rohatgi-Mukherjee[110] show that in water/methanol mixtures k_t increases with the water content and the quantum yield of I_3^- formation in 0.1 M I^- solution increases with polarity in protic solvents (up to 0.052 in water) and with the fraction of the protic component in nearly isodielectric solvent mixtures. Braathen et al.[121] provided direct evidence for the oxidation of I^- by measuring simultaneously the $O_2(^1\Delta_g)$ decay and the I_3^- formation, reporting $k_t = 8.7 \times 10^5$ M^{-1} s^{-1} in aqueous solution. The proposed mechanism involves the reaction of the initially formed peracid (HOOI) with I^-.

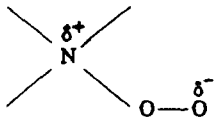
V. Nitrogen-Containing Compounds

V.1. Amines

The efficiency of $O_2(^1\Delta_g)$ quenching by amines increases when the ionization potential of the amine decreases. This dependence leads to the general sequence

$$(k_t)_{tertiary} > (k_t)_{secondary} > (k_t)_{primary}$$

Ogryzlo and Tang[122] explained this sequence through a mechanism involving a charge-transfer complex, and several workers have obtained reasonable correlations between the rate constant and the ionization potential, or the σ Hammett parameter, of the amines[27,36,123,124] supporting the formation of a complex with partial charge separation. Similar to the results obtained in most systems involving $O_2(^1\Delta_g)$ deactivation and/or reaction, quenching of $O_2(^1\Delta_g)$ by DABCO or triethylamine is an entropy-controlled process,[44,122] implying the rapid formation of a reversible complex (Scheme 1). However, for the quenching by amines, the role of the solvent is more complicated than a simple stabilization of this complex as a consequence of its polarity and polarizability, and other properties of the solvent (e.g., the presence of acidic hydrogens) must also be considered.[38] Data showing the dependence of k_t with solvent are collected in Table 4. Encinas et al.[39] and Clennan et al.[129] have analyzed in detail the dependence of the total interaction rate with the solvatochromic parameters (α, β, and π^*) of the solvent. Encinas et al.[39] measured high k_t values in solvents of high π^* and low α. Since the π^* scale is a measure of the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect and the α scale describes the ability of the solvent to donate a proton in a solvent-to-solute hydrogen bond,[131] the results are compatible with a mechanism involving a complex such as along the reaction coordinate. Solvents having a large π^* value stabilize the complex, and solvents with a high α value preclude its formation by protecting the nitrogen lone pair. A similar solvent dependence has been reported



by Clennan et al.,[129] who found that k_t values change by factors as large as 10^4 when acetonitrile or trifluoroethanol is employed as solvent. For piperidine, the amine for which more solvents were analyzed, the data shown in Table 4 were fitted by

$$\log k_t = 8.10 - 2.87\alpha \quad (4)$$

while the data obtained by Encinas et al.[39] for triethylamine could be fitted to

$$\log k_t = 7.72 + 0.36\pi^* - 2.18\alpha + 1.82\beta \quad (5)$$

A strong negative dependence on the value of the α parameter has also been reported for several hydrazines.[128] The data for tetramethylhydrazine show that the quenching rate (dominated by physical deactivation) decreases by a factor ca. 160 when the solvent changes from benzene to 2,2,2-trifluoroethanol. Similar changes have been reported for other hydrazines. However, for some amines higher reaction rates have been measured in water than in other solvents of lower α values, indicating that, at least in aqueous solution, factors other than the α parameter are determining the rate of the process. Lion et al.[130] reported k_t values for 2,2,6,6-tetramethyl-4-piperidinol and DABCO nearly 2 orders of magnitude higher in water than in ethanol. This trend can be explained in terms of the predominance of the π^* parameter or be a consequence of the peculiar properties of water as a solvent for bimolecular processes involving relatively nonpolar reactants.[132] Furthermore, it has to be considered that highly constrained amines, such as 2,2,6,6-tetramethylpiperidine and its derivatives, react in a variety of solvents, producing the stable nitroxide radicals,[133] and hence the mechanism of the process could be different from that proposed for other amines.

An interesting effect of the solvent was obtained by a comparison of the behavior of *n*-butyldimethylamine and its hydroxy analogue, 4-hydroxy-*n*-butyldimethylamine.[129] In the strongly hydrogen bonding solvent 2,2,2-trifluoroethanol, both N atoms are similarly protected and show similar reactivity. On the other hand, in solvents of low α, the hydroxy derivative reacts slower than the *n*-butyldimethylamine. This difference can be understood in terms of intramolecular hydrogen bond formation in the 4-hydroxy derivative. The difference in rates in benzene corresponds to a free energy variation of 1.2 kcal/mol at 298 K, which should be considered as a measure of the intramolecular hydrogen bridge free energy.

Quenching of $O_2(^1\Delta_g)$ by amines partly takes place through a chemical path generally leading to hydrogen peroxide production ($\Phi \approx 0.2$ for triethylamine in methanolic solution).[39] The mechanism of this process, most likely involving the formation of the anion superoxide and/or its protonated acid, HOO$^\bullet$, has been extensively discussed by Bellus.[27] Saito et al.[134] reported the formation of anion superoxide via one-electron transfer from substituted *N,N*-dimethylanilines to $O_2(^1\Delta_g)$ in phosphate buffer. Both the yield of superoxide and the quenching rate constant correlated well with the oxidation potential of the amines, tetramethyl-*p*-phenylenediamine (TMPD) being the compound studied with the highest superoxide yield. The one-electron-transfer process was only possible for aromatic amines with oxidation potential <0.5 V vs SCE in aqueous media. The formation of anion superoxide and the amine-derived cation can arise from the dissociation of the charge-transfer complex to produce solvent-stabilized ions. In agreement with these considerations, Manring and Foote[124] reported that the formation of $TMPD^+$ is only detectable in aqueous solvents.

V.2. Hydroxylamines, Nitroxides, and Nitrones

N,N-Substituted hydroxylamines, nitroxy radicals, and nitrones are closely related compounds whose reactions with $O_2(^1\Delta_g)$ have been analyzed, including the effect of the solvent. *N,N*-Diethylhydroxylamine (DEHA) in methanol[39] and acetonitrile[135] react with $O_2(^1\Delta_g)$ by a chemical pathway that can be represented by

$$R_2NOH + O_2(^1\Delta_g) \rightarrow [R_2NO\text{-}\,\text{-H-}\,\text{-OO}] \rightarrow R_2NO^\bullet + HOO^\bullet \quad (6)$$

where formation of the intermediate is the rate-limiting step and it can arise from the charge-transfer complex or by an independent free-radical-like hydrogen abstraction process. Subsequent reactions of the hydroperoxy radical lead to hydrogen peroxide with quantum yields of 0.85 in methanol[39] and up to 0.45 in acetonitrile.[135] A similar process has been invoked for the interaction of $O_2(^1\Delta_g)$ with *N,N*-dibenzylhydroxylamine in carbon tetrachloride[136] and could also contribute to the quenching of $O_2(^1\Delta_g)$ by desferrioxamine.[137]

The effect of solvent on k_t for alkylhydroxylamines is noticeably different from that obtained employing alkylamines such as diethylamine and triethylamine.[39] In particular, k_{DEHA} values are similar in *n*-hexane, benzene, acetone, and acetonitrile, implying that the solvent π^* value is almost irrelevant. Furthermore, in solvents of low π^* value (*n*-hexane) and high α value (formamide) $k_{DEHA} > k_{diethylamine}$, while in solvents of high π^* and low α values the opposite is found. These differences are compatible with a rate-limiting chemical pathway leading to a free-radical-like hydrogen abstraction, as depicted in eq 6. The low value of k_t reported in water, $\approx 10^5$ M^{-1} s^{-1},[135] and the fact that the effect of the solvent for the triethylhydroxylamine reaction closely resembles that observed for triethylamine and diethylamine[39] are compatible with this interpretation.

Darmanyan and Tatikolov[138] have measured the quenching of $O_2(^1\Delta_g)$ by stable nitroxy radicals and concluded that the quenching occurs exclusively via the electron-exchange interaction in collision complexes. Quenching rate constants and pre-exponential *A* factors are only weakly solvent dependent. Thus, log *A* in toluene ranged from 6.2 to 7.4 for the various nitroxy radicals considered, while values of 5.1 and 6.3 were measured in chloroform for the same radicals.[138] The weak solvent dependence was attributed to the different degree of solvation of the nitroxy radicals.

Nitrones have been extensively employed for spin-trapping experiments in complex biological systems to determine the extent of free-radical reactions under conditions of oxidative stress. In these systems, $O_2(^1\Delta_g)$ is frequently present, and hence it is important

Table 5. Bimolecular Total Rate Constant (k_t) for the Quenching of $O_2(^1\Delta_g)$ by Nitrones[a]

nitrone/ solvent	α-phenyl-N-phenyl[e,c]	α-p-toluyl-N-phenyl[e,c]	α,α-diphenyl-N-phenyl[e,c]	α-phenyl-N-tert-butyl
cyclohexane	0.8	2.1	0.5	
benzene	3.7	5.5	3.9	0.8[f,c]
toluene				0.9[g,c]
methanol	5.1	7.7	1.0	
chloroform				0.4[g,c]
acetonitrile	3.3	4.6	3.3	1.8[g,c]
water				14[h,c]

[a] k_t values are given in 10^7 M^{-1} s^{-1}. Superscripts a–d as described in Table 1. [e] Reference 141. [f] Reference 140. [g] Reference 142. [h] Reference 139.

to evaluate the rate of its reactions with nitrones, as well as the products obtained. Harbour et al.[139] have reported a rate constant of 1.4×10^8 M^{-1} s^{-1} for α-phenyl-*N-tert*-butylnitrone (PBN) in aqueous solution. The quenching process involves the formation of diamagnetic product(s) and hydrogen peroxide. Reversion of the oxygen consumption by catalase indicates that nearly 30% of the reaction leads to hydrogen peroxide. Darmanyan and Moger[140] measured the kinetics of the interaction of $O_2(^1\Delta_g)$ with PBN in benzene. The results were interpreted in terms of a reversible electron-transfer process with a rate constant of 8.2×10^6 M^{-1} s^{-1} and a chemical reaction channel with a rate constant of 1.4×10^5 M^{-1} s^{-1}. These values are considerably smaller than those measured in water and imply that the incorporation of nitrones to membranes would protect them from the reaction with $O_2(^1\Delta_g)$.

From laser flash photolysis studies of aromatic nitrones, Cyr et al.[141] reported higher rate constants in polar (acetonitrile and methanol) than in nonpolar (cyclohexane) solvents. Furthermore, these data together with that obtained for α-phenyl-*N-tert*-butylnitrone (Table 5), show that the rate constant depends on the value of the solvent parameter α as previously discussed for the amines. Although some of the data have been obtained without a direct monitoring of $O_2(^1\Delta_g)$, the reported differences are too high to be due to experimental errors and are compatible with results obtained in other systems where $O_2(^1\Delta_g)$ reactions are particularly fast in aqueous solutions.

VI. Sulfur-Containing Compounds

Several kinds of sulfur-containing compounds, such as dialkyl,[143-145] diaryl,[146,147] vinyl,[148] and allyl sulfides,[149,150] thiiranes,[151,152] and thiols,[153,154] are readily oxidized by $O_2(^1\Delta_g)$, particularly in protic solvents. On the other hand, Devasagayam et al.[154] were unable to find any reaction in aqueous media between disulfides (cystine, reduced glutathione, and dimesna) and $O_2(^1\Delta_g)$.

