Kinetic Studies of Singlet Oxygen [4 + 2]-Cycloadditions with Cyclic 1,3-Dienes in 28 Solvents

Jean-Marie Aubry,*,† Bernadette Mandard-Cazin,‡ Michel Rougee,§ and René V. Bensasson*,§

Contribution from the Equipe de Recherches sur les Radicaux Libres et l'Oxygène Singulet, CNRS UA 351, Faculté de Pharmacie de Lille, B. P. 83, 59006 Lille Cedex, France, Laboratoire de Recherches Organiques, CNRS UA 476, ESPCI, F-75231 Paris, France, and Laboratoire de Biophysique, Museum National d'Histoire Naturelle, INSERM U 201, CNRS UA 481, 43 rue Cuvier, 75231 Paris Cedex 05, France

Abstract: The [4 + 2]-cycloaddition of singlet oxygen with 1,4-dimethylnaphthalene (DMN) and derivatives has been studied in 28 solvents by laser flash photolysis and steady state photolysis. The bimolecular rate constants of singlet oxygen quenching by DMN, *via* a physical process (k_q) and *via* a chemical reaction (k_r), are solvent-dependent and increase by more than 2 orders of magnitude from cyclohexane to formamide. This significant solvent dependence is in contrast with previous investigations conducted in six or seven solvents. It is discussed in terms of the solvatochromic properties of the different solvents. Moreover, for seven water-soluble 1,3-dienes, the overall rate constant k_0 ($= k_r + k_q$) is much higher in water than in methanol. Our results are consistent with a two-stage mechanism implying as a first step an equilibrium producing an exciplex with charge transfer character. A shift toward the formation of this exciplex leading to the cycloaddition product occurs by an increase (i) in the Hildebrand solubility parameter δ_H, (ii) in the dipolarity−polarizability parameter π^* of the solvent, and (iii) in the solvophobicity of the diene.

Introduction

Olefins can undergo three types of reactions with the lowest singlet excited state of molecular oxygen O_2 ($^1\Delta_g$) giving an allylic hydroperoxide (ene reaction), a dioxetane ([2 + 2]-cycloaddition), or an endoperoxide ([4 + 2]-cycloaddition), respectively.[1] Solvent effects on these reactions were mainly studied with acyclic 1,3-dienes which undergo, concomitantly, these three modes of reaction.[2] From the ratio between the different peroxides obtained, it was concluded that the rate of [2 + 2]-cycloaddition clearly increases with solvent dipolarity, whereas the ene reaction is only slightly solvent-dependent. In contrast, the rate of [4 + 2]-cycloaddition seemed to be practically solvent-independent in agreement with a concerted mechanism.[2e] Gollnick and Griesbeck[3] confirmed these conclusions using three specific substrates, 2,3-dimethyl-2-butene, 1,3-cyclohexadiene, and benzvalene which yielded allylic hydroperoxide, endoperoxide, and dioxetane, respectively. Due to the lack of appreciable solvent effects, Clennan[2h] also suggested a concerted mechanism for $^1O_2$ [4 + 2]-cycloadditions with cyclic 1,3-dienes such as furans and cyclopentadienes, as far as they are symmetrically substituted.

However, we have previously noticed that the chemical reactivity of singlet oxygen with a conjugated diene such as disodium 3,3'-(naphthalene-1,4-diyl)-dipropionate (NDP) was much higher in water than in methanol.[4] In the present work, we have broadened this observation by conducting a kinetic study of the singlet oxygen [4 + 2]-cycloaddition for different types of cyclic 1,3-dienes in 28 solvents, improving on previous investigations which were conducted using only six or seven solvents.[2,3] Using time-resolved and steady-state photolysis techniques, we have determined the rate constants for the physical and chemical reactions involved. We have discussed the solvent effects on kinetics in terms of solvatochromic parameters including dipolarity/polarizability (π^*) and Hildebrand solubility (δ_H) parameters.

Most of our work was carried out with naphthalene derivatives since they exhibit three useful properties:

(i) A low reactivity toward $^1O_2$ in common solvents such as methanol makes the observation of a large accelerating effect in highly dipolar solvents much easier.

(ii) A reaction with $^1O_2$ takes place exclusively through [4 + 2]-cycloaddition (reaction 1).

