# 11. The Effect of Solvent on Competing Hydroperoxide and Dioxetane Formation on Photo-Sensitized Oxygenation of Olefins

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## *Summary*

The rates of the competitive photo-sensitized oxygenation of 2-isobutylidene-adamantane (**1**) and 2-propylidene-adamantane (**2**) with 1,1-di-*t*-butyl-2-methoxy-ethane (**3**) in various solvents were determined. The rates for **1** and **2** were independent of solvent, whereas that for **3** varied markedly with solvent polarity. Compounds **1** and **2** gave only hydroperoxides while **3** gave dioxetane. These results are interpreted in terms of two competing processes involving little and much charge separation leading to hydroperoxide and dioxetane, respectively.

Although information is sparse, it appears that the nature of the solvent has a negligible effect on the rates of photo-oxygenation of those olefins which give exclusively either allylic hydroperoxides [1] or 1,2-dioxetane [2]. In contrast, the

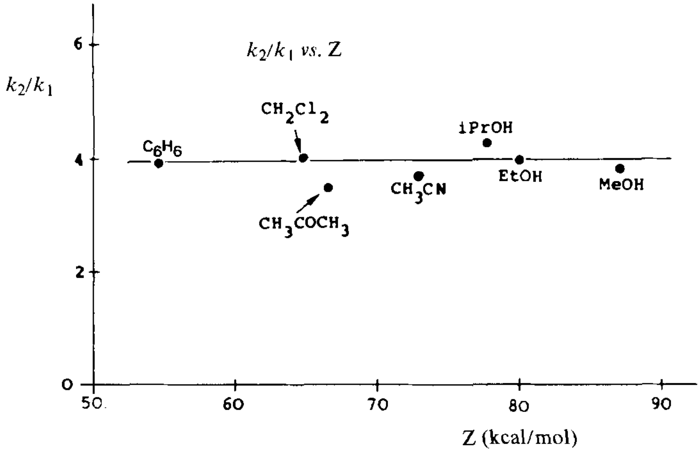

Fig. 1. *Rates of photo-oxygenation of olefins* **1** *and* **2** *in various solvents.*
Olefin concentrations: $1.3 \times 10^{-1}$M, except 4: ($6.5 \times 10^{-2}$M). Sensitizers: *meso*-tetraphenylporphin ($3.3 \times 10^{-3}$M); for solvent 1, and methylene blue ($5.3 \times 10^{-3}$M); for solvents 2, 3, 5, 6, and 7, and ($2.7 \times 10^{-3}$M) for 4.

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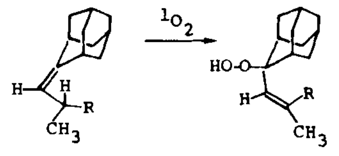
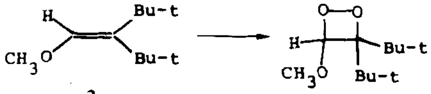
reactions of olefins, which are structurally capable of giving *both* hydroperoxide and dioxetane, are acutely sensitive to solvent. Notable examples are furnished by 2,5-dimethyl-2,4-hexadiene [3], dihydropyran [4], methyl-2,3-dihydro-$\gamma$-pyran [5], methoxymethylidenecyclohexane [6], 1-ethylthio-2-ethyl-1-hexene, and its 1-ethoxy analogue [7]. In all these cases products originating from an ene-type reaction and a competing [2+2]-cycloaddition are obtained. The perennial mechanistic question is to know whether the two reaction courses stem from a common intermediate or arise from two different transition states.

In an attempt to provide an answer, we now report on the photo-oxygenation[1]) of 2-isobutylidene-adamantane (**1**), 2-propylidene-adamantane (**2**) and 1,1-di-*t*-butyl-2-methoxyethene (**3**)[2]). Only hydroperoxides (**4** and **5**) were formed by **1** and **2**, while **3** gave solely the dioxetane **6**[3-5]). Furthermore, the three olefins exhibit similar reactivities towards singlet oxygen, which makes them particularly suitable for competitive rate studies[6]).