Sulfides have been the most thoroughly investigated compounds. The electrophilic character of the reaction has been established from Hammett-type plots of substituted aryl sulfides. Thus, a ρ-value of ≈−1.6 has been reported for substituted thioanisoles in methanol[146] and in chloroform.[147]

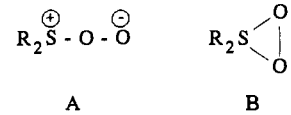
The interaction between sulfides and $O_2(^1\Delta_g)$ leads to physical quenching and chemical reaction, the relative rates of these processes being different in protic and aprotic solvents[155-157] and strongly dependent on temperature.[157,158] At room temperature, almost quantitative product formation has been reported in protic and coordinating solvents,[143,145,157,158] while in aprotic solvents physical quenching predominates.[157-159] k_t values have been found to be almost independent on the temperature,[145,158] but the ratio k_r/k_t depends strongly on it, particularly in aprotic solvents. The photooxidation rate of diethyl sulfide in acetone or ether shows a 30–50-fold increase when the temperature changes from 24 to −78 °C.[158] Otherwise, k_t values have been found to be almost insensitive to the solvent (from benzene to methanol)[145,146,156,158] (Table 6), the increase in k_r in protic solvents taking place at the expense of the physical quenching. On the other hand, the oxidation of electron-rich thioanisoles shows a remarkable solvent effect, at least when the solvent changes from benzene to methanol/water (1:1) (see Table 6). In the latter solvent mixture, *p*-hydroxythioanisole follows the reactive pathway almost quantitatively.[160] In phosphate buffer (pH 7.5) the formation of 2% superoxide ion was reported and explained in terms of an electron-transfer pathway from the highly polar intermediate (Scheme 1).

Table 6. Total Rate Constant (k_t) for $O_2(^1\Delta_g)$ Quenching by Sulfur-Containing Compounds

compound	solvent	$k_t \times 10^{-6}$, M^{-1} s^{-1}	ref[a]
thioanisole	benzene	0.8	160
	chloroform	2.3	147
	methanol	2	146
	methanol/H_2O (1:1)	23	160
p-hydroxyanisole	benzene	11	160
	methanol/H_2O (1:1)	162	160
p-methylanisole	benzene	1.5	160
	chloroform	4.6	147
	methanol	3.1	146
	methanol/H_2O (1:1)	32	160
p-methoxyanisole	benzene	2	160
	chloroform	7.6	147
	methanol	5.3	146
	methanol/H_2O (1:1)	46	160
diethyl sulfide	benzene	20	146
	methanol	17.1, 16.6	146, 158
	toluene	13.7	158
	acetone	26.9	158

[a] All of the values were measured by indirect steady-state method.

Several intermediates have been proposed to explain the effect of the solvent and temperature upon product distribution. Kinetic studies involving competitive trapping experiments with diphenyl sulfide or diphenyl sulfoxide (both unreactive toward singlet oxygen[145,146,161,162]) were carried out in both protic (methanol) and aprotic (benzene and acetonitrile) solvents.[145,156,157,162,163] Competitive behavior takes place in methanol, suggesting the presence of a dipolar persulfoxide (A) as single intermediate. On the other



A B

hand, the results obtained in benzene and acetonitrile indicate that sulfide and diphenyl sulfoxide react through different intermediates, suggested to be the dipolar persulfoxide (A) and the thiadioxirane (B).[156]

A mechanism comprising two independently formed intermediates is supported by the results obtained by

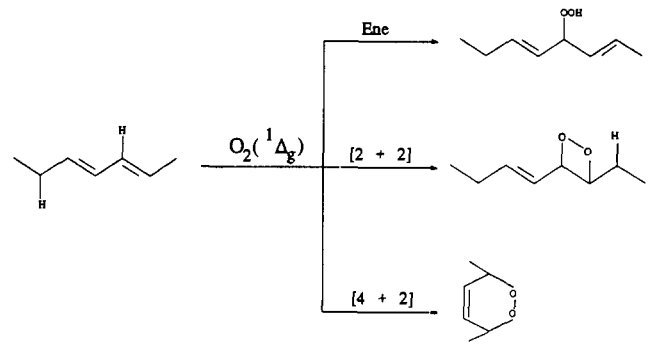
Watanabe et al.[157] for sulfides in aprotic solvents. In this reaction, sulfoxide and sulfone are the major products at the initial stage of photooxidation and they are differently affected by various parameters. The sulfoxide formation is more sensitive to the electronic effect of substituents, whereas steric retardation is more significant for sulfone formation. The addition of 0.1 M protic or coordinating solvents to benzene accelerates the sulfoxide formation without affecting sulfone formation. The apparent activation energy for sulfone formation is positive, in contrast to the sulfoxide, whose formation yield decreases when the temperature is raised. These results, together with $^{18}O_2$ tracer experiments which show that the two oxygen atoms in the sulfone come from the same oxygen molecule, indicate that both products arise from independently generated intermediates, being the thiadioxirane (B) the sulfone precursor.[157] Solvent and temperature determine the relative rate of the production of these intermediates. If both intermediates arise from the reversibly formed charge-transfer complex, the proposed mechanisms are not contradictory to the general Scheme 1. Furthermore, in aqueous solvents, electron transfer in the initially formed charge-transfer complex could lead directly to the partial production of superoxide anion.[160]

The reaction of cyclic sulfides with $O_2(^1\Delta_g)$ presents some differences with those discussed for the open compounds. The smallest cyclic sulfides, thiiranes, react with $O_2(^1\Delta_g)$ giving thiirane oxide in nonnucleophilic solvents. In methanol, the primary products are sulfinic esters at low substrate concentration and thiirane oxide at high concentrations, the results being explained in terms of a peroxythiiane oxide intermediate.[151] Results obtained for other cyclic disulfides[164,165] also show striking differences with those obtained employing dialkyl sulfides.

The interaction of thiols with $O_2(^1\Delta_g)$ has been proposed to play a protective role against skin photosensitivity[153] and the photodamage to lens proteins.[166,167] However, for all of the SH-containing compounds studied, it has been found that the physical quenching contributes less than 5% to the overall rate of $O_2(^1\Delta_g)$ scavenging, supporting the proposal that photooxidation of cysteine by $O_2(^1\Delta_g)$ could be one of the early events in the photomodification of the lens crystallin proteins.[166,167] The major oxidation products identified in the photooxidation of glutathione, in D_2O at pD 7.4, were disulfide, sulfoxide, sulfonate, and sulfinate.[154] The observed rate constants are strongly dependent on pH, indicating that only the unprotonated form of the thiol reacts with $O_2(^1\Delta_g)$.[153,154]

Clennan and Chen[149,150] have analyzed the effect of the solvent on the diastereoselective oxidation of allylic phenyl sulfoxides, sulfones, and sulfides. In the oxidation of 1-[(4-methylphenyl)sulfinyl]-2,3-dimethyl-2-butene, although the temperature changes the product distribution, identical regio- and stereoisomer ratios were obtained in acetone-d_6 and methanol-d_4.[149,150] On the other hand, a solvent-dependent and remarkably high diastereoselectivity was observed in the oxidation at the sulfur atom when a hydroperoxy group was present at the β position, suggesting an internal anchimeric assistance. The diastereoselectivity decreases with temperature and is lower in CD_3OD than in acetone-d_6 or $CDCl_3$. This latter result is the expected one if in the hydroxylic solvent, external anchimeric assistance competes with the internal assistance afforded by the hydroperoxy group.

Scheme 2



The photooxidation of thiocarbonyl compounds mediated by $O_2(^1\Delta_g)$ has been extensively studied by Ramamurthy et al.[168-173] Total quenching rate constants are in the 10^5–10^6 M^{-1} s^{-1} range, with diarylthiones being the most reactive compounds.[169] The mechanism proposed involves the interaction of the π^* empty orbital of the $O_2(^1\Delta_g)$ with the filled n orbital of the thiocarbonyl, leading to a zwitterionic or diradical-like intermediate that closes to 1,2,3-dioxathietane (with subsequent formation of the ketone) or forms the sulfine by oxygen elimination. Electron-releasing substituents in diaryl and alkylaryl thioketones favor the formation of ketones, whereas electron-withdrawing substituents favor sulfine formation.[168-171] The distribution of the products obtained from most thioketones is independent of the solvent. An exception to this rule are bicyclo-[2.2.1]heptanethiones, whose photooxidation gives considerably more sulfines in methanol than in aprotic solvents.[171]

Scurlock et al.[174] have measured quenching rate constants by organoselenium compounds exhibiting glutathione peroxidase activity. The quenching rate constants are approximately 1 order of magnitude higher than those of the S-containing analogues. A linear correlation is observed between log k_t and the Hammett constant σ_{ortho} with $\rho = -0.89$, the results being closely similar in CD_3OD and in perdeuterated benzene.

VII. Unsaturated Compounds

Interaction of $O_2(^1\Delta_g)$ with mono- or polyolefins proceeds by physical deactivation producing endoperoxides, hydroperoxides, and dioxetans, according to Scheme 2.

These products have been proposed to arise from a variety of intermediates, and several reviews have been devoted to discuss the mechanism of the different processes.[175-178] Clennan[179] has recently reviewed the different mechanisms proposed for the various reactions of 1,3-dienes. They include seven reaction paths for the [2 + 4] cycloaddition and six for the [2 + 2] dioxetane formation. The main process, and the dominant pathway, is determined by the structure of the olefin and the properties of the solvent. Considering the differences in polarity of the possible intermediates, it is not surprising that the solvent frequently modifies the product distribution. Furthermore, the solvent can specifically interact with some of the intermediates (or even the products), increasing the possible primary (and secondary) reactions and the number of products. On the other hand, it is generally accepted that the solvent

Table 7. Bimolecular Rate Constants for the Total (k_t) and Reactive (k_r) Quenching and Ene Reaction (k_{ene}) for the Interaction of $O_2(^1\Delta_g)$ with Olefinic Compounds

compound	solvent	k_t[a]	k_r[a]	k_{ene}[a]	ref[b]
trans-4-octene	chloroform	0.022	0.004		188[a]
	acetonitrile	0.025	0.01		188[a]
2-methyl-2-pentene	benzene	0.72			182[d]
	dichloromethane	0.97			182[d]
	acetone	0.81			182[d]
	acetonitrile	1.2			182[d]
	methanol	0.67			182[d]
2,3-dimethyl-2-butene	cyclohexane	15			191[c]
	toluene	40			191[c]
	acetone	40			191[c]
	acetonitrile	72			191[c]
2,5-dimethyl-2,4-hexadiene	benzene	3.6	<0.25	0.14	182[d]
	dichloromethane	5.2	1.4	1.3	182[d]
	acetone	3.9	0.74	0.34	182[d]
	acetonitrile	6.3	1.6	1.7	182[d]
	methanol	2.6	2.5	0.29	182[d]
1-methoxycyclopentene	cyclohexane	2.4			191[c]
	toluene	12			191[c]
	acetone	16			191[c]
	acetonitrile	25			191[c]
	methanol	13			191[c]
2-methoxy-2,3-butene	cyclohexane	2.5			191[c]
	toluene	12			191[c]
	acetone	11			191[c]
	acetonitrile	24			191[c]
	methanol	13			191[c]
retinol	cyclohexane	<2			42[c]
	benzene	<12			42[c]
	2-propanol	16.5			42[c]
	acetone	14			42[c]
	acetonitrile	26			42[c]
	N-methylformamide	85			42[c]

[a] k values are given in 10^6 M^{-1} s^{-1}. [b] Superscripts are as defined in Table 1.

plays only a minor role in determining the total rate of the interaction of $O_2(^1\Delta_g)$ with monoolefins or 1,3-dienes.[179-183] Possibly, this is due to the fact that these reactions have only been studied in solvents of relatively low polarity (up to acetonitrile or methanol) and not in aqueous mixtures or in solvents of high polarity (such as formamide) where the reactive channels could be considerably faster.