(iii) The quantitative regeneration of the starting compound on thermolysis of the endoperoxide provides a simple and unambiguous test to check that [4 + 2]-cycloaddition is the sole oxidation pathway as indicated below (reaction 1):
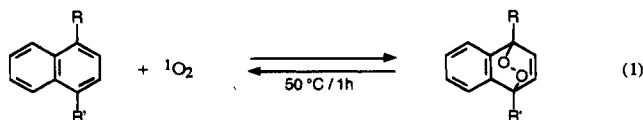
Experimental Section

Chemicals. Porphines were obtained from Midcentury (Posen, IL). Rose Bengal, solvents, naphthalene (h_8 and d_8), 1,4-dimethylnaphthalene (DMN), and 1,2,4-trimethoxybenzene (TMB) were purchased from

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‡ ESPCI.
§ Museum National d'Histoire Naturelle.
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Aldrich. Deuterated formamide, $DCOND_2$ (98% d_3), was prepared by the Commissariat à l'Energie Atomique (CEA, Saclay, France). Sodium 1,3-cyclohexadienyl-1,4-diethanoate (CHDDE),[5] disodium 3,3'-(naphthalene-1,4-diyl)dipropionate (NDP),[6] sodium 3-(4-methyl-1-naphthyl)-propionate (MNP),[7] [2-(4-methyl-1-naphthyl)ethyl]trimethylammonium chloride (MNEA),[8] and disodium 3,3'-(anthracene-9,10-diyl)dipropionate (ADP)[9] were synthesized according to known procedures.
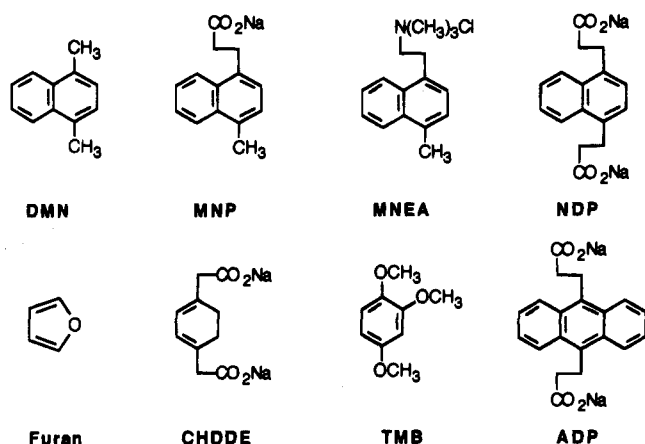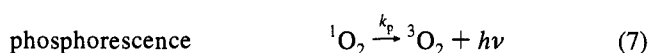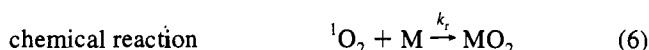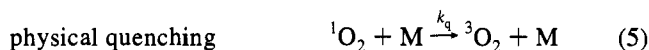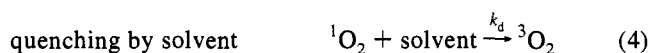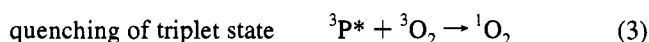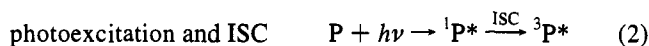

Flash Photolysis. The photosensitized production of $^1O_2$ was carried out by energy transfer from a photosensitizer to $^3O_2$ using a flash photolysis system[11] coupled with a dectector already described by Rodgers and Snowden.[10]

Steady-State Photolysis. A solution of the naphthalenic substrate 2.5×10^{-3} M and a photosensitizer (Rose Bengal) 3×10^{-5} M was saturated with oxygen and irradiated in a Pyrex cell at 5 °C with a halogen lamp (600 W, Osram). Control experiments were performed to ensure that the naphthalenic substrate alone does not act as a photosensitizer under these conditions. The photochemical reaction was monitored by HPLC analysis on an RP 18 column. The solutions of the naphthalenic endoperoxides were then decomposed by heating for 1 h at 50 °C, and the quantitative regeneration of the starting compound was checked by HPLC. The rate of $^1O_2$ production was determined by replacing naphthalenic substrate with two efficient $^1O_2$ scavengers, α-terpinene 5×10^{-2} M in organic solvents and CHDDE 2×10^{-2} M in D_2O, which trap completely photogenerated singlet oxygen.

Results

The photosensitized production of singlet oxygen ($^1\Delta_g$) and its different pathways of decay are presented in Scheme 1:[12]

Scheme 1

photoexcitation and ISC	$P + h\nu \rightarrow {}^1P^* \xrightarrow{ISC} {}^3P^*$	(2)
quenching of triplet state	${}^3P^* + {}^3O_2 \rightarrow {}^1O_2$	(3)
quenching by solvent	${}^1O_2 + \text{solvent} \xrightarrow{k_d} {}^3O_2$	(4)
physical quenching	${}^1O_2 + M \xrightarrow{k_q} {}^3O_2 + M$	(5)
chemical reaction	${}^1O_2 + M \xrightarrow{k_r} MO_2$	(6)
phosphorescence	${}^1O_2 \xrightarrow{k_p} {}^3O_2 + h\nu$	(7)

k_d is the intrinsic first-order rate constant of singlet oxygen decay in the solvent, k_q and k_r are the bimolecular rate constants for the decay of singlet oxygen by interaction with a substrate M, and k_p is the first order rate constant of phosphorescence decay.

