Is Water the Best or the Worst Solvent for [2 + 4] Cycloadditions of Singlet Oxygen to Aromatic Compounds?

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An accelerating effect of water, greater than two orders of magnitude, is observed for the photo-oxygenation of disodium 3,3′-(1,4-naphthylidene)dipropionate at variance with the current assumption on the constancy of the rate constant of $^1O_2$ [2 + 4] cycloadditions in various solvents.

Only four equations, (1)—(4), are necessary to account for the kinetics of peroxidation of an aromatic compound (A) in the presence of a source of singlet oxygen, $^1O_2$ ($^1\Delta_g$). The rate of peroxidation of (A) can be expressed as a function of the rate of $^1O_2$ formation ($d[^1O_2]_f/dt$) [equation (5)]. Thus, with a given rate of $^1O_2$ formation, the peroxidation of (A) will proceed more rapidly with higher values of k_r and τ ($= 1/k_d$). Until now, kinetic studies of $^1O_2$ [2 + 4] cycloadditions support the constancy of k_r for a given substrate in a wide range of solvents;[1] on the other hand, τ varies within three orders of magnitude from H_2O (4.2 μs)[2] to C_6F_6 (3900 μs).[3] Hence, water seems to be the worst solvent for the peroxidation of conjugated dienes *via* $^1O_2$. We now report that, in contrast, a large increase of k_r in water compensates for the short $^1O_2$ lifetime in this medium.

$$\text{Source of singlet oxygen} \longrightarrow {}^1O_2 \qquad (1)$$

$$(A) + {}^1O_2 \xrightarrow{k_r} (A)O_2 \qquad (2)$$

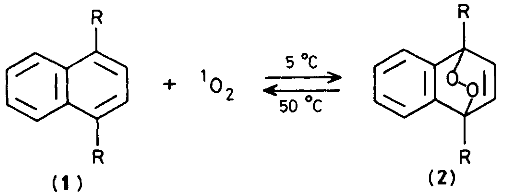
$$(A) + {}^1O_2 \xrightarrow{k_q} (A) + {}^3O_2 \qquad (3)$$

$$^1O_2 \xrightarrow{k_d} {}^3O_2 \qquad (4)$$

$$-\frac{d[(A)]}{dt} = \frac{d[^1O_2]_f}{dt}\left\{\frac{k_r[(A)]}{k_d + (k_r + k_q)[(A)]}\right\} \qquad (5)$$

This result was obtained by studying the sensitized photo-oxygenation of the hydrophilic derivative (**1a**) of 1,4-dimethylnaphthalene[4] in various mixtures of water and methanol. This trap is suitable for this study because it is highly soluble in both solvents and its low reactivity towards $^1O_2$ enables us to obtain evidence for the accelerating effect of water. Moreover, the lack of side oxidation products is checked easily, as the endoperoxide (**2a**) regenerates (**1a**) quantitatively on thermolysis (reaction 6). Methanol was chosen as the organic solvent because it is similar to water both in its chemical behaviour and the $^1O_2$ lifetime (10.4 μs in methanol).[2]

Solutions of (**1a**) {2.5×10^{-3} M; at this concentration, $k_d \gg (k_r + k_q)$ [(A)]} and Rose Bengal (3×10^{-5} M), in water–methanol mixtures, were irradiated at 5 °C for various times in order to obtain 20% disappearance of (**1a**). The solutions were then heated for 1 h at 50 °C to check for the quantitative regeneration of (**1a**). The results in Figure 1 show that the photo-oxygenation of (**1a**) appears to be 28 times faster in H_2O than in MeOH, although the $^1O_2$ lifetime is 2.5 times longer in the latter solvent. Moreover, even a low proportion of water accelerates greatly the peroxidation



(1) (2) (6)

a; R = $CH_2CH_2CO_2Na$
b; R = Me

Table 1. Rate constants (k_r ± 10%/dm^3 mol^{-1} s^{-1}) for photo-oxygenation of (**1a**) and (**1b**) in various solvents.[a]

Solvent	H_2O	MeOH–H_2O (80 : 20 v/v)	MeOH	EtOH–H_2O (86 : 14 v/v)	Pr^{n}OH–H_2O (73 : 27 v/v)
ε[b]	80.4	43.5	32.3	32.3	32.3
$\tau/\mu s$	4.2	8.0	10.4	11.3	9.3
$10^{-4} k_r$, (**1a**)	142	5.8	1.0	6.0	13.4
$10^{-4} k_r$, (**1b**)	—	37.1	4.2 (1.2[c])	12.7	23.5

[a] For mixed solvents, k_r was inferred from known or calculated values of k_d (ref. 2) and from determination of d[$^1O_2$]$_f$/dt with α-terpinene which traps all $^1O_2$ generated by photosensitization (k_r [(A)] $\gg$ k_d + k_q [(A)]). In water, a 'static' competition technique was adopted for the estimation of k_d/k_r using potassium rubrene-2,3,8,9-tetracarboxylate (J. M. Aubry, J. Rigaudy, and Nguyen Kim Cuong, *Photochem. Photobiol.*, 1981, **33**, 155) as a reference acceptor. A solution of this trap in sealed air-saturated water, was irradiated, with and without the substituted naphthalene, until oxygen consumption was complete (Cf. B. Stevens, J. A. Ors, and C. N. Christy, *J. Phys. Chem.*, 1981, **85**, 210). [b] G. Akerlöf, *J. Am. Chem. Soc.*, 1932, **54**, 4125. [c] From B. Stevens, S. R. Perez, and J. A. Ors, *J. Am. Chem. Soc.*, 1974, **96**, 6846.