Yamaguchi et al.[184] employed intermolecular perturbation and configuration interaction calculations to elucidate the mode of attack of $O_2(^1\Delta_g)$ to electron-rich monoolefins and discussed the role of the solvent from this point of view. The calculations predict, for example, that for group III olefins (those with allylic hydrogens and electron-donating groups on both sides in a symmetric manner,[185,186] such as stilbestrol) polar solvents would increase the concerted ene reaction and decrease concerted [2s + 2a] reactions. These predictions are not fully compatible with the reported experimental data (vida infra).

It has been proposed that the total reactivity of a given compound comprising one or several olefinic double bonds can be obtained as the sum of the reactivity of the various structural units.[43,187] In these compounds, the saturated alkyl chain contributes to the $O_2(^1\Delta_g)$ interaction rate by increasing the rate of the physical pathway.[188] The contribution is proportional to the length of the alkyl chain and was considered similarly to a "solvent" deactivation.

VII.1. Monoolefins

Early studies[180,189] on solvent effects on the reaction of $O_2(^1\Delta_g)$ with olefins (e.g., 2-methyl-2-pentene) show that the ratio of $O_2(^1\Delta_g)$ decay rate to reaction rate is only slightly solvent dependent, a result interpreted in terms of an ene reaction taking place through a concerted six-center transition state, although a perepoxide intermediate was not completely excluded.

2-Methyl-2-pentene gives only ene products with the OOH group in the original C-2 (1a) or C-3 (2a) position.[180,182] The ratio 2a/1a varies only slightly with the temperature (e.g., from 1.10 to 0.75 in acetone when the temperature changes from 22 to −78 °C) and the solvent (e.g., 1.29 in dichloromethane and 1.39 in acetonitrile at 22 °C).[182] The lack of dependence of the product distribution with solvent is generally observed for the ene reaction of monoolefins, even in complex systems. For example, (+)-limonene gives rise to six products whose proportions are almost identical in methanol and in carbon tetrachloride.[190]

Reported data concerning the solvent effect on the total interaction rate of monoolefin with $O_2(^1\Delta_g)$ reacting exclusively through the ene reaction, are given in Table 7. At least in the considered solvents, these data indicate that the total rate of the process is slightly solvent dependent. Similar conclusions have been reached by Gollnick and Griesbeck[183] for 2,3-dimethyl-2-butene and 2-methyl-2-butene in solvents ranging from benzene to acetonitrile and methanol. If the carbon tetrachloride data are disregarded,[183] the data reported for cyclohexene,[192] an olefin of very low reactivity, gave limited solvent dependence. Results obtained for polyunsaturated fatty acids derivatives, which also react to produce hydroperoxides,[41,193,194] would indicate only a modest solvent effect over the range of solvents considered.[194]

A larger solvent dependence of the total rate is observed for compounds that preferentially follow the dioxetane pathway such as enol ethers[191] and benzvalene[183] (see Table 7). The total rate for $O_2(^1\Delta_g)$ interaction increases with the solvent polarity and, for benzvalene, gives almost a linear dependence when plotted against $(\epsilon-1)/(2\epsilon-1)$. For this compound, the Kirkwood–Laidler–Eyring model gives a value of μ = 6.7 D for the transition state, pointing to significant charge separation and polar intermediates such as perepoxides or zwitterions.[183] The sensitivity of the [2 + 2] addition to the polarity of the solvent explains the increase in dioxetane products in polar solvents reported for enol ethers.[195–197] Asveld and Kellog[196] reported that dioxetane yield in the reaction of $O_2(^1\Delta_g)$ with the enol ether (methyl cyclohexenylidene ether) increased from 3 to over 50% as the solvent polarity increased.

Hurst and Schuster[198] found an essentially solvent-independent 10^4-fold variation in reaction rate for different simple olefins that was almost entirely determined by changes in the activation entropy, proposing the intermediacy of an exciplex which was not in the required reaction geometry. Movement to the right geometry (or crossing to the right potential surface) would be the irreversible step that determines the value of the pre-exponential factor. No role is played by the solvent along this path. A similar proposal has been put forward by Gorman et al.,[191] who measured Arrhenius parameters for four enol ethers in five solvents. In spite of the fact that the reactivity of the compounds covered almost 2 orders of magnitude, no clear trend in activation energies could be observed; all values are 0 ± 1.0 kcal/mol. The differences in reactivity, almost totally due to changes in the pre-exponential factors, interpreted according to transition-state theory, would imply $\Delta S^{\ddagger}$ values ranging from −23 to −34 eu. The solvent effect, significant in some systems, is related to solvation entropy requirements at the transition state leading from exciplex to product, particularly in the case of dioxetane formation.

VII.2. Polyolefins

The mechanistic aspects, including the role of the solvent, of 1,3-diene photooxidations by $O_2(^1\Delta_g)$ have been recently discussed in detail by Clennan.[178,179] These compounds can undergo the three processes, ene reaction and [2 + 2] and [4 + 2] additions. k_t values reported for 2,5-dimethyl-2,4-hexadiene show only a minor solvent influence (Table 7). The reported Arrhenius parameters for the reaction of 2,5-dimethyl-2,4-hexadiene indicate that both the total rate and the ene process are limited by a negative activation entropy, whose values are similar in acetone and in methanol.[182] Larger dependences on the solvent have been reported for polyconjugated olefins[42] (Table 7), the reaction rate being extremely fast in *n*-methylformamide, the more polar solvent considered. These results were considered by the authors to be relevant in the extrapolation of data from solution to cell membranes.[42]

For compounds where several reaction paths compete, the product distribution is considerably solvent dependent and the prevalence of [2 + 2] processes in polar solvents has been associated with the involvement of a zwitterionic intermediate along this reaction path.[181,182,197,199] It is interesting to speculate that this type of process, taking place at the polar interfaces of membranes, could lead to the formation of dioxetanes during the photooxidation of lipids.

Trapping of an intermediate by nucleophilic solvents (such as methanol) has been reported for dienes which give [2 + 2] adducts, such as 2,5-dimethyl-2,4-hexadiene[181] and indenes.[181,200,201] These results have been explained in terms of the nucleophilic attack by methanol of a perepoxide intermediate. A somewhat different and more complex mechanism has been proposed by Gollnick and Griesbeck[202] to explain the product distribution during the interaction of $O_2(^1\Delta_g)$ with 2,5-dimethyl-2,4-hexadiene, in polar and nonpolar solvents. Besides the three processes (ene, [2 + 2], and [2 + 4]) and physical quenching, they propose a "vinilog ene-reaction". From an analysis of each rate as a function of the solvent, it is concluded that only the rates of the dioxetane and ene product formation are solvent dependent. Different intermediates are proposed for the different processes and even for a given process in different (protic and aprotic) solvents. Clennan et al.[203–206] carried out detailed studies on product formation of different isomeric 1,4-dialkoxy-1,3-butadienes. Taking into account the influence of the steric hindrance on product distribution and on the thermodynamic parameters, as well as the dramatic response of the reaction to changes in solvent composition, the authors proposed zwitterionic intermediates that can rotate in competition with closure to dioxetanes. The zwitterions should be stabilized in more polar solvents, and as a result their rotation should compete with closure more effectively than in less polar solvents. Reactions of the zwitterionic intermediate with the solvent were invoked to explain the product adducts observed in the reaction of $O_2(^1\Delta_g)$ with 2,4-hexadienes in methanol.[207]

The lack of dependence on the solvent of k_t and Arrhenius parameters for the $O_2(^1\Delta_g)$–olefin interaction and the strong solvent effect upon the yield and distribution of products can be interpreted in terms of Scheme 1 provided that the critical intermediates, such as the zwitterions, are derived from the charge-transfer complex. However, a different mechanism has been recently proposed by Clennan et al.,[179] which differs from that shown in Scheme 1 by considering that the quenching in aprotic solvents takes place exclusively from the zwitterionic intermediate and that the ene and [2 + 2] reactions are consecutive and not competing processes.

VII.3. Furan Derivatives

Furan and dihydrofuran reactions with $O_2(^1\Delta_g)$ strongly parallel those described in previous sections for the olefins and open enol ethers. Furans mainly react by a [2 + 4] pathway to give endoperoxides that rearrange or enter into bimolecular processes with a minimal contribution from physical quenching.[179,208,209] Clennan and Mehrsheikh-Mohammadi[210,211] determined k_t values for several substituted furans in dichloromethane and found a good correlation between the rate of the process and the electron-donating (or electron-withdrawing) character of the substituents. Gollnick and Griesbeck[208] measured k_r values for several substituted furans in methanol; the values obtained were similar to those in dichloromethane,[210] indicating that in the latter solvent the process was dominated by chemical interaction. These results also indicate that [2 + 4] cycloaddition is insensitive toward the solvent.

Table 8. Reactive Rate Constant (k_r) for the Reaction of $O_2(^1\Delta_g)$ with Diphenylisobenzofuran

solvent	$k_r \times 10^{-8}$, M^{-1} s^{-1}	ref[a]
hexane	2.6	215
cyclohexane	4.5	191
methylcyclohexane	3.7	215
toluene	6.7	191
acetone	6.4	191
acetonitrile	11, 14.2	191, 215
methanol	8.1, 7.2	191, 215

[a] All values were measured by flash photolysis and direct method.

Furans without labile allylic hydrogens react exclusively to give unstable endoperoxides.[208,212] Due to the extensive use of diphenylisobenzofuran (DPBF) as a $O_2(^1\Delta_g)$ probe, it has been the furan derivative most thoroughly investigated, and numerous efforts have been devoted to evaluate k_t and the reaction yield in different solvents.[191,209,213,214] In all of the solvents considered, the interaction is dominated by the chemical pathway, leading to a bleaching quantum yield of nearly one.[212] Wilkinson and Brummer's[28] compilation lists 104 determinations of k_t in 39 solvents, and the number has kept growing over the past decade. These data did not establish a clear dependence of DPBF reactivity on solvent properties, but more recent work employing direct detection of $O_2(^1\Delta_g)$ emission led to the assessment of a distinct solvent effect,[191,215] characterized by a small increase in k_t with increasing solvent polarizability (Table 8). In toluene, activation parameters have been measured by Gorman et al.,[216] and in spite of a rate change of nearly 2 orders of magnitude for furan and DPBF (1.1×10^7 and 8.1×10^8 M^{-1} s^{-1}, respectively), activation energies of 0.0 ± 0.4 kcal/mol were obtained for both compounds.

The logarithm of k_r of various furans with $O_2(^1\Delta_g)$ in methylcyclohexane increases linearly with the applied pressure. Treatment of the data according to the transition-state theory yields an activation volume of -17 cm^3/mol, whereas these plots for DPBF are curved significantly downward or show maximum values depending on the solvent.[217] These results indicate diffusional control at high pressures. The activation volume of the chemical step is nearly independent of the solvent (acetonitrile, methanol, methylcyclohexane, and 2,2,4,4,6,8,8-heptamethylnonane) and similar to that obtained when furan was employed as substrate, indicating that most of the effect is due to the structural change associated with the complex formation.[217] These results, as well as the zero activation energies measured in toluene,[216] are fully compatible with a reaction mechanism as that depicted in Scheme 1. According to this scheme, the activation volume mainly reflects the change associated with the reversible formation of the complex intermediate.