The decay of singlet oxygen by reactions (4), (5) and (6) competes with the radiative process (7). The overall lifetime, τ, of singlet oxygen is determined by all radiative and non-radiative deactivation channels. In solution, the non-radiative pathways predominate the total deactivation process. In usual solvents, the phosphorescence process has a very small quantum yield and decays with a rate constant, k_p, in the range 0.2–3 s^{-1}. The k_p values are lower by many orders of magnitude than the k_r [M] and k_q [M] values of the nonradiative pathways of singlet oxygen decay.[13] Thus, the deactivation channel by phosphorescence (7) can be neglected. However, the deactivation of this phosphorescence is a very convenient method for monitoring the kinetics of singlet oxygen. Using this $^1O_2$ phosphorescence detection, we have measured the rate constants, k_d and k_o (= $k_r + k_q$), via the laser flash photolysis technique, whereas, using an HPLC analysis, we have determined the rate constant, k_r, of the endoperoxide MO_2 produced via the steady-state photolysis technique.

Flash Photolysis. In aerated solutions, after laser excitation, the production of $^1O_2$ is completed via reactions 2 and 3 within less than 2 μs. Following this, singlet oxygen decays via reactions 4, 5, and 6 according to (8):

$$-\frac{d[^1O_2]}{dt} = k_{obs}[^1O_2] = [k_d + (k_r + k_q)[M]][^1O_2] \quad (8)$$

Under our experimental conditions, the concentration of the substrate [M] is not modified during irradiation, as M is present in excess of the initial concentration of singlet oxygen $[^1O_2]_0$. Therefore, integration of (8) gives (9):

$$[^1O_2] = [^1O_2]_0 \exp-(k_{obs}t) = [^1O_2] \exp-[k_d + (k_r + k_q)[M]]t \quad (9)$$

The exponential decay of $^1O_2$ was monitored through its phosphorescence. The values of $k_{obs} = k_d + (k_r + k_q)[M]$ were derived from single-exponential fittings of the decay curves and the overall bimolecular rate constant for quenching of $^1O_2$, k_o = $(k_r + k_q)$, was obtained by a Stern–Volmer kinetic analysis which plots k_{obs} as a function of five different substrate concentrations, [M]. The value of k_o is the slope of the straight line obtained and k_d is its intercept with the Y-axis. This value of k_d was always very similar to that measured in the absence of M. Table 1 reports the experimental lifetimes of $^1O_2$ ($1/k_d$) in the different solvents, compared with literature values, and also gives the values of the overall rate constant k_o obtained for 1,4-dimethylnaphthalene (DMN) in the same solvents.

To study the particular case of water we used a water-soluble derivative of DMN, disodium 3,3'-(naphthalene-1,4-diyl)dipropionate (NDP), which is also soluble in other dipolar solvents such as methanol and formamide.

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Table 1. Singlet Oxygen Lifetimes in Different Solvents Characterized by Their Solvatochromic Parameters δ_H^{20} and π^{*21}

solvent	$1/k_d = \tau_\Delta$ (μs)		δ_H (M Pa^{0,5})	π^*	$k \times 10^{-4}$ (M^{-1} s^{-1})	
	a	b			k_r	$k_r + k_q$
acetic acid	25		21.4	0.64		9.3
acetone	51	50	19.6	0.71	1.6	7.0
acetonitrile-d_3	714	554	24.8	0.75		26.2
acetonitrile-h_3	67	62	24.8	0.75	5.4	26.7
anisole	9		20.2	0.73		9.6
benzene-d_6	637	626	18.6	0.59		3.5
benzene-h_6	30	30	18.6	0.59		2.2
carbon tetrachloride	1300	15 000	17.8	0.28		1.4
chloroform	120	260	19.0	0.58		7.3
cyclohexane	23	23	16.8	0.00		0.8
dichloromethane	97	86	19.8	0.82	2.9	7.6
ethanol	14	12	26.0	0.54	1.55	7.6
ethyl acetate	43		18.1	0.55	0.8	2.3
ethyl formate	36		19.3	0.61		9.7
formamide-d_3	212^c		39.3	0.97		356
formamide-h_3	11.5		39.3	0.97	124	324
Freon 113	820	16 000	14.8			0.9
hexafluorobenzene	1700	3900	16.6	0.33		0.9
hexafluoroisopropanol	57	53^{22}		0.65		86
hexane	30	31	15.0	−0.08		0.9
methanol-d_4	230	227	29.6	0.60	3.0	12.5
N-methylformamide	12		30.3	0.90	17.7	110
nitrobenzene	11		22.2	1.01		26.8
nitromethane	49		26.4	0.85	8.2	66.4
propylene carbonate	39		27.3	0.83		42.8
tetrahydrofuran	22	25	18.5	0.58	0.3	2.4
trifluoroethanol	31	24^{22}		0.73	23.8	90.0
water-d_2	65	67	51.9	1.09		