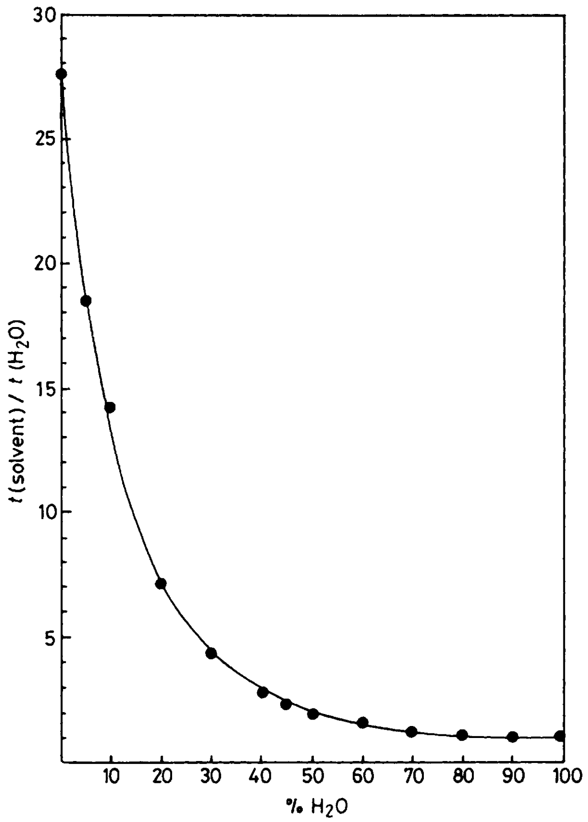


Figure 1. Variation of irradiation time (t) with the proportion (v/v) of water in the water–methanol mixture.

process; this result has already been used for preparative purposes.[4] However, k_r cannot be inferred directly from these results as d[$^1O_2$]$_f$/dt (equation 5) depends slightly on the solvent.[5] Hence k_r values were measured precisely for three compositions (Table 1).

The accelerating effect of water on k_r for (**1a**), relative to methanol, reaches a value of 142 (Table 1); to rule out the possible influence of carboxylic groups, it was checked that H_2O also enhances the photo-oxygenation rate of the parent compound (**1b**). The low solubility of 1,4-dimethylnaphthalene in H_2O compelled us to use the mixed solvent MeOH–H_2O (80 : 20) instead of pure water, but nevertheless a nine-fold increase in k_r for (**1b**) was observed for these solvents compared with only a six-fold increase in the case of (**1a**) (Table 1). Such an important influence of H_2O points to a significant modification of the peroxidation mechanism. However, this effect cannot be explained by the involvement of a non-singlet oxygen process as the photo-oxygenation of (**1a**) proceeds 14 ± 1 times faster in D_2O than in H_2O as expected from the known deuterium effect on $^1O_2$ lifetime [$\tau(D_2O)/\tau(H_2O)$ = 13],[2] making the reasonable assumptions that k_r and d[$^1O_2$]/dt are similar in D_2O and H_2O.

Recent work of Gollnick indicates the importance of the dielectric constant ε on the rate constant, k_r, for [2 + 2] additions and ene reactions of $^1O_2$.[6] This work suggests that the high polarity of water (ε 80) could account for the acceleration observed, although such an effect was not observed for [2 + 4] cycloadditions of $^1O_2$; however the solvents examined in this study had much lower polarities ($\varepsilon \leqslant$ 36.2) than water. Thus rate constants of (**1a**) and (**1b**) were measured in three solvents of the same dielectric constant (32.3); the results are summarized in Table 1. They show that k_r increases with increase in proportion of water and that the average dielectric constant is not a convenient parameter to predict the value of k_r. Thus, water acts in a more specific way, although the high polarity of H_2O is probably involved in the process. It is noteworthy that an enhancing effect of water was also observed in [2 + 4] cycloadditions (Diels–Alder reactions) of ground state molecules.[7] We tentatively explain the action of water assuming the reversible formation of an exciplex between (A) and $^1O_2$ (A · · · $^1O_2$).[8] Solvation by water molecules would either increase the electrophilicity of $^1O_2$ or stabilize the transient species and makes its evolution into endoperoxide more likely.

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