Solvent Polarity Controls Oxidizing Species in the Photosensitized Oxidation of *N,N*-Dibenzylhydroxylamine

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A kinetic analysis of the 9,10-dicyanoanthracene-sensitized photooxidation of *N,N*-dibenzylhydroxylamine, giving α-phenyl-*N*-benzylnitrone and hydrogen peroxide in quantitative yields, reveals the participation of superoxide in acetonitrile and singlet oxygen in carbon tetrachloride as the major oxidizing species.

Photosensitized oxygenation of substituted alkenes and aromatics with 9,10-dicyanoanthracene (DCA) in polar solvents proceeds by a singlet oxygen ($^1O_2$)[1] or a superoxide ($O_2^{\cdot-}$)[2] mechanism or both[3] depending on the structure of electron-rich substrates being subject to photooxygenation. The fact that little information is available regarding DCA-sensitized photooxidation of hydroxylamines[4] stimulated us to undertake an investigation of the DCA-sensitized photooxidation of *N,N*-dibenzylhydroxylamine (DH) as a model compound. We now report the first observation that either $^1O_2$ or $O_2^{\cdot-}$ is involved as the main oxidizing species in this sensitized photooxidation depending on solvent polarity.

Irradiation