^{a} This work. ^{b} Mean values of lifetimes reported in ref 1b. Values of chemical (k_r) and overall $k_o = (k_r + k_q)$ rate constants for 1,4-dimethylnaphthalene in the same solvents. ^{c} The experimental value (157 μs) has been corrected to take into account the 2% residual protons of perdeuterated formamide.

Table 2. Chemical (k_r) and Overall Rate Constants ($k_r + k_q$) for Disodium 3,3'-(Naphthalene-1,4-diyl)dipropionate, NDP

rate constants for NDP	methanol	formamide	water
$10^{-4}k_r/M^{-1}$ s^{-1}	1.0		142
$10^{-4}(k_r + k_q)/M^{-1}$ s^{-1}	6.2	65	282

Table 3. Overall Quenching Rate Constants ($k_r + k_q$) for Various Cyclic 1,3-Dienes in Water-d_2 and Methanol-d_4

	NDP	MNP	MNEA	ADP	TMB	CHDDE	furan
$10^{-4}(k_r + k_q)/$ M^{-1}s^{-1} in D$_2$O	282	694	143	9760	5447	2578	4481
$10^{-4}(k_r + k_q)/$ M^{-1}s^{-1} in CD$_3$OD	6.2	9.1	2.4	997	799	1095	1364

The experimental results reported in Table 2, show that the reactivity of the naphthalenic substrate is, by far, the largest in water. It can be concluded that the accelerating effect does not arise from the sodium carboxylate groups since it is also observed with six other hydrophilic 1,3-dienes (Table 3).

Steady-State Photolysis. Solutions containing the substrate M and a photosensitizer S (Rose Bengal) were irradiated with a continuous light source. The disappearance of the substrate M and the formation of the peroxide MO$_2$ were monitored using UV spectroscopy and HPLC analysis. Under stationary conditions, processes 2−6 lead to eq 10 for the rate of M disappearance, where v_f is the rate of production of singlet oxygen.[12]

$$-\frac{d[M]}{dt} = v_f \frac{k_r[M]}{[k_d + (k_r + k_q)[M]]} \qquad (10)$$

In order to measure v_f, we used highly reactive substrates capable of trapping the total amount of $^1O_2$ produced. A

requirement for the complete scavenging of $^1O_2$ is that k_r [M] $\gg k_d + k_q$[M], i.e., the chemical quenching of $^1O_2$, is the predominant process in the scheme of deactivation of $^1O_2$ (reactions 4−6). Moreover, the trap M must be transparent to the incident light in order to avoid any autophotooxidation. Under these conditions, the rate of M disappearance, $-d[M]/dt$, is equal to the rate of $^1O_2$ formation, v_f. All these conditions are fulfilled with α-terpinene 5 $\times$ 10^{-2} M in organic solvents and with CHDDE 2 $\times$ 10^{-2} M in D$_2$O.[1,10] On the other hand, when the substrate M has a low reactivity toward $^1O_2$, deactivation by solvent (reaction 4) becomes the main pathway for the disappearance of $^1O_2$ ($k_d \gg (k_r + k_q)$[M]) and expression 10 is simplified into expression 11. Integration of this equation between t_0 and t gives expression 12.

$$-\frac{d[M]}{dt} = v_f \frac{k_r}{k_d}[M] \qquad (11)$$

$$\ln [M]_t = \ln [M]_0 - v_f \frac{k_r}{k_d}t \qquad (12)$$

Plotting $\ln [M]_t$ versus irradiation time gives a straight line, the slope of which is $v_f(k_r/k_d)$. The chemical quenching rate constant, k_r, calculated from known values of k_d and experimental determination of v_f, is reported in Table 1. To check that $^1O_2$ cycloaddition was the sole chemical reaction involved, we used the thermoreversibility properties of the naphthalenic endoperoxides (reaction 1). Thus, we controlled by HPLC, the complete regeneration of the starting compound, after warming the irradiated solution at 50 °C for 1 h.