Dihydrofuran derivatives, as monoolefins, react by two competing paths, ene and [2 + 2] processes. Early works[218-220] on the photooxidation of dihydropyrans showed that the ratio of [2 + 2] cycloaddition to ene reaction varies over a 35-fold range as the solvent is changed from benzene to acetonitrile. Gollnick et al.[221,222] carried out a study on the effect of the solvent on the rates and product distribution of 2,3-dihydrofurans (2,3-dihydrofurans, 5-methyl-, 4,5-dimethyl-, and 4-carbomethoxy-5-methyl-2,3-hydrofuran) and the six-membered ring enol ether 5,6-dimethyl-3,4-dihydro-2*H*-pyran. Data collected in Table 9 show that the yield of the [2 + 2]-derived products from 2,3-hydrofurans increase with solvent polarity, mostly due to an increase in the rate of the process leading to these products. For other hydropyran derivatives (e.g., 3,4-dihydro-2*H*-pyran and 4-methyl-3,4-dihydro-2*H*-pyran) a notable increase in the dioxetane yield in polar solvents has also been reported.[221,223] However, 4,5-dimethyl-2,3-dihydrofuran gave predominantly the dioxetane in a variety of solvents ranging from benzene and carbon tetrachloride to acetonitrile and methanol,[221] and for 5,6-dimethyl-3,4-dihydro-2*H*-pyran, a compound also of relatively high reactivity, the product distribution was almost solvent independent.[222]

Table 9. Rate Constants for the Chemical Quenching (k_r) for the [2 + 2] Cycloaddition Reaction (k_{2+2}) and Ene Reaction (k_{ene}) of $O_2(^1\Delta_g)$ with 2,3-Dihydrofurans

2,3-dihydrofuran derivative	solvent	k_r[a]	k_{2+2}[a]	k_{ene}[a]
2,3-dihydrofuran	CCl_4	1.55	0.37	1.18
	benzene	2.09	0.67	1.42
	dichloromethane	3.15	2.33	0.82
	acetone	2.75	1.95	0.78
	acetonitrile	4.69	3.28	1.41
	methanol	2.45		
5-methyldihydrofuran	benzene	14.6	7.6	7.02
	acetone	28.3	22.06	6.22
	acetonitrile	34.4		
	methanol	13.8		
4-carbomethoxy-5-methyl-dihydrofuran	benzene	0.19	0.008	0.19
	acetone	0.61	0.24	0.37
	acetonitrile	0.88	0.39	0.49
	methanol	0.73	0.21	0.52

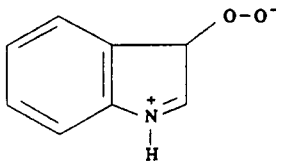
[a] k values are given in 10^6 M^{-1} s^{-1}. Data from ref 221. All values were obtained by steady-state method.

The dependence of k_t with temperature in the reaction of 5,6-disubstituted 3,4-dihydro-2*H*-pyrans with $O_2(^1\Delta_g)$ was reported by Chan et al.[223] in acetonitrile, chloroform, and carbon tetrachloride. In all of the solvents the process takes place with negative activation energy, implying entropic restrictions even larger than those reported for the furan derivatives.[216]

VII.4. Indole Derivatives

The reactions of indole derivatives with $O_2(^1\Delta_g)$, in particular those concerning tryptophan, have been extensively studied since this amino acid is one of the main targets when $O_2(^1\Delta_g)$ reacts with proteins.[224-228] In these systems, the reactivity of a tryptophan residue is extremely dependent on its location,[229-231] a dependence that can be related both to differences in the $O_2(^1\Delta_g)$ accessibility[232,233] and to microproperties of the medium where the amino acid target is located.[231,234] The fact that indole reactions are far from the diffusion-controlled limit and, in the case of proteins, slower than the tryptophan triplet quenching by molecular oxygen[235] would favor the predominance of a polarity effect in determining the reactivity of protein-bound tryptophan groups. Furthermore, data obtained in dipeptides[236,237] and tripeptides[238] show that, in a given solvent, the rate constant of the free amino acid can be considerably different from that of the same amino acid inserted in a peptidic chain.

It is well established that indole and its derivatives interact with $O_2(^1\Delta_g)$ by a process that involves a charge-transfer intermediate.[239-243] The process can be de-



scribed according to Scheme 1, where the reactive channel takes place through a zwitterionic peroxidized intermediate which can decay to a dioxetane[244] or to an ene-derived hydroperoxide[239-241] or be trapped by the solvent.[240,241] This proposal is sustained by the correlation observed between the rate of the process and the solvent polarity[245-247] (Table 10), the dependence of the total rate on the electron-withdrawing ability of the substituents in the indolic ring,[216,247] the sensitivity of the product distribution to the solvent, and the formation of solvent-derived products in protic media.[239] Most of the reported data also indicate that k_r is more solvent dependent than k_t. Similar to other systems reacting by a mechanism such as that depicted in Scheme 1, the process takes place with a rate constant nearly temperature independent.[216] This implies that in nonpolar solvents (such as toluene) the rate of the process is determined by the pre-exponential factor that, for indole, is as low as 7.7×10^5 M^{-1} s^{-1}. These results contrast with those reported for the temperature dependence of the chemical reaction of tryptophan in aqueous solution, which takes place with a pre-exponential factor of 3.7×10^{10}.[249] Similar high pre-exponential factors have been measured for imidazole, furfuryl alcohol, and dimethyl-*p*-nitrosoaniline. These results could be explained in terms of hydrophobic contributions to the stabilization of the transition state in aqueous solution.[249]

The yield and distribution of products obtained in the dye-sensitized oxidation of tryptophan and other indole derivatives have been shown to be extremely dependent on pH and the sensitizer (rose bengal, riboflavin, lumiflavin, methylene blue, and porphyrins). The dependence with pH found when methylene blue was employed as sensitizer has been interpreted in terms of a $O_2(^1\Delta_g)$-mediated mechanism and different pathways for the decomposition of the initially produced 3-hydroperoxyindolenine.[250] On the other hand, the differences observed when other dyes[251-253] were employed most probably result from a competition between type I and type II mechanisms.

VII.5. Aromatic Compounds

Polycyclic aromatic hydrocarbons quench $O_2(^1\Delta_g)$ by a chemical pathway to produce endoperoxides. Early reports by Stevens and Pérez[66] and by Monroe[254] pointed to a weak change of the reaction rate of $O_2(^1\Delta_g)$ with aromatic compounds (anthracene, rubrene, and 9,10-dimethylanthracene) when the solvent varies from carbon tetrachloride to methanol. The reported differences (up to a factor of 4 for 9,10-dimethylanthracene) are even smaller when more recently determined τ_Δ values are employed to obtain the addition rate constants. Opriel et al.[255] reported similar values of k_t for several anthracene derivatives in benzene and carbon disulfide. On the other hand, Rubio et al.[37] considered a wider range of solvents and found a noticeable increase in the reaction rate in aqueous mixtures and in pure water (Table 11). These data were obtained by following the aromatic derivative

Table 10. Rate Constants for the Total (k_t) and Reactive (k_r) Quenching of $O_2(^1\Delta_g)$ by Tryptophan

solvent	$k_t \times 10^{-7}$, M^{-1} s^{-1}	$k_r \times 10^{-7}$, M^{-1} s^{-1}	ref[a]
N-methylformamide	13		245
ethanol	<0.5		245
methanol	0.6		245
ethanol/acetonitrile (8:2)	0.63	0.048	237
D_2O/methanol (1:9)	1.3		246
D_2O/methanol (7:3)	6.0		246
H_2O/methanol (5.5:3)	3.0		245
D_2O/formamide (1:9)	8.7		246
D_2O/formamide (7:3)	5.2		246
D_2O (pD 7.4)	7.2	3.6	246
D_2O (pD 8.4)	5.1	3.0	248
H_2O (pH 7)		3.2	237

[a] All values were measured by flash photolysis and direct method except refs 220 and 245 (steady-state method).

consumption and indicate an increase of nearly 50 in the [2 + 4] addition rate (for 9-methylanthracene) when the solvent changes from methanol to water. Closely similar results have also been reported by Cazin et al.,[38] who studied the photooxidation of (1,4-naphthylidene)-dipropionate disodium salt and 1,4-dimethylnaphthalene (Table 11). For the former compound, k_r is 140 times larger in water than in methanol. The rate of the process in water/alcohol mixtures does not correlate with the bulk ϵ of the mixture, and a more specific role of water was proposed. However, data obtained in our laboratory indicate that bleaching of anthracene derivatives is also extremely fast in formamide and other polar solvents such as ethylene glycol. k_r values are only very weakly correlated with polarity parameters such as the polarity–polarizability or E_T. If the data obtained when 9-(hydroxymethyl)anthracene was used are expressed in terms of solvatochromic parameters, the largest coefficient is that of the π^* parameter, pointing to a prevalence of the solvent polarizability in determining k_r. However, in bimolecular reactions involving nonpolar reactants (such as $O_2(^1\Delta_g)$ and aromatics), the rate of the process that takes place with a negative activation volume[217] should be influenced by the cohesive energy (or internal pressure) of the solvent.[132] Since these parameters are somehow correlated to polarity parameters such as the E_T values,[257] it is difficult to establish whether in solvents of high polarity (such as formamide or water) the high rate of the process is due to an increased stability of the critical transition intermediate as a consequence of its dipolar character or its smaller volume. Nevertheless, the fact that additives with salting-in capacity (such as tetraethylammonium chloride or urea) increase the rate of the process would argue against a significant role of the latter effect.[132] The reported increase in k_r with salt addition[117] can be considered as a result of stabilization of the polar intermediate.

1,8-Dihydroxy-9-anthrone is a poor $O_2(^1\Delta_g)$ quencher in benzene ($k_t \approx 2.8 \times 10^4$ M^{-1} s^{-1}).[256,258] However, its anion readily reacts in acetonitrile solution ($k_t = 3.1 \times 10^8$, $k_r = 2.1 \times 10^8$ M^{-1} s^{-1}). In aqueous solution, the photooxidation rate increases with pH and, while the neutral species is almost unreactive, the trihydroxyanthracene anion has a total rate constant of ca. 3×10^8 M^{-1} s^{-1}, very close to that measured in acetonitrile.[256]

Mesodiphenylhelianthrene (MDH) is the most reactive $O_2(^1\Delta_g)$ acceptor.[259] k_r values for this compound are very close to the diffusion-controlled limit in a

Table 11. Total Rate Constant (k_t) for the Reaction of Aromatic Hydrocarbons with $O_2(^1\Delta_g)$

compound	solvent	$k_t \times 10^{-7}$, M^{-1} s^{-1}	ref[a]
9,10-dimethylanthracene	benzene	2.5	37
	ethanol	4.6	37
	methanol	6.9	37
	methanol/H_2O (8:2)	20	37
	ethanol/H_2O (1:1)	20	37
9-methylanthracene	benzene	0.23	37
	ethanol	0.2	37
	methanol	0.2	37
	ethanol/H_2O (1:1)	1.7	37
	H_2O	9.6	37
1,4-dimethylnaphthalene	methanol	0.004	38
	methanol/H_2O (8:2)	0.037	38
	2-propanol/H_2O (73:27)	0.0235	38
(1,4-naphthylidene)dipropionate	methanol	0.001	38
	methanol/H_2O (8:2)	0.006	38
	H_2O	0.14	38
1,8-dihydroxy-9-anthrone	benzene	0.003	256
1,8-dihydroxy-9-anthrone (anion)	acetonitrile	31	256
	D_2O, buffer	30	256

[a] All values were measured by indirect steady-state method except ref 256 (direct method).

variety of solvents (from cyclohexane to acetone). This implies that $k_r \geq k_{-d}$. Hence, during its self-sensitized photooxidation a significant in-cage reaction may take place prior to $O_2(^1\Delta_g)$ diffusion. In agreement with this conclusion, nearly 17% of the geminate pair reacts prior to its dissociation in toluene.[259] An even larger value can be expected in solvents of higher viscosity and/or at lower temperatures.