**1** R=$CH_3$
**2** R=H



**4** R=$CH_3$
**5** R=H



**3** **6**

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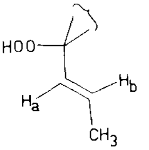
[1]) Photo-oxygenation was performed according to our procedure [8].

[2]) The dioxetane **6** cleaved cleanly giving di-*t*-butyl ketone. No addition products were detected from **3** in methanol.

[3]) Compounds **4** and **5** gave characteristic spectral data. **4**: IR. (NaCl, $cm^{-1}$): 3420*s* (br., OOH); 1663*m* (C=C). - NMR. ($CDCl_3$): 7.06 (*s*, OOH); 5.3 (*sept*, $J = 1.5$ Hz, H); 1.90 (*d*, $J = 1.5$ Hz, $CH_3$) and 1.84 (*d*, $J = 1.5$ Hz, $CH_3$).



**5**: IR. (NaCl): 3430*s* (br., OOH); 1640 (C=C). - NMR. ($CDCl_3$): 7.09 (*s*, OOH); 5.89 (*d*×*qa*, $J(H_b,H_a) = 16$ Hz, $J(H_b, CH_3) = 6.5$ Hz, $H_b$); 5.46 (*d*×*qa*, $J(H_a,H_b) = 16$ Hz, $J(H_a,CH_3) = 1.5$ Hz, $H_a$); 1.82 (*d*×*d*, $J(CH_3,H_b) = 6.5$ Hz, $J(CH_3,H_a) = 1.5$ Hz, $CH_3$).

[4]) Dioxetane **6** was isolated as a pale yellow oil by florisil column chromatography and was a reasonably stable compound having a half-life in $CDCl_3$ of 57.5 h at 29° - NMR. ($CDCl_3$): 6.02 (*s*, 1 H); 3.45 (*s*, 3 H); 1.30 (*s*, 9 H); 1.23 (*s*, 9 H).

[5]) Steric hindrance in **2** favouring the conformation shown accounts for the *E* configuration of **5** (*cf.* [9]).

[6]) The intermediacy of singlet oxygen was confirmed by quenching experiments with DABCO (1,4-diazabicyclo[2.2.2]octane), a *bona fide* quencher of singlet oxygen. The addition of DABCO (52 mM) to the reaction mixture of **1/3** and **2/3** in methanol (olefin concentrations of 130 mM) decreased the observed *pseudo*-first order rate constants ($k_1$ and $k_3$) and ($k_2$ and $k_3$) by factors of 8.4 and 9.1, and 4.9 and 5.2, respectively. However, the ratios $k_3/k_1 = 2.2$ and $k_3/k_2 = 0.54$ remained unchanged. (*Cf.* absence of DABCO, $k_3/k_1 = 2.4$ and $k_3/k_2 = 0.57$).

Accordingly, solutions of pairs of olefins, *e.g.* **1/2**, **1/3** and **2/3** containing sensitizer were irradiated with a 500 W sodium lamp under oxygen at 10°6)). Samples of the reaction mixture were withdrawn at intervals and analyzed by gas-liquid chromatography. The concentrations of the olefins were determined from the ratios of their peak areas to that of dodecane taken as internal standard, thereby giving the *pseudo*-first order rate ratios for each pair of olefins, *viz.* $k_2/k_1$, $k_3/k_1$ and $k_3/k_2$.

These rate ratios now need to be plotted against a reliable index of solvent polarity [10]. Good straight lines were obtained with several empirical parameters of solvent polarity obtained by spectroscopic methods, as exemplified by the Z [11], $E_T$ [12], $\chi_R$ or $\chi_B$ [13] values. For the hydroperoxide-producing reactions it is seen that the plot $k_2/k_1$ *vs.* Z for seven solvents is a straight line of zero slope *(Fig. 1)*. Consequently, solvent effects are either inoperative or affect the two reactions equally. When hydroperoxidation is allowed to compete with dioxetane formation, marked solvent discrimination is observed. The plots of $k_3/k_1$ and $k_3/k_2$ against Z (*Fig. 2* and *3*) give straight lines of pronounced slope. In both cases, passing from benzene to methanol favours dioxetane formation by a four-fold enhancement of rate. The relative solvent effects on dioxetane and hydroperoxide formation are therefore expressed by the linear relationship: $k_3/k_1 = (-2.85 \pm 0.57) + (6.10 \pm 0.80) \times 10^{-2}$ Z; $k_3/k_2 = (-0.70 \pm 0.15) + (1.48 \pm 0.21) \times 10^{-2}$ Z.