Discussion

1. Vibrational Deactivation of $^1O_2$. Deactivation by Solvents. Our experimental values for the lifetime of $^1O_2$ in solvents agree with literature data (Table 1), except for chloroform and perhalogenated solvents (carbon tetrachloride, Freon 113, hexafluorobenzene). These solvents exhibit a much shorter lifetime than the published values despite the fact that we used samples of the purest quality commercialy available. In the case of chloroform, this discrepancy probably arises from the small amount of ethanol used by the supplier to stabilize this solvent. For perhalogenated solvents, it is known that the real lifetime can be measured only when special requirements are fulfilled, specifically low energy of irradiation and low concentrations of photosensitizer and oxygen.[13] Regardless of these discrepancies, the determination of the overall rate constant, k_o (= $k_r + k_q$), by flash photolysis is not influenced by the lifetime value of the solvent.

Table 1 also presents unreported $^1O_2$ lifetimes for 10 unusual solvents. The most remarkable of these are amides which exhibit good solubilizing properties for both organic and ionic substrates although they are scarcely used as solvents for photooxidation. Disinterest in amides is probably due to the possible quenching of $^1O_2$ by the group −NR$_2$ through a reversible electron transfer similar to that observed for amines.[14b] Surprisingly, the lifetime of $^1O_2$ in amides is relatively long (12 μs) and even very long in perdeuterated formamide (212 μs). This observation can be explained by considering that the

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Table 4. Second-Order Rate Constants of $^1O_2$ Deactivation by Naphthalenes-h_8 and -d_8 in Benzene-d_6 Solutions (the Value Given for $C_{10}D_8$ Is Corrected To Account for the 2% Residual Protons)

quencher	k_q (M^{-1} s^{-1})	quencher	k_q (M^{-1} s^{-1})
$C_{10}H_8$	3300	$C_{10}D_8$	278
CH_{napht}	413	CD_{napht}	35
CH_{benz}	470	CD_{benz}	23

free electron pair of nitrogen is no longer available for electron transfer since it is delocalized on the carbonyl group.

Deactivation by the Oscillators of 1,4-Dimethylnaphthalene. The vibrational deactivation of $^1O_2$ by a nonreactive molecule may be explained by an energy transfer from $^1O_2$ to the sole terminal bonds of the molecule.[13,14] Thus, with benzene, only C—H bonds contribute to the deactivation process but C—C bonds and π electrons of the aromatic core have no effect. This is not true for anthracene which reacts with $^1O_2$ on the electron-rich carbons 9, 10 through [4 + 2]-cycloaddition to give an endoperoxide.[17] The behavior of the intermediate aromatic compound naphthalene was less clear, and so we determined the rate constants for $^1O_2$ deactivation by naphthalenes-h_8 and -d_8 in order to examine whether a chemical reaction occurs. We have observed that naphthalenes-h_8 and -d_8 are not photooxidized as their UV spectra remain identical when irradiated under the conditions used to oxidize DMN. Thus, we can conclude that k_r is negligible for naphthalene and that the overall rate constant, k_o, of $^1O_2$ deactivation measured by flash photolysis is equal to k_q. This rate constant k_q was found to be 3300 M^{-1} s^{-1} for naphthalene-h_8 and 344 M^{-1} s^{-1} for naphthalene-d_8. Using these values we have calculated the incremental rate constants for the oscillators (C—H)$_{napht}$ and (C—D)$_{napht}$ (Table 4).[15,16]

The k_q values presented in Table 4 for the the C—H bonds of naphthalene-h_8 and of benzene-h_6 were found to be very similar. For deuterated molecules, the k_q values for the C—D bonds are both very low, but differ significantly. Their difference may arise either from impurities of the commercial sample of $C_{10}D_8$ or from a lower ratio of deuteriation than the value indicated by the supplier (98%). This similarity between the quenching rate constants of terminal bonds of benzene and naphthalene confirms the absence of a chemical reaction channel during the photolysis of unsubstituted naphthalene. We estimate the vibrational rate constant of $^1O_2$ deactivation by the six CH_{napht} bonds and the six CH_{aliph} bonds of 1,4-dimethylnaphthalene to be $k_{DMN}^{vib} = 6 \times 413 + 6 \times 390 = 0.48 \times 10^4$ M^{-1} s^{-1}.

This rate constant should be independent from the solvent used. It contributes to the overall quenching rate constant, k_o ($= k_r + k_q$), determined by flash photolysis as its lower limiting value.

2. Interaction of 1,4-Dimethylnaphthalene with $^1O_2$. Comparison of Chemical and Physical Quenching. DMN quenches $^1O_2$ both chemically and physically. We determined the corresponding rate constants, k_r and k_q, with two complementary techniques. Steady state photolysis associated with HPLC analysis of the reacting medium gave us the chemical rate constant, k_r, and flash photolysis coupled with time-resolved detection of $^1O_2$ phosphorescence led us to the overall quenching rate constant, k_o (Table 1).

