

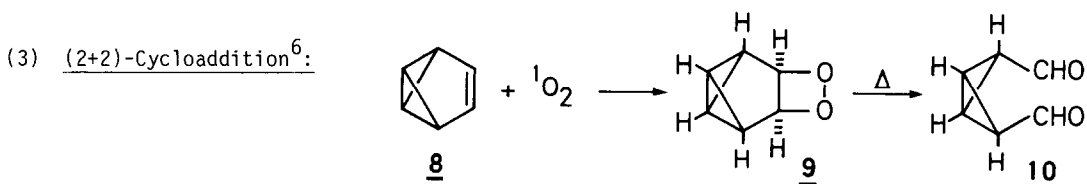
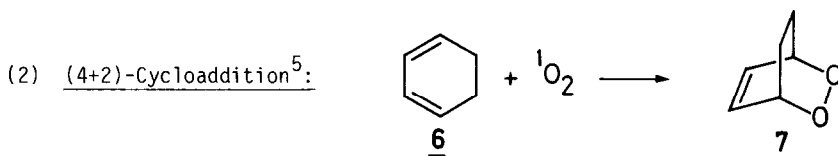
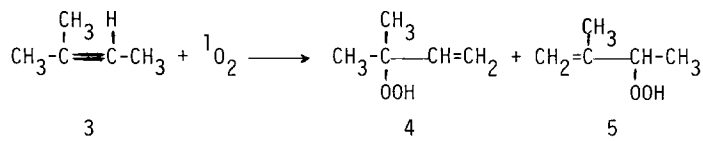
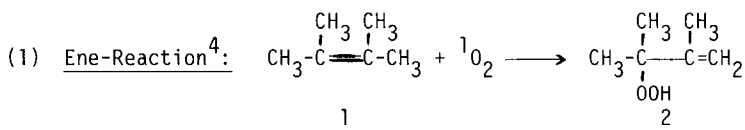
SOLVENT DEPENDENCE OF SINGLET OXYGEN / SUBSTRATE INTERACTIONS
 IN ENE-REACTIONS, (4+2)- AND (2+2)-CYCLOADDITION REACTIONS

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Summary: Product formation of singlet oxygen reactions with simple olefins occurring as ene-reactions, (4+2)- and (2+2)-cycloaddition reactions is independent on solvent polarity. Thus, 2,3-dimethyl-2-butene (1) and 2-methyl-2-butene (3), 1,3-cyclohexadiene (6), and benzvalene (8) yield allylic hydroperoxides (2) and (4) (54%) + (5) (46%), endoperoxide (7), and dioxetane (9), respectively. The rates of the ene-reactions and (4+2)-cycloaddition reactions are only slightly dependent, those of the (2+2)-cycloaddition reaction, however, are clearly dependent on solvent polarity. "Physical" quenching of singlet oxygen by the olefins is negligible, but substantial by the sensitizer tetraphenylporphin (TPP) in chlorinated solvents.

For a study on the solvent dependence of products and rates of the three types of singlet oxygen/olefin interactions¹, we have chosen substrates 1, 3, 6, and benzvalene (8)². The latter was shown to yield dialdehyde 10 upon irradiation in ether in the presence of O₂ and of tetraphenylporphin (TPP) as a sensitizer, presumably via dioxetane 9 as the primary (unstable) product³.