VII.6. Phenolic Compounds

Photoprocesses involving phenolic compounds have received extensive attention, mostly due to the role they could play as $O_2(^1\Delta_g)$ scavengers in biological systems[260-262] and the potential use of $O_2(^1\Delta_g)$-mediated photooxygenation of waste water contaminated with phenolic pesticides.[263-265] The value of k_t, as well as the fraction of reactive quenching, is strongly dependent on the structural properties of the phenol, on the solvent, and on the phenol protonation status. Extensive early work by Thomas and Foote[266] indicates that in methanol, para-substituted 2,6-di-*tert*-butylphenols show a linear correlation between log k_t and their half-wave oxidation potential. The dependence is rather similar to that obtained when phenol methyl ethers are employed,[267] suggesting that the phenolic hydrogen does not play any significant role in the quenching process.

Most of the reported data bearing on the effect of solvent upon k_t and k_r for several phenolic compounds are collected in Tables 12 and 13. The latter shows data on α-tocopherol, the compound most widely studied due to its relevance as an antioxidant in biological systems.[261] Tables 12 and 13 show that k_t values considerably increase with solvent polarity and that the differences between the various phenols increase in more polar media. These results are compatible with a mechanism comprising the formation of charge-transfer intermediates.[40,237,270,277,278]

The interaction between phenolic compounds and $O_2(^1\Delta_g)$ can be explained in terms of Scheme 1. An interesting feature of the data is that, in all solvents and for all compounds considered, activation energies are negative, the selectivity being determined by differences in the pre-exponential factors.[270] If the excited-state formalism applies to these processes (and differences in transmission coefficients due to possible nonadiabaticies are disregarded), the latter observation implies that the controlling factor is a large, negative, activation entropy.[270] The main product in the interaction of $O_2(^1\Delta_g)$ and phenol is the corresponding hydroperoxide,[266] whose decomposition can lead to quinones and to a variety of other products.[266,277,279]

Dihydroxybenzenes react via a mechanism similar to that for monophenols. The values of k_t (and to some extent also the products) depend on the solvent polarity, being faster and giving fewer products in polar solvents.[40] However, most probably the effect of the solvent is due to different pathways in the decomposition of a common primary product and not to different pathways from the charge-transfer complex. Mártire et al.[40] have measured k_t and k_r for several dihydroxybenzenes and chlorinated derivatives in several solvents of variable polarity (Table 12), finding a general correlation of k_t with the dielectric constant of the medium. An interesting feature of the data is that k_r/k_t values are much lower in acetonitrile than in water (acidic), indicating that the reactive dissociation of the encounter complex is enhanced in aqueous solution. For resorcinols, the chemical pathway in water is the only significant channel for the complex dissociation.

Since the reaction of phenols is dependent of their donor–acceptor properties, the rate of the process depends, in addition to the medium polarity, upon their protonation status. This dependence can be particularly important with regard to the reactivity of phenolic compounds in biological systems. The data obtained for tyrosine and tyrosine dipeptides are given in Table 12. These data show that the rate of the quenching process, and particularly that of the reactive pathway, is considerably faster for the phenolate anion.

The reactions of $O_2(^1\Delta_g)$ with monochloro- and mononitrophenols,[269] polychlorophenols,[264,268] and dihydroxybenzenes and their chlorinated derivatives[40] have been extensively investigated in a variety of media (Table 12) and show that even under basic conditions the processes are considerably faster in aqueous solutions.

VIII. Microheterogeneous Systems

The diffusion length of $O_2(^1\Delta_g)$ molecules can be estimated to be ca. 780 nm in aqueous solution.[280,281] In

Table 12. Rate Constants for the Total (k_t) and Reactive (k_r) Quenching of $O_2(^1\Delta_g)$ by Phenolic Compounds

compound	solvent	$k_r \times 10^{-7}$, M^{-1} s^{-1}	$k_r \times 10^{-7}$, M^{-1} s^{-1}	ref[a]
phenol	benzene/methanol (3:2)	$<10^{-3}$		268[a]
	benzene/methanol/OH^-	7.0		268[a]
3-chlorophenol	methanol/OH^-	1.5		269[b]
	H_2O (pH 11.5)	110	1.5	269[b]
4-chlorophenol	methanol/OH^-	3.3		269[b]
	H_2O (pH 11.5)	40	3.1	269[b]
2,4-dichlorophenol	benzene/methanol (3:2)	$<10^{-3}$		268[a]
	benzene/methanol (3:2)/OH^-	5.7	0.45	268[a]
	H_2O (pH 10)	200	11.4	268[a]
2,6-dichlorophenol	benzene/methanol (3:2)	$<10^{-3}$		268[a]
	benzene/methanol (3:2)/OH^-	5.4	0.37	268[a]
	H_2O (pH 10)	110	5.7	268[a]
2,4,6-trichlorophenol	benzene/methanol (3:2)	$<10^{-3}$		268[a]
	benzene/methanol (3:2)/OH^-	2.2	0.4	268[a]
	H_2O (pH 10)	60	5.9	268[a]
2-nitrophenol	benzene/methanol (3:2)/OH^-	0.3		269[b]
	H_2O (pH 10)	150	1.6	269[b]
4-methyl-2-nitrophenol	benzene/methanol (3:2)/OH^-	4.5		269[b]
	H_2O	8		269[b]
	H_2O (pH 10)	430	2.8	269[b]
2,4,6-triphenylphenol	benzene	2.2		266[c]
	acetonitrile	1.45		266[c]
	methanol	25.2		266[c]
2,4,6-tri-*tert*-butylphenol	cyclohexane	0.06		270[c]
	toluene	0.14		270[c]
	acetone	0.24		270[c]
	acetonitrile	0.25		270[c]
	methanol	0.28, 0.34		270,[c] 266[c]
1,4-dihydroxybenzene	dioxane	1.9		40[d]
	acetonitrile	2.8		40[d]
	D_2O	29		40[d]
1,3-dihydroxybenzene	dioxane	0.055		40[d]
	acetonitrile	0.39	0.015	40[d]
	D_2O	2		40[d]
1,2-dihydroxybenzene	dioxane	0.13		40[d]
	acetonitrile	0.29		40[d]
	D_2O	5.4		40[d]
tyrosine	ethanol/acetonitrile (8:2)/H^+	0.55	<0.0055	237[d]
	ethanol/acetonitrile (8:2)	0.62	0.31	237[d]
	ethanol/acetonitrile (8:2)/OH^-	18	3.0	237[d]
	H_2O (pH 7)	2.7		237[d]
	H_2O (pH 10)		3.8	237[d]
	H_2O (pH 11.5)		5.2	237[d]
tyrosine–glycine	ethanol/acetonitrile (8:2)/H^+	0.42	0.005	237[d]
	ethanol/acetonitrile (8:2)	0.43	0.21	237[d]
	ethanol/acetonitrile (8:2)/OH^-	12	1.0	237[d]
	H_2O (pH 11.5)		4.3	237[d]
glycine–tyrosine	ethanol/acetonitrile (8:2)	0.35	0.03	237[d]
	ethanol/acetonitrile (8:2)/OH^-	9.4	0.27	237[d]
	H_2O (pH 11.5)		1.9	237[d]

[a] Superscripts are as defined in Table 1.

Table 13. Rate Constants for the Total (k_t) and Reactive (k_r) Quenching of $O_2(^1\Delta_g)$ by α-Tocopherol

solvent	$k_r \times 10^{-7}$, M^{-1} s^{-1}	$k_r \times 10^{-7}$, M^{-1} s^{-1}	ref[a]
freon	3.1	0.19	271[a]
cyclohexane	9, 8.4	0.1	272,[b] 270[c]
hexadecane	4.2		273[a]
isooctane	12		274[b]
benzene	17		272[b]
toluene	22		270[c]
acetone	43		270[c]
pyridine	25	0.2	274[b]
ethanol/chloroform (1:1)	28	0.36	275[b]
acetonitrile	59		270[c]
methanol	67, 70, 30	4.6	276,[a] 274,[a] 270[c]
D_2O/ethanol (1:1)	45		275[b]

[a] Superscripts are as defined in Table 1.

other solvents where the decay is slower, diffusion lengths are even larger (ca. 2500 nm in D_2O). The type of kinetics observed for $O_2(^1\Delta_g)$ reactions in microheterogeneous systems depends upon the relationship between the $O_2(^1\Delta_g)$ diffusion length and the intra- and intermicrophase distances.[26,280,281] Furthermore, the characteristics of the process differ for diffusion-controlled and non-diffusion-controlled cases. In the former the rate will depend on whether the diffusion control is due to the capture of the externally generated $O_2(^1\Delta_g)$ by the microphase or by the intramicrophase diffusion.[281] For the reaction of $O_2(^1\Delta_g)$ with a microphase-associated target molecule, the rate of the process depends on the size and concentration of the microphase, the partition of $O_2(^1\Delta_g)$ between the solvent and the microphase, the intramolecular reactivity, the concentration and localization of the target molecules, and the locus of $O_2(^1\Delta_g)$ generation. This latter point has been the most thoroughly considered in terms of photodamage and phototherapy,[282,283] but it is intimately linked to all of the other factors. Furthermore, the presence of microphases can modify the sensitizer

Table 14. Experimental Rate Constant for $O_2(^1\Delta_g)$ Reactions in Micellar Solutions

quencher	micelle	$k_r \times 10^{-8}$, M^{-1} s^{-1}	ref[a]
DPBF	SDS (0.1 M)	11, 10	307, 115
	CTAB (0.1 M)	6.5, 6.7	307, 115
	Igepal (0.1 M)	6.5	307
	Brij 35 (0.1 M)	6.6	307
2,3-dimethylindole	SDS (0.1 M)	7.0	115
	CTAB (0.1 M)	4.4	115
pentamethylchromanol	SDS (0.1 M)	4.0	115
	CTAB (0.1 M)	4.1	115
9,10-dimethylanthracene	SDS (0.1 M)	1.5	37
	CTAB (0.015 M)	2.0	37
	CTAC (0.1 M)	2.7	37
	Triton X-100 (0.1 M)	2.6	37
9-methylanthracene	SDS (0.1 M)	4.9	37
	SDS (0.6 M)	3.5	37
	SDS + hexane[e]	4.9	37
	SDS + heptanol[f]	2.2	37
	CTAC (0.1 M)	6.1	37
	CTAC + heptanol[f]	4.0	37
	Triton X-100 (0.1 M)	5.4	37
	CTAB (0.015 M)	5.7	37
9-(hydroxymethyl)anthracene	SDS (0.1 M)	1.3	281
	CTAB	1.8	281
9-anthracenecarboxylic acid	CTAB	0.74	281
azide	CTAB (0.1 M)	8.2	115
	DTAC[g] (0.1 M)	18	118

[a] References 115 and 307, flash photolysis and indirect method. References 37, 118, and 281 by steady-state and indirect method. [e] Saturated in hexane. [f] Heptanol 56 mM. [g] DTAC, dodecyltrimethylammonium chloride.

aggregation[284-289] and/or its properties,[290-294] thus changing the $O_2(^1\Delta_g)$ production rate[288,289,292-296] as well as the relative relevance of type I and type II processes[290,297] by separating (or concentrating in a reduced volume) the sensitizer and the target molecule. On the other hand, the pH difference between the bulk solution and the charged interfaces can influence the efficiency of $O_2(^1\Delta_g)$ production[298-300] and the reactivity of those substrates whose reactions are pH sensitive.[299,301-305]