The overall quenching rate constant, k_o, appears to be always much higher than the vibrational rate constant calculated above (0.48 × 10^4 M^{-1} s^{-1}). Moreover, physical quenching (k_q) is always prevalent over chemical quenching (k_r). Thus, $^1O_2$ interacts mainly with DMN by a physical quenching that is

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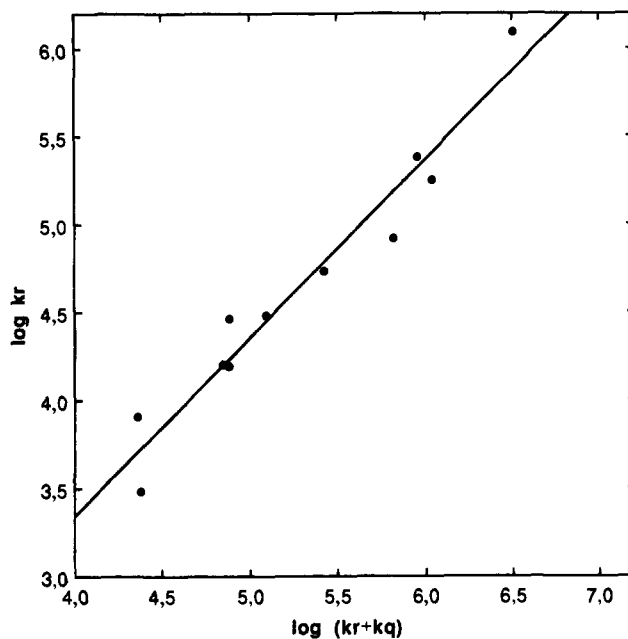
Figure 1. Comparison of the chemical quenching rate constants k_r with the overall quenching rate constants k_o ($= k_r + k_q$) in a double-logarithmic plot.

different from a simple energy transfer to vibrational levels of DMN. Since the graduation of these rate constants covers several orders of magnitude, comparison of k_r and k_o can reasonably be examined only on logarithmic scales (Figure 1).

The experimental dots shown in Figure 1 are fairly aligned (r = correlation coefficient = 0.94), and the slope of the best fitted straight line is very close to 1 (= 0.98). This result suggests the existence of a common intermediate for both chemical and physical quenching. Intercept led to a value of 0.29 for the ratio k_r /($k_r + k_q$). This value represents the maximum proportion of $^1O_2$ able to react chemically with DMN when the substrate concentration is high enough to make the deactivation by solvent negligible.

Solvent Effect on the Quenching of $^1O_2$ by 1,4-Dimethylnaphthalene. Since the rate constants, k_r and k_o, change in the same way when the solvent is modified, we preferred to focus our attention on the overall quenching rate constant, k_o, which may be more easily and more accurately measured than the chemical rate constant k_r. The results reported in Table 1 show that, in nonpolar solvents such as alkanes, the overall rate constant is very small, whereas in highly dipolar solvents such as formamide it increases up to 400 times. This strong solvent effect is in contrast with earlier studies[2,3] which have been carried out for a limited number of solvents. In our study, the diene is much less reactive, the range of solvents examined is much wider, and the rate constants span over almost 3 orders of magnitude.

In an attempt to rationalize the observed solvent effect, we used the semiempirical approach of Taft and Kamlet *et al.*[21a,b] These authors characterized an extensive range of solvents with four main descriptors: the π^* scale which accounts for the dipolarities and polarizabilities of solvents, the α scale which is related to their hydrogen bond donor ability, the β scale which indicates their hydrogen bond acceptor ability, and the Hildebrand parameter, δ_H, which is the square root of the solvent cohesive energy density.[19] In other words, this last parameter,

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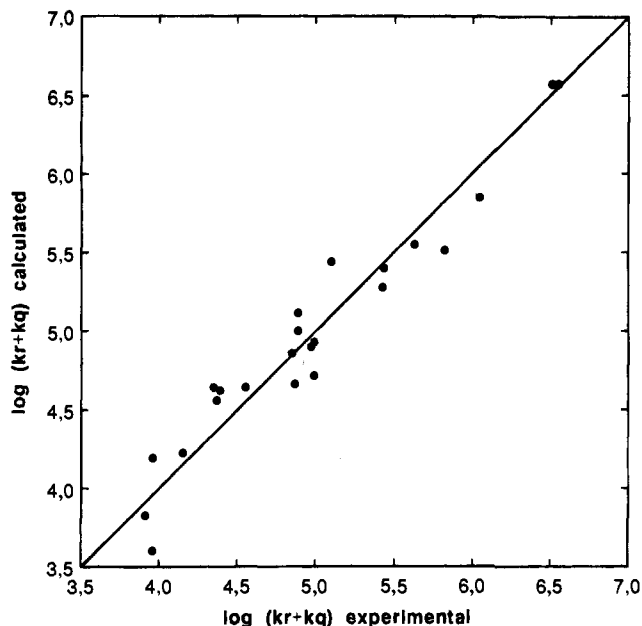
Figure 2. Double-logarithmic plot of calculated vs experimental overall constants $(k_r + k_q)$ in various solvents.
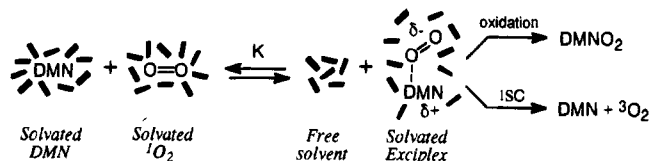