If the second equation is multiplied by $k_2/k_1$ ($\simeq 4.0$), then the values obtained are very nearly those found for the first equation, namely $k_3/k_2 \times k_2/k_1 = (-2.8 \pm 0.6) + (5.9 \pm 0.8) \times 10^{-2}$ Z. This means that the relative influence of solvents on the photo-oxygenation of **3** compared to **1** is the same as that experienced for **2**.

These findings permit the following conclusions: *(i)* There is little or no charge separation in the transition state for the hydroperoxidation; *(ii)* The transition state leading to 1,2-dioxetane is much more polar, possibly implicating perepoxide7)) or zwitterionic peroxide [15] intermediates.

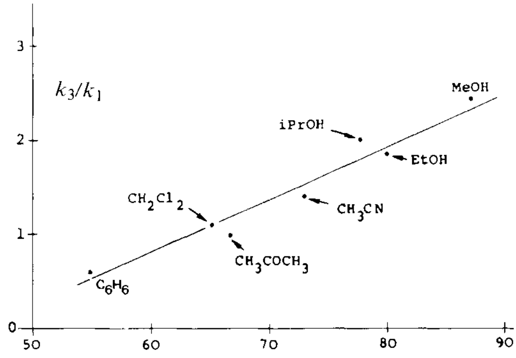


Fig. 2. $k_3/k_1$ vs. *Z in various solvents.*

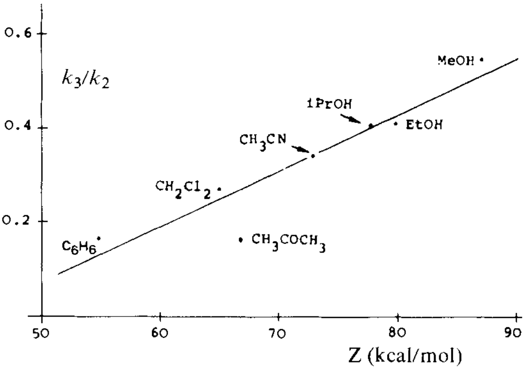


Fig. 3. $k_3/k_2$ vs. *Z in various solvents.*

Olefin concentrations: $1.3 \times 10^{-1}$M except 4: ($6.5 \times 10^{-2}$M). Sensitizer data: same as in *Fig. 1.*

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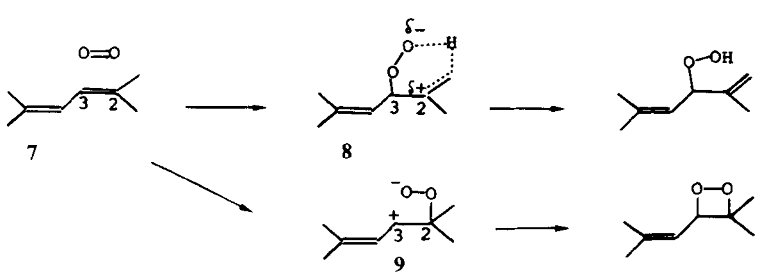
7) According to calculations, a regular perepoxide would have a dipole-moment of 5.6 D and a zwitterionic peroxide a moment of 10.1 D [14].



These findings may be extrapolated to those substrates which give both hydroperoxide and dioxetanes or products deriving therefrom, *e.g.* 2,5-dimethylhexadiene (**7**). Two distinct processes may be envisaged depending on the solvent. In solvents like benzene the preferred transition state **8** arises from primary attack by oxygen at C(3) leading to a feebly polarized 'ene'-type process. In polar, protic solvent, *e.g.* methanol, the preferred transition state derives from initial attack at C(2) giving a zwitterionic peroxide **9** in which the cationic center is allylically stabilized[8]).

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[8]) For a general discussion of the possibilities of one-step *vs.* two-step processes with **7** see [16].