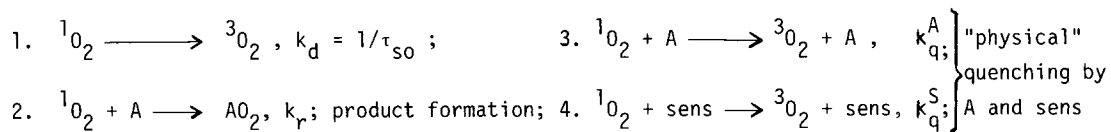
First, we wish to report the isolation of dioxetane 9 from benzvalene (8). 8 irradiated⁷ at 13°C in oxygen-saturated acetonitrile or methylene chloride in the presence of rose bengale (RB) or TPP, respectively, consumes one mole of oxygen per molecule of 8. The ¹H-nmr-spectra (80 MHz, TMS as internal standard) taken of these solutions at 13°C and those taken at -70°C in CDCl₃/CFCl₃ (3:1) after MeCN and CH₂Cl₂ were removed at -60°C/10⁻⁵ Torr are identical and in accord with structure 9 (benzvalenedioxetane = 7,8-dioxatetracyclo [4.2.0.0^{2,4}.0^{3,5}]octane): δ = 2.24 (m, 2H); 2.79 (m, 2H); 5.23 (s, 2H). 9 was isolated by removing the solvent at -25°C/10⁻⁵ Torr followed by distillation of the residue into a trap cooled to -78°C. If the distillate was warmed up to -20°C/760 Torr, it decomposed violently; no elemental analysis and molecular weight determination could thus be made. If the distillate was diluted with CDCl₃/CFCl₃(3:1), the sensitizer-free solution of 9 yielded the same nmr-signals as those containing RB and TPP. Only 9 was observed if the nmr-spectra were taken immediately after 8 was photooxygenated at 13°C in the other solvents of Table 1. Thus, 9 appears to be rather stable at room temperature in polar and non-polar solvents. However, a slow rearrangement to the dialdehyde 10 (¹H-nmr: δ = 2.43 (t, 2H); 3.20 (dt, 2H); 9.47 (d, 2H)) occurred in all these solvents.

Second, in accord with our earlier report⁸, there is only formation of 2 from 1, of 7 from 6, and of 4 (54±1 %) + 5 (46±1 %) from 3 in all solvents used, as was shown by ¹H-nmr-spectra and, in case of 4 + 5, by vpc-determination of the corresponding alcohol mixture after reduction.

Third, we wish to report on the solvent dependence of B-values and absolute rate constants, k_r, of ¹O₂-reactions with substrates 1, 3, 6, and 8.

In order to determine B-values defined as B = k_d/k_r (M), we use 2,5-dimethylfuran (DMF) as a standard which allows to determine the value of I_A·Φ(¹O₂) for a given sensitizer/solvent combination. In all the solvents used, DMF absorbs one mole of O₂ during photooxygenation with a rate that is independent of the DMF-concentration since k_r^{DMF}[DMF]/(k_r^{DMF}[DMF] + k_d) = 1 as long as [DMF] ≅ 5·10⁻⁴ M (in MeOH) and [DMF] ≅ 5·10⁻⁶ M (in CCl₄). Furthermore, in all the solvents, the primary product is the endoperoxide of DMF; its subsequent thermal reactions do not interfere with the singlet oxygen reaction⁹. Finally, there is evidence that in all solvents k_q^{DMF} ≪ k_r^{DMF} and k_q^S ≪ k_r^{DMF} (for sens = RB and TPP)¹⁰.

None of the substrates used appear to quench the triplet states of RB and TPP¹⁰. We may therefore consider only the reaction steps which follow the formation of ¹O₂:



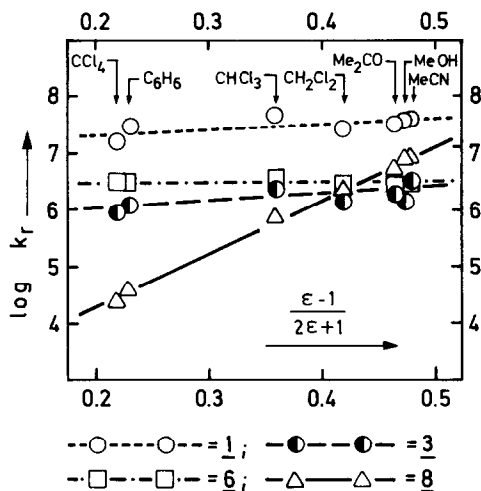
with τ_{sO} = lifetime of ¹O₂, A = substrate, and sens = RB and TPP. The rate of oxygen consumption is then given by equ. 1 :

Table 1 : β -Values of Olefins 1, 3, 6 and 8 for Non-polar and Polar Solvents

| Solvent | $10^{-4}k_d^a$ (s^{-1}) | $10^3\beta(\underline{1})$ (M) | $10^3\beta(\underline{3})$ (M) | $10^3\beta(\underline{6})$ (M) | $10^3\beta(\underline{8})$ (M) |
|---------------------------|--------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| CCl_4 ^{b,c} | 0.14 | 0.10 | 1.51 | 0.44 | 59.07 |
| C_6H_6 ^{b,d} | 4.20 | 1.32 | 34.63 | 14.84 | 1074.12 |
| $CHCl_3$ ^{b,e} | 1.70 | 0.36 | 7.22 | 4.30 | 20.22 |
| CH_2Cl_2 ^{b,f} | 0.95 | 0.40 | 5.80 | 3.21 | 4.87 |
| Me_2CO ^{g,d} | 3.80 | 1.17 | 19.92 | 12.75 | 7.23 |
| $MeOH$ ^{g,d} | 14.30 | 4.00 | 95.93 | 37.49 | 18.84 |
| $MeCN$ ^{g,d} | 3.30 | 0.76 | 11.00 | 9.38 | 3.96 |