VIII.1. Micelles

Micelles are rather small structures ($d \approx 3$ nm) in which a higher oxygen solubility than in the surrounding aqueous solution can be expected. The relative $O_2(^1\Delta_g)$ concentration can be expressed in terms of the partition constant (K), defined as the ratio between the molar concentrations in the micellar pseudophase and the aqueous phase. Values of K of 2.8 in sodium dodecyl sulfate (SDS) and 4.0 in cetyltrimethylammonium bromide (CTAB) have been measured.[23,25] These values are very close to that reported for the partition of ground-state oxygen.[306]

In micellar solutions, the average $O_2(^1\Delta_g)$ diffusion length is considerably larger than the mean distance between micelles and, in the absence of high concentrations of scavengers in the aqueous solution, a $O_2(^1\Delta_g)$ molecule hits several micelles during its lifetime. For an entrance rate (k_+) equal to that of the ground-state oxygen molecule ($k_+ \geq 1.3 \times 10^{10}$ M^{-1} s^{-1}),[281] the above-mentioned partition constants imply that the average residence time of a $O_2(^1\Delta_g)$ molecule inside a micelle (the inverse of the exit rate k_-) will be ca. 2.3 and 5.9 ns in SDS and cetyltrimethylammonium chloride (CTAC) micelles, respectively. If the intramicellar concentration ($[Q]_{intra}$) of a target molecule is ca. $0.1n$, where n is the solute mean occupation number, it can be concluded that only targets with $k_{intra} \geq 10^9$ M^{-1} s^{-1} will compete with the exit, leading to diffusion-controlled quenching. These simple calculations imply that, irrespective of their locus of generation, $O_2(^1\Delta_g)$ molecules will escape to the aqueous solution[307-309] and visit several micelles prior to reaction or deactivation.[281,310] Furthermore, the kinetics of the system will be similar to that observed in homogeneous solutions, and the $O_2(^1\Delta_g)$ will decay monoexponentially with

$$(\tau_\Delta)^{-1} = (\tau_\Delta^\circ)^{-1} + (k_{intra}[Q]_{intra})Kf \quad (7)$$

where τ_Δ° is the lifetime in the absence of quenchers and f is the volume fraction occupied by the micellar solution. τ_Δ values in the presence of micelles have been measured by several groups,[23,307,311,312] and they are very similar to those measured in aqueous solution, at least for the ionic surfactants.[311]

For an equilibrium distribution of $O_2(^1\Delta_g)$ maintained throughout the system, the experimentally determined value of k_t, defined in terms of the analytical quencher concentration, is related to the intramicellar bimolecular rate constant k_{intra} by

$$k_t = Kk_{intra}/[(1-f) + fK] \quad (8)$$

At low f values, as those of most micellar solutions, this relationship reduces to

$$k_t = Kk_{intra} \quad (9)$$

Since micelles are inhomogeneous microsystems, both the $O_2(^1\Delta_g)$ local concentration and the microenvironment properties (that condition k_{intra}) will depend upon the substrate localization and are modified by the presence of additives or any other factors (such as the surfactant concentration and/or the solution ionic strength) that modify the properties of the micelles and/or the probe localization. An analysis of the reactivity in micelles pointing to the relevance of the probe localization or its orientation has been carried out in a limited number of systems, and most of the obtained data are given in Table 14.

DPBF has been the compound most frequently employed as a $O_2(^1\Delta_g)$ quencher in micellar solu-

tions.[23,118,214,307,310,313-315] Most of the results have been interpreted in terms of a diffusion-limited process with a very efficient,[23] or partially limited,[118,310] incorporation. However, a restricted incorporation of $O_2(^1\Delta_g)$ molecules ($k_+ < k_{encounter}$), such as that proposed to regulate the reactivity of tryptamine,[303] seems incompatible with the considerably higher rates of fluorescence quenching by oxygen reported in micellar solutions.[281]

Most of the data in Table 14 indicate that the reactivity in micelles is rather similar to that measured in organic solvents. However, large differences have been observed in some systems. DABCO reactivity in micelles is considerably lower than that measured in most organic solvents, a result explained in terms of the nitrogen lone pair hydrogen bonding.[115] On the other hand, an increase between 1 and 2 orders of magnitude in the rate constant of $O_2(^1\Delta_g)$ quenching by poly(chlorophenols) in CTAC micelles has been reported by Bertolotti et al.[302]

The data in Table 14 show that k_t values are generally larger in SDS than in CTAC micelles. This conclusion is further stressed if k_{intra} values are considered. Since the rate constants of the compounds (phenols, indole derivatives, furans, and anthracenes) increase with solvent polarity, the differences between k_{intra} values in both detergents could reflect a higher exposure to water in SDS micelles than in CTAC as a consequence of its smaller, more open structure.[316] However, since those reactions take place with negative activation volume,[215] the observed differences between both micelles could be accounted for, at least partially, by the smaller Laplace pressure of the larger micelles.[317] On the other hand, the larger rate constant measured for the quenching by azide in cationic micelles (see Table 14) can be ascribed to the ionic strength effect upon k_t already discussed in section IV.

The influence of the target localization on k_t has been discussed by Lissi and Rubio,[281] employing several anthracene derivatives as substrates and taking advantage of the high sensitivity of their rate constants to the solvent. Incorporation of 9-methylanthracene into both SDS and CTAB micelles reduced its rate of reaction with $O_2(^1\Delta_g)$, relative to that measured in aqueous solution. A similar protection has been reported by Moore and Burt[309] for anthracene. These results, contrary to expectations based on the higher intramicellar $O_2(^1\Delta_g)$ concentration, reflect the relevance of the intramicellar microenvironment where the reaction takes place. If the difference in oxygen concentration is taken into account, k_{intra} values are similar to those obtained in ethanol/water (1:1) mixtures (Table 11). However, there exist noticeable differences among the various compounds considered[281] that can be rationalized in terms of their different intramicellar location. Exposure of the probe to the aqueous pseudophase (moving it toward the interface) should increase its specific rate constant but will, possibly, also decrease the local $O_2(^1\Delta_g)$ concentration. The interplay of these two factors determines the reaction rate. The fact that 9,10-dimethylanthracene, the most deeply incorporated substrate, presents the smallest $k_{intra}/k_{ethanol:water}$ ratio indicates that the effect of the medium polarity is more important than the possible gradient in intramicellar $O_2(^1\Delta_g)$ concentration.[281]

The effect of additives which modify the micellar capacity to dissolve oxygen and the microproperties of the incorporated probe surroundings have been the object of few studies. Early results indicate that ethanol addition increases the rate of DPBF photobleaching in dodecyltrimethylammonium chloride (DTAC) micelles.[118] The data in Table 14 show that addition of 1-heptanol or increasing the surfactant concentration produces a significant decrease in 9-methylanthracene k_t values, as expected from the decrease in the polarity of the probe surroundings.[318-320] On the other hand, addition of *n*-hexane does not change the k_t value, implying a compensation between a less polar environment[319] and a higher intramicellar $O_2(^1\Delta_g)$ concentration.

Regardless of the fact that incorporation of solutes into micelles may modify the product distribution or the relevance of chemical pathways, few studies have been carried out to quantitatively evaluate micellar effects on photooxidations. Hovey[321] reported a cleaner production of sulfoxides during the 10-methylphenothiazine-mediated photooxidation of several sulfides in SDS micelles. Ohtani et al.[283] reported almost equal probabilities for the formation of C_9 and C_{13} hydroperoxides and an equal ratio of trans,trans/trans,-cis products for the oxidation of methyl 9-*cis*, 12-*cis*-octadecadienoate in acetonitrile and in aqueous emulsion. A noticeable effect of micelles has been reported by Horsey and Whitten[285] upon the production distribution during the photooxidation of protoporphyrin IX methyl ester. However, the formation of superoxide-mediated products cannot be completely disregarded in the micellar solution.

VIII.2. Reverse Micelles

Few $O_2(^1\Delta_g)$ processes have been studied in reverse micelles[322-325] or water in oil microemulsion,[290] although these media could facilitate the use of direct $O_2(^1\Delta_g)$ detection methods employing water-soluble sensitizers.[326]

The kinetics of $O_2(^1\Delta_g)$ processes in reverse micelles can be described in terms similar to those used previously for the micellar solutions,[281] the only difference being that the intramicellar $O_2(^1\Delta_g)$ concentration in reverse micelles is smaller than in the surrounding solvent, and hence incorporation of $O_2(^1\Delta_g)$ molecules from the organic solvent into the micelles can be a rather inefficient process.[327,328] Furthermore, the characteristics of the micelle[329] and the localization of micelle-incorporated probes[330,331] can be changed drastically by modifying the water/surfactant ratio (R).

Quenching of $O_2(^1\Delta_g)$ in reverse micelles has been carried out employing tryptophan,[324,332] azide,[322,324] DPBF,[323] and anthracene derivatives.[325] The results for azide in sodium bis(2-ethylhexyl)sulfosuccinate (AOT) reverse micelles indicate a noticeable decrease in k_t when R decreases (k_t values of 2.7×10^6, 6.6×10^6, 1.9×10^7, and 4.2×10^7 M^{-1} s^{-1} were reported at R values of 1.1, 4.5, 9, and 22, respectively[324]). The last value is still smaller than the value found in aqueous solution, if the $O_2(^1\Delta_g)$ partition constant (K) between the micelle and the organic solvent is taken as 0.11.[25] The extremely low values observed at low R, where a water pool is not present,[327] most probably reflect the localization of azide ions in a small region of high viscosity as well as a reduced $O_2(^1\Delta_g)$ incorporation. At high R values, azide ions will be pushed by electrostatic

repulsion toward the water pool. Alternatively, tryptophan may remain partially bound to the micellar interface even at rather high R ratios.[331] k_t values for this compound in AOT reverse micelles range from ca. 3.2×10^6 M^{-1} s^{-1} at low R to 4.2×10^6 M^{-1} s^{-1} at $R \approx 20$. These results were interpreted in terms of a rather high k_{intra} value of 3×10^7 M^{-1} s^{-1} at high R, and a moderate decrease at lower R values. At low R values, tryptophan is a more efficient $O_2(^1\Delta_g)$ quencher than azide, a result that can be explained in terms of different localization sites in the "dry" reverse micelle.[328]

Rubio and Lissi[325] carried out a study of the reactivity of different anthracene derivatives toward $O_2(^1\Delta_g)$ in AOT reverse micelles over a wide range of R values. The reactivity of 9,10-dimethylanthracene, a compound that can be assumed to remain in the organic solvent, is independent of both AOT and water concentration. For solutes totally incorporated into the micelles (e.g., anthracenecarboxylic acid and ethyldimethyl[3-(9-anthracenyl)propyl]ammonium bromide), the consumption rate was independent of AOT concentration but increased for higher R values. The dependence on R was larger for 9-anthracenecarboxylic acid, a result explained in terms of a displacement of this compound toward the micellar core. Accordingly, at high R values the intramicellar reactivity becomes similar to that in bulk water. For (hydroxymethyl)anthracene, partitioned between the solvent and the micelles, the value of k_t changes both with AOT concentration and with R. The results are quantitatively described in terms of the partition and an intramicellar bimolecular rate constant of 1.1×10^7 M^{-1} s^{-1}. This value is larger than that obtained when ethanol is employed as solvent.