Figure 3. Mechanism of the physical and chemical quenching of singlet oxygen by 1,4-dimethylnaphthalene.

Table 5. Ratio of the Overall Rate Constants k_o ($= k_r + k_q$) of Various Water-Soluble Cyclic 1,3-Dienes Measured in Water-d_2 and Methanol-d_4

substrate	$\dfrac{(k_r + k_q) \text{ in } D_2O}{(k_r + k_q) \text{ in } CD_3OD}$	substrate	$\dfrac{(k_r + k_q) \text{ in } D_2O}{(k_r + k_q) \text{ in } CD_3OD}$
NDP	45	TMB	6.8
MNP	76	CHDDE	2.4
MNEA	60	furan	3.3
ADP	10		

δ_H, is a measure of the solvent–solvent interactions that are interrupted in creating a solute cavity in the solvent.[18]

According to the procedure of Taft and Kamlet *et al.*,[21a,b] the logarithm of the rate constant of a given reaction in a series of solvents may be expressed by a simple relation including these four parameters:

$$\log k = \text{constant} + h\delta_H + s\pi^* + a\alpha + b\beta \qquad (13)$$

A multilinear least-squares fit of $\log (k_r + k_q)$ versus these parameters shows a fair correlation with δ_H and π^*, but not with α and β:

$$\log (k_r + k_q) = 2.62 + 0.07\delta_H + 1.18\pi^* \qquad (14)$$

This satisfactory agreement ($r = 0.96$) is shown graphically in Figure 2 by plotting $\log (k_r + k_q)$ calculated from eq 14 versus the experimental logarithm of the overall rate constant, k_o. This agreement indicates that the solvent stiffness or "structuredness", expressed by δ_H, and the solvent dipolarity, expressed by π^*, play a prevalent role in the singlet oxygen [4 + 2]-cycloadditions.

This multiparameter eq 14 is an improvement when compared to correlations established with a single parameter. It is now considered that the simple concept of polarity as a universal solvent characteristic is an inadequate simplification. In the reaction reported here, $\log (k_r + k_q)$ shows a less satisfactory correlation with any of the polarity indices that our two parameters approach: $r = 0.81$ for the dipolarity/polarizability parameter π^*; $r = 0.78$ for the Kirkwood function, $(\epsilon - 1)/(2\epsilon + 1)$; $r = 0.78$ for the Dimroth and Reichardt polarity index, E_T^N.

Taking into account both solvent parameters π^* and δ_H, it is possible to describe the solvent effect on the different steps of the reaction of $^1O_2$ with DMN (Figure 3).

The first step involves the reversible formation of an exciplex. The intermediacy of an exciplex is supported by the zero or negative activation enthalpies observed for various $^1O_2$ reactions.[14b] This exciplex exhibits a charge transfer character due to the strong electron attraction by singlet oxygen and is characterized by an equilibrium constant, K. Since the correlation of $\log (k_r + k_q)$ with the Hildebrand parameter is positive, the reactants form a more compact activated complex. Thus, the formation of the exciplex is accompanied by the release of free solvent molecules.[18]

In a second step, the solvated exciplex yields either a DMN endoperoxide *via* a pathway characterized by a rate constant k_r or an intact DMN and an oxygen molecule in the ground state *via* a pathway characterized by a rate constant k_q, these rate constants being approximately related by the ratio $k_r/k_q = 0.4$ calculated from the data of Figure 1.