a see ref. 12; b sens = TPP; c $k_q^S = 2.9 \cdot 10^7 M^{-1} s^{-1}$; d $k_d/k_r \gg k_q^S[sens]/k_r$; e $k_q^S = 3.0 \cdot 10^7 M^{-1} s^{-1}$; f $k_q^S = 1.8 \cdot 10^7 M^{-1} s^{-1}$; g sens = RB

Figure 1 : Solvent Dependence of Ene-Reactions, (4+2)- and (2+2)-Cycloaddition Reactions with 1O_2



$$v_{O_2} = I_A \cdot \Phi(^1O_2) \cdot k_r[A] / [(k_r + k_q^A)[A] + k_d + k_q^S[sens]] \quad (\text{equ. 1})$$

with I_A = number of light quanta absorbed per unit time and volume, and $\Phi(^1O_2)$ = quantum yield of singlet oxygen formation. Since $v_{O_2}^{DMF} = I_A \cdot \Phi(^1O_2)$, we get

$$v_{O_2}^{DMF} / v_{O_2} = (1 + k_q^A/k_r) + (k_d/k_r + k_q^S[sens]/k_r) \cdot [A]^{-1} \quad (\text{equ. 2})$$

which shows that plotting $v_{O_2}^{DMF} / v_{O_2}$ vs. $[A]^{-1}$ allows to determine (a) the "physical" quenching of 1O_2 by the substrate A from the intercept of the curve with the ordinate, and (b) the slope containing β and the "physical" quenching of 1O_2 by the sensitizer^{10,11}. If the slope is independent of the sensitizer concentration, β is derived directly from the slope. If it depends on $[sens]$, a plot of the slope of equ. 2 vs. $[sens]$ allows to determine a β -value extrapolated to zero sensitizer concentration and k_q^S from the slope of equ. 3 :

$$\text{slope of equ. 2} = k_d/k_r + (k_q^S/k_r) \cdot [sens] \quad (\text{equ. 3})$$

β -values thus derived are shown in Table 1, from which k_r -values were obtained by using singlet oxygen lifetimes determined by Merkel and Kearns¹². "Physical" quenching of 1O_2 by 1, 3, 6 and 8 appears to be negligible since $(1 + k_q^A/k_r)$ of equ.2 was always found to be 1 ± 0.15 . There is, however, quenching of 1O_2 by TPP in chlorinated solvents (see k_q^S -values, Table 1).

A plot of $\log k_r$ vs. solvent polarity given as $(\epsilon - 1)/(2\epsilon + 1)$ (Figure 1) shows that (a) the (4+2)-cycloaddition reaction is nearly independent, (b) the ene-reaction is slightly dependent, whereas (c) the (2+2)-cycloaddition reaction is clearly dependent on the solvent polarity. Applying the Kirkwood-Laidler-Eyring model^{8,13} with $\mu(^1O_2) = 0$ D, $\mu(\underline{1}) = 0$ D, $\mu(\underline{3}) = 0.92$ D⁸, $\mu(\underline{6}) = 0.38$ D¹⁴, and $\mu(\underline{8}) = 0.88$ D¹⁵ allows to calculate the dipole moments of the transition states of the ene-reactions (= 2.1 D¹⁶), of the (4+2)-cycloaddition reaction (= 1.0 D), and of the (2+2)-cycloaddition reaction (= 6.7 D). Charge separation is thus very weak at the transition states of ene-reactions and (4+2)-cycloaddition reactions, but clearly present at the transition states of (2+2)-cycloaddition reactions. Whereas the first two reactions are best described as occurring in concerted mechanisms^{4,5} possibly via peroxide-like transition states^{8,17}, the latter reaction appears to proceed via intermediates such as peroxides or zwitterions⁶.

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