The structure of Nafion swollen in water resembles that of a reverse micelle, where the hydrated sulfate head groups are clustered together in water-containing pockets of ca. 5 nm in diameter which are interconnected by short channels within the perfluorocarbon matrix.[333] The value of τ_Δ in vacuum-dried Nafion powder is 320 μs, while values of 55, 270, and 38 μs have been reported when the powders are swollen with water, D_2O, and methanol, respectively.[334] The value in water-swollen Nafion was interpreted in terms of partitioning of $O_2(^1\Delta_g)$ between the water pools and the fluorocarbon backbone, with a partition constant of ca. 0.21. Quenching of $O_2(^1\Delta_g)$ by Ni^{2+}, Cu^{2+}, and $Co(NH_3)_6^{3+}$ was smaller than in bulk solution,[334] particularly in air-dried Nafion, as a result of the adsorption of the ions to the charged interfase. Niu et al.[335] measured the methylene blue-sensitized photooxidation of anthracene, 9,10-diphenylanthracene, and 2-(dimethylamino)anthracene in Nafion, finding a photooxidation efficiency higher than that observed in ethanolic solution, as expected from the longer τ_Δ value and a more favorable $O_2(^1\Delta_g)$ distribution. The increase in efficiency, relative to that in ethanol, is somewhat larger for the more hydrophobic substrates, pointing to a modest relationship between localization and relative reactivity.

VIII.3. Vesicles

In this section, the term vesicle is used to describe spherical or ellipsoidal, single- or multicompartment, closed bilayer structures, regardless of their chemical composition.[286] The properties of a vesicle are determined by its composition, the number of compartments (uni- or multilamellar), and the size (small, diameter $\leq$30 nm, or large). Photoprocesses in these systems are actively investigated since they can be considered simple systems that mimic biological membranes. In contrast to micelles, inter- and intravesicular distances can be similar or even larger than the $O_2(^1\Delta_g)$ average diffusion length.[281] This possibility introduces a series of factors (gradient of $O_2(^1\Delta_g)$ concentration in a given pseudophase, nonequilibrium distribution of oxygen between the aqueous phase and vesicles, multiexponential decay for $O_2(^1\Delta_g)$) that lead to complex kinetics, as well as the possibility that the rate of the process depends upon the locus of $O_2(^1\Delta_g)$ generation. The latter point, together with the possibility that $O_2(^1\Delta_g)$ generated intravesicularly reacts inside the same vesicle or with target molecules located in other vesicles, has been the central point addressed in most studies in these systems, and the results have been frequently contradictory. Employing sonicated vesicles of didodecyldimethylammonium bromide (DDAB), Rodgers and Bates[336] observed normal kinetics for the consumption of DPBF (lipid soluble) and anthracene dipropionic acid (ADPA) (water soluble) in the presence of $O_2(^1\Delta_g)$ quenchers of different hydrophobicity, regardless of the sensitizer location. These results, which imply fast exchange between vesicles and aqueous solution and even among vesicles, can be explained in terms of the high surfactant concentrations employed (40 mM) and the small size of the vesicles (the solutions were optically clear). These conditions lead to intervesicular distances smaller than the average oxygen diffusion length. In agreement with these considerations and the low fraction of the solution volume occupied by the vesicles, the measured τ_Δ values in the absence of quenchers were similar to those reported in aqueous solutions.[311,336] Nonell et al.[337] obtained similar τ_Δ values in the presence of small unilamellar vesicles (SUV) (ca. 26 nm radius, 26 nM in vesicles) of dipalmitoylphosphatidylcholine (DPPC) as in neat D_2O solution, irrespective of the sensitizer, concluding that $O_2(^1\Delta_g)$ diffuses quickly through the lipid bilayer and a partition equilibrium is attained before decay occurs. In this equilibrium situation, $O_2(^1\Delta_g)$ is mostly located in the aqueous phase. When the sensitizer mesotetrakis(4-sulfonatophenyl)porphine was located in the buffer, τ_Δ became nearly independent of the DPBF concentration at high quencher concentration. The measured time (40 μs) was determined by the decay in the solvent and the irreversible capture of $O_2(^1\Delta_g)$ by the DPBF-loaded vesicles with $k_+ \approx 2 \times 10^{11}$ M^{-1} s^{-1}.

Reddi et al.[338] reported that during the photooxidation by liposome-bound hematoporphyrin in DPPC small unilamellar vesicles (SUVs) in the presence of 50 μM DPBF a significant fraction of the $O_2(^1\Delta_g)$ escapes to the water phase, leading to a subsequent, slow DPBF bleaching. Similarly, Grossweiner et al.[292,339,340] concluded that the protection of egg phosphatidylcholine (EPC) SUVs damage photosensitized by incorporated sensitizers, afforded by water-soluble agents, provides evidence that even in vesicles containing reactive (unsaturated) lipids, a significant fraction of $O_2(^1\Delta_g)$ molecules reach the external medium. On the other hand, in a study of the photooxidation of single bilayer vesicles (25–30 nm diameter) of EPC, Dearden[341] concluded that the rate of photooxidation of unsaturated fatty acids is strongly dependent upon the location of the sensitizer in the bilayer. In this work, it is

considered that the unimolecular decay can be expressed as

$$k_d = g_w(k_d)_w + g_{intra}(k_d)_{intra} \quad (10)$$

with $(k_d)_w$ and $(k_d)_{intra}$ the unimolecular decay rates in water and inside the vesicles and g_w and g_{intra} the fractions of $O_2(^1\Delta_g)$ present in the aqueous phase and inside the vesicles, respectively. After considering that k_d is greater than k_r [lipid], it was concluded that most of the oxygen is present inside the vesicles ($g_{intra} > g_w$) even when water-soluble (rose bengal) sensitizers were employed. This conclusion was derived from the partial efficiency of azide as quencher and from the rather small enhancement in photooxidation rate elicited by changing the solvent from water to D_2O. However, several peculiar properties of the vesicles render difficult the evaluation of g values by the proposed procedure. In the first place, eq 10 is only valid under conditions of fast exchange between the vesicles and the solvent. Second, the intravesicular double-bond concentration is relatively high (>0.1 M), and hence reaction inside the vesicles can compete with decay or exit. Furthermore, for an oxygen molecule leaving a vesicle, there will be a high probability of re-entry to the same vesicle (the same applies to those oxygen molecules diffusing into the inner water pools). This probability strongly decreases with the elapsed time and hence will be slightly dependent on τ_Δ in the aqueous phase. In any case, the data clearly indicate that "micelle-like" kinetics do not apply and that significant $O_2(^1\Delta_g)$ gradients are established. Similar considerations apply to the work of Hoebeke et al.[342] on the reactions of ADPA (water soluble) and 9,10-dimethylanthracene (lipid soluble) in dimyristoylphosphatidylcholine (DMPC) large unilamellar vesicles (LUVs) (diameter $\approx$ 100 nm) and to the work of Singh et al.[51] regarding merocyanine 540 photobleaching in dilaurylphosphatidylcholine (DLPC) LUVs. From the enhancement effect of D_2O and the inhibitory effect of sodium azide Hoebecke et al.[342] concluded that $O_2(^1\Delta_g)$ molecules spend more than 87% of their lifetimes in a lipidic environment and that ca. 40% of them remain inside the liposome where they are originally generated. Although a quantitative analysis of the data by the proposed procedure is not warranted (by the above considerations regarding the use of eq 10 and the fact that it is not established if the substrate (ADPA) or the azide ions reach the inner pool), they also show that $O_2(^1\Delta_g)$ gradients are important and that the equilibrium distribution of these species between the aqueous solution and the vesicules is not established. This is a rather general situation in LUVs and is supported by data reported by Rubio and Lissi[281] showing that, in dioctadecyldimethylammonium chloride (DODAC) LUVs, there is a smaller steady-state $O_2(^1\Delta_g)$ concentration inside the intravesicular water pool than in the aqueous solution when the sensitizer is located in the external solution.

The above considerations imply that, while equilibrium distribution of $O_2(^1\Delta_g)$ can be assumed (particularly in SUVs and in the absence of high intravesicular concentration of quenchers) with most $O_2(^1\Delta_g)$ present in the water phase, high inhomogeneities will be produced in other situations, rendering difficult the evaluation of meaningful bimolecular rate constants in those systems. Employing DPPC SUVs, Valduga et al.[343] followed the bleaching of DPBF using the vesicle-bound sensitizer Zn(II) phthalocyanine. A linear relationship between the inverse of the bleaching yield and the inverse DPBF concentration was obtained, leading to an apparent k_t value of ca. 5×10^9 M^{-1} s^{-1}. However, since at low DPBF concentration the τ_Δ must be controlled by the unimolecular decay in water while at high DPBF concentrations all of the process will remain almost exclusively intravesicular, it is unlikely that a single equation can represent the data over the whole DPBF concentration range. A smaller value ($k_t = 6.2 \times 10^8$ M^{-1} s^{-1}) has been reported for DPBF in DDAB vesicles,[336] this value being similar to those obtained in homogeneous solvents. Handa et al.[344] reported that incorporation of the dye (tetraphenylporphyrin) or the target (methyl orange) to soybean phosphatidylcholine vesicles greatly reduced their oxidation rate. For methyl orange, the consumption rate as a function of the vesicle concentration indicates, if the partition constant for $O_2(^1\Delta_g)$ is taken as equal to 5, that $k_{intra}/k_{water} = 1.7 \times 10^{-2}$ mainly as a consequence of the reduced polarity of the medium.

Bachowski et al.[345] measured, in LUVs ($d \approx 100$ nm) of EPC and diacetyl phosphate (10:1), the protection by azide of the lipid peroxidation and lactate dehydrogenase inactivation promoted by chloroaluminum phthalocyanine tetrasulfonate irradiation. Although linear Stern–Volmer plots were obtained, the k_t values depended on the substrate considered, implying a strongly inhomogeneous $O_2(^1\Delta_g)$ distribution. Kinetic analysis of $O_2(^1\Delta_g)$ reactions in fully saturated DMPC and DLPC vesicles, monounsaturated 1-palmitoyl-2-oleoylphosphatidylcholine (POPC) vesicles, and erythrocyte membranes has been carried out employing merocyanine 540 as sensitizer.[51,346,347] Extensive oxygen consumption was observed in DMPC vesicles only in the presence of histidine, while in POPC vesicles and in erythrocyte membranes oxygen consumption takes place even in the absence of histidine due to the reaction with the unsaturated lipids or other components of the membrane.[346,347] From a comparison of the rates of merocyanine 540 and DPBF consumption a value of k_r was estimated for the dye of 9.1×10^7 M^{-1} s^{-1}. This value is 3 times larger than that measured in ethanol/water (1:1).[51] However, the employed procedure implies knowledge k_{intra} for DPBF and the assumption of similar locations of the merocyanine and DPBF molecules, rendering a comparison with homogeneous solutions unwarranted. Values of k_t by azide of 3×10^8 and 1.7×10^8 M^{-1} s^{-1} were obtained in DMPC vesicles from the protection of histidine and merocyanine bleaching, respectively.[51,347] These values are smaller than those measured in homogeneous solution (Table 3) and were interpreted in terms of the "heterogeneous nature" of the system, emphasizing the difficulties associated with the interpretation of kinetic data in microheterogeneous solutions.

Most of the above-mentioned uncertainties can be avoided by employing low concentrations of targets of low reactivity. This procedure has been applied by Encinas et al.[348] in the evaluation of the reactivity of anthracene derivatives in DODAC vesicles by following the bleaching of the substrate under steady-state conditions employing water-soluble sensitizers. The data are shown in Table 15, together with other related bimolecular rate constants reported for these systems.