3. Reactivity of 1,3-Dienes in Water. Influence of Hydrophilic Groups. The index of dipolarity/polarizability π^* of water (1.09) and formamide (0.97) are close to each other. On the contrary, Hildebrand's parameter, δ_H, is much higher for water (51.9 MPa$^{0.5}$) than for formamide (39.3 MPa$^{0.5}$) or any other organic solvent.[20] The correlation established with DMN suggests that an even higher increase in the rate constant should be observed in water than in formamide. The poor solubility of DMN in water required the use of a water-soluble derivative, disodium 3,3'-(naphthalene-1,4-diyl)dipropionate, NDP, to investigate this solvent. In a previous study,[4] we showed that the corresponding chemical quenching rate constant k_r is 142 times higher in water than in methanol. We have confirmed this solvent effect by measuring the overall rate constants k_o ($= k_r + k_q$) of NDP in water, methanol, and formamide (Tables 2 and 5). As expected, this rate constant k_o is 45 times higher in D_2O than in CD_3OD and 4 times higher in D_2O than in formamide-d_3.

To check that this variation in the overall rate constant is really due to the solvent and not to a stabilization of the exciplex by the carboxylate functions $-COO^-$ Na^+, we determined k_o values for two other water-soluble naphthalenic compounds. The first, sodium (4-methyl-1-naphthyl)-3-propionate, MNP, has only one carboxylate function, and the second, [2-(4-methyl-1-naphthyl)ethyl]trimethylammonium chloride, MNEA, has a quaternary ammonium function $-NR_3^+$ Cl^- as the water-solubilizing group. For these substrates, the overall rate constant is, respectively, 76 and 60 times higher in water than in methanol (Table 5), confirming that the solvent effect results from the solvation of the exciplex and not from the carboxylate functions of NDP.

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Influence of the Diene Structure. Singlet oxygen can react through [4 + 2]-cycloaddition with several types of dienes: cyclic dienes such as cyclohexadienes, aromatic dienes (electron-rich benzenic compounds, naphthalenes, anthracenes), and heterocyclic dienes such as furan. Thus, the reactivity toward $^1O_2$ of four typical water-soluble dienes of different structures, ADP, TMB, CHDDE, and furan, has been investigated in D_2O and CD_3OD. With all four substrates, the overall rate constant, k_r, is much higher in water than in methanol but the solvent effect is less pronounced than with naphthalenic compounds (Table 5).

This different behavior may result partly from the higher intrinsic reactivity of these dienes. Effectively, with highly reactive substrates, the energy of activation is approaching zero and one expects the solvent effect to be much weaker than with poorly reactive compounds such as naphthalenic derivatives.

However, this explanation does not hold for the anthracene derivative, ADP, which exhibits a more pronounced solvent effect than CHDDE and furan (Table 5) although its intrinsic reactivity is the highest (Table 3). This can be rationalized considering that these dienes are both smaller, more polar, and more hydrophilic than ADP, and thus, the solvation energy of these substrates by polar solvents is already important. Therefore, the gain in energy arising from the solvation of the slightly more polar exciplex is rather small, and the solvent effect is limited. On the other hand, the large anthracenic core of ADP is very hydrophobic and the stabilization of the polar exciplex is comparatively high resulting in a notable expected solvent effect. In agreement with this proposal, 1,3-diphenylisobenzofuran, which is much bigger and more hydrophobic than furan, has been reported to be 8.5 times more reactive in water than in methanol although its intrinsic reactivity is one of the highest known.[12]

Conclusion

In contrast to previous investigations performed using a limited number of solvents,[2,3] the rate constant of singlet oxygen [4 + 2]-cycloadditions with 1,3-dienes was found to be herein highly solvent-dependent *via* experiments conducted using 28 solvents. Our results indicate a shift toward the formation of an exciplex leading to a cyclooxidized product (Figure 3) by

an increase in (i) the Hildebrand solubility parameter δ_H, (ii) the dipolarity-polarizability parameter π^* of the solvent, and (iii) the solvophobicity of the diene. The accelerating effect, which we have observed in highly "structured" solvents such as formamide and water, may have useful consequences in organic synthesis when faintly reactive substrates have to be oxidized by singlet oxygen.[6] This process must be related to the enhanced reaction rates observed in aqueous solutions for Diels–Alder [4 + 2]-cycloadditions by Rideout and Breslow.[23] In both singlet oxygen and Diels-Alder cycloadditions, hydrophobic interactions between the reactants are involved and lead to higher reaction rates for more hydrophobic dienes.

In the past, the lack of appreciable solvent effects and the topographic similarity of [4 + 2] singlet oxidations and Diels–Alder reactions have induced many workers to describe the former as concerted cycloadditions,[2,3] assumed to proceed *via* isopolar activated complexes. In fact, our results on the singlet oxygen [4 + 2]-cycloadditions are consistent with a two-stage mechanism implying as a first step an equilibrium producing an exciplex with charge transfer character (Figure 3) as proposed *via* theoretical considerations by Yamaguchi.[24]

Supporting Information Available: Details about the laser-flash and the steady-state photolysis systems. Discussion about the vibrational deactivation of $^1O_2$ by the oscillators of solvents (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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