The values of k_t/k_w (Table 15) range from 0.077 to 0.3, implying a reduced reactivity as a consequence of

Table 15. Quenching Rate Constant (k_t) of $O_2(^1\Delta_g)$ by Different Substrates in Vesicular Media

quencher	vesicle[e]	$k_t \times 10^{-7}$, M^{-1} s^{-1}	k_t/k_w[f]	ref[a]
DPBF	DDAB (SUVs)	62		336[b]
	DPPC (SUVs)	88		338[b]
2,3-dimethylindole	DDAB (SUVs)	4.8		336[b]
9,10-dimethylanthracene	EPC (SUVs)	32		341[a]
	DODAC (LUVs)	1.8		348[a]
	DODAC (SUVs)	4.1		348[a]
9-methylanthracene	DODAC (LUVs)	0.84	0.15	348[a]
	DODAC (SUVs)	0.69	0.12	348[a]
9-(hydroxymethyl)anthracene	DODAC (LUVs)	0.4	0.3	348[a]
	DODAC (SUVs)	0.26	0.2	348[a]
3-(9-anthryl)propionic acid	DODAC (LUVs)	0.37	0.077	348[a]
	DODAC (SUVs)	0.52	0.11	348[a]
9-anthracenecarboxylic acid	DODAC (LUVs)	0.087	0.15	348[a]
	DODAC (SUVs)	0.094	0.16	348[a]

[a] Superscripts are as defined in Table 1. [e] LUVs, large unilamellar vesicle. SUVs, small unilamellar vesicles. [f] Ratio between k_t in the vesicular solution and the values measured in water (k_w).

substrate incorporation to the vesicles. This decrease reflects a smaller k_{intra} value due to the reduced polarity of the medium. The values of k_t for a given aromatic compound depend on the size of the vesicle. For those compounds where the aromatic moiety is deeply incorporated into the bilayer (e.g., 9,10-dimethylanthracene and 3-(9-anthryl)propionic acid), the values are smaller in the large vesicles, probably as a consequence of a lower oxygen solubility or a less polar microenvironment in these more closely packed vesicles. On the other hand, for those compounds for which the aromatic group can be located near the interface (e.g., 9-(hydroxymethyl)anthracene, 9-anthracenecarboxylic acid, and 9-methylanthracene), the values are similar or even slightly higher in the large vesicles, suggesting a more exposed location in these structures, similar to that observed for other aromatic compounds.[349] A different location of the aromatics in the vesicle could also explain the small difference in reactivity between 9-methylanthracene and 9,10-dimethylanthracene (a factor of nearly 2 in LUVs), compared to that observed in homogeneous solvents (e.g., a factor 20 in ethanol).

A relevant $O_2(^1\Delta_g)$ reaction in vesicles is that with unsaturated lipids that can lead to substantial structural damage and lysis.[339,346,350-355] Eisenberg et al.[356] reported the lysis of EPC vesicles by $O_2(^1\Delta_g)$ generated in the gas phase, and a detailed analysis of the photooxidation of individual lipid components has been carried out by Dearden et al.,[357] who show that the reactivity follows the order C18:1 < C16:1 < C18:2 < C20:4. These values approximately correspond to the double-bond character, with the difference between C18:1 and C16:1 consumption rates (a factor of nearly 2) reflecting the relevance of the intravesicular location. It is noteworthy that as time of irradiation and fluidity of the bilayer increase, as measured by fluorescence depolarization,[358] the relative reactivities of the different lipids change, with a noticeable increase in the rate of C20:4 consumption. This indicates that structural changes in the membrane organization can modify both the total and the relative reactivities of different biomolecules. An increase in the lipid peroxidation in EPC LUVs with cholesterol (that modifies their fluidity) has also been reported[355] but was mostly attributed to variations in $O_2(^1\Delta_g)$ generation rates, although changes in the solubilization or reactivity of the $O_2(^1\Delta_g)$ cannot completely be excluded. Korytowski et al.[359] have carried out a comparison of the relative yields or 3β-hydroxy-5α-cholest-6-ene 5-hydroperoxide (5α-OOH) and 3β-hydroxycholest-4-ene 6β-hydroperoxide (6β-OOH) in homogeneous solvents, unilamellar vesicles, erythrocyte ghost membranes, and L1210 leukemia cells. The results indicate that environmental factors make photogeneration of 6β-OOH in the lipid bilayers more favorable than in homogeneous solution.

The fluidity of the vesicles can be altered by incorporation by solutes or by changes in temperature. The influence of these factors upon the reactivity of substrates incorporated into vesicles toward $O_2(^1\Delta_g)$ has been analyzed by Rubio et al.[117] 1-Octanol addition to LUVs of DODAC led to a notable decrease in k_t values for 9,10-dimethylanthracene and 3-(9-anthryl)propionic acid, in spite of the increased solubility/mobility of oxygen molecules inside the vesicles.[349] These results imply a noticeable reduction in k_{intra} due to changes in the polarity of the microenvironments of the probe or movements toward less polar regions. The possibility of probe displacement is supported by the larger effect of 1-octanol addition upon the reaction rate of 9,10-dimethylanthracene.

The fluidity of DODAC LUVs increases sharply at temperatures above the bilayer phase transition.[349,360] In spite of this, the reactivity of anthracene derivatives located inside the vesicles is only slightly dependent on the temperature, increasing by less than a factor of 2 when the temperature changes from 15 to 42 °C.[117] These results, which contrast with the change in the diffusion-controlled rate constant for the deactivation of pyrene derivatives by oxygen,[349,361] are attributed to a combination of effects. The increase in $O_2(^1\Delta_g)$ solubility should be offset by the decrease in k_{intra} due to the decreased local polarity at the locus of the anthracene moiety location.[117] On the other hand, Suwa et al.[362] reported that the yield of the cholesterol-derived 5α-OOH hydroperoxide produced in the photosensitized oxygenation of cholesterol in liposomal membranes increases 6–7-fold above the transition temperature of DPPC and DMPC membranes.

VIII.4. Biological Membranes, Organelles, and Cells

The photooxidation of biological membranes, organelles, and cells mediated by $O_2(^1\Delta_g)$ has been extensively investigated,[351,363-365] but few kinetic data have been reported in these complex systems, since the same considerations are applicable as discussed for vesicles, with the additional complexity offered by the

presence of various environments and reactive substrates. These factors, together with the larger size of intra- and intercellular distances and the short τ_Δ values expected (due to the presence of reactive biomolecules), render the kinetics extremely complex and dependent on the locus of $O_2(^1\Delta_g)$ generation. Pooler[366] has shown that in most in vitro systems the $O_2(^1\Delta_g)$ molecules which diffuse away from a cell could rarely reach another cell before being quenched by the solvent. The damage (and protection) will be nearly site-specific,[367-370] and the scavenging efficiency of a given $O_2(^1\Delta_g)$ acceptor, as well as the enhancement produced by D_2O incorporation, will vary considerably from one system to another, and in very few systems total protection can be expected.[366,369,371-378] Similarly, lack of protection by a given $O_2(^1\Delta_g)$ scavenger or lack of D_2O effect cannot be taken as proof against mechanisms involving $O_2(^1\Delta_g)$.[372,379,380]

The deleterious effect of $O_2(^1\Delta_g)$ in cells can be due to damage of membrane components, DNA damage, or enzyme inactivation. DNA strand breaks are produced when $O_2(^1\Delta_g)$ is generated by sensitizers that penetrate the cell wall.[376,378,381-383] Studies on $O_2(^1\Delta_g)$-mediated damage of nucleic acids, nucleotides, and bases show that guanine and its derivatives are the most susceptible to photooxidation, the other bases being at least 2 orders of magnitude less reactive.[383-386] A rate constant of 5×10^6 M^{-1} s^{-1} has been reported for D-guanosine in neutral solution.[385,386] The reactivity undergoes a significant enhancement in basic media. A value of 5.7×10^7 M^{-1} s^{-1} has been measured for D-guanosine at pH 10.[386] DNA molecules react with $O_2(^1\Delta_g)$ more slowly than could be expected from their guanine content,[386] implying a slower reactivity of these bases when incorporated to the macromolecule. This effect can be related to a smaller $O_2(^1\Delta_g)$ concentration inside the matrix or differences in the intramatrix bimolecular rate constant. There are no data bearing on the effect of the medium upon the reactivity of guanine bases to allow an estimation of the influence of this factor.

Damage to membranes is a general feature of $O_2(^1\Delta_g)$ presence in biological systems. The action of $O_2(^1\Delta_g)$ on the membrane components can lead to lysis[371,373] due to lipid oxidation[387] or protein damage.[371,388-390] Frequently, other species derived from type I reactions or secondary reactions can also contribute to the observed damage.[364,391,392] However, the capacity of $O_2(^1\Delta_g)$ to promote the hemolysis of erythrocytes has been unequivocally demonstrated by generating it in the gas phase.[393]

The value of τ_Δ has been estimated[394] or measured[26,369,395,396] in biological systems. Kanofsky[396] measured a $\tau_\Delta = 1.04 \pm 0.03$ μs in human plasma, mainly determined by the reactions of $O_2(^1\Delta_g)$ with plasma proteins. Firey and Rodgers[395] observed $O_2(^1\Delta_g)$ luminescence with $\tau_\Delta = 46$ μs in a suspension of mesotetrakis(4-sulfonatophenyl)porphine-labeled ghosts. This value was rather close to the lifetime in the deuterium oxide solvent employed. This result implies that the detected $O_2(^1\Delta_g)$ molecules are those that diffuse out into the buffer[26] due to the small thickness of the red cell membrane[397] and the high rate of intramembrane diffusion of oxygen molecules.[398] The rise and decay kinetics of the $O_2(^1\Delta_g)$ luminescence measured in aqueous suspensions of porphyrin-containing yeast cells also indicate that the emitting molecules are located outside the cells.[399] The value of τ_Δ from unsealed ghosts, labeled with 5-(*N*-hexadecanoyl)aminoeosin and suspended in deuterium oxide buffer, has also been measured by Kanofsky.[26] The τ_Δ measured was dependent upon the membrane concentration. In dilute solutions, τ_Δ was 23 μs and, as evidenced by the strong quenching by azide, is determined by its diffusion into the buffer solution.[26] Extrapolation of the data to 100% ghost concentration yielded τ_Δ values from 24 to 130 ns inside the membranes. Data obtained regarding the yield of $O_2(^1\Delta_g)$ production and the effect of added D_2O also suggest a high reactivity of $O_2(^1\Delta_g)$ inside the red cell membrane,[367] mostly as a consequence of protein quenching. From the mutual photobleaching of two sensitizers in NHIK 3025 cells, Moan and Berg[394] estimated that the $O_2(^1\Delta_g)$ diffusion length was ca. 0.01–0.02 μm and that the lifetime inside them was between 0.01 and 0.04 μs. Extrapolation of τ_Δ values obtained in a suspension of L1210 leukemia cells to "100%" cell concentration yield a limiting lifetime between 0.17 and 0.32 μs.[369] The theoretical contributions of various types of biological molecules within the L1210 cell to the total $O_2(^1\Delta_g)$ quenching were calculated from their concentrations and their quenching rate constants in homogeneous solution. The data indicate that proteins are the biomolecules that most contribute to the $O_2(^1\Delta_g)$ quenching. However, the assumptions involved in the calculations render the results only qualitative.[369] Other works also indicated a very short intracellular τ_Δ,[365,400,401] rendering unsuccessful the attempts to directly determine it.

Rate constants for azide quenching were determined by Stern–Volmer analysis of competitive kinetic data in ghosts employing different sensitizers and targets.[377] Surprisingly, although Stern–Volmer plots were linear up to values of 10, the derived k_t values were extremely dependent upon the localization of the sensitizer and the target considered. The values obtained ranged from 2.4×10^7 (lipids as target) to 1.4×10^9 M^{-1} s^{-1} (lactate dehydrogenase as target) when chloroaluminum phthalocyanine tetrasulfonate was employed as sensitizer. The proposal that azide can intercept any $O_2(^1\Delta_g)$ escaping to (or formed in) the medium but has limited access to $O_2(^1\Delta_g)$ generated in the membrane and reacting (or being quenched) near its site of origin is compatible with the occurrence of linear Stern–Volmer plots only if emission from inside the membrane is negligible.[377] In any case, the reported data emphasize the complexity of the processes taking place even in the simplest biological membranes.

IX. Acknowledgments

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X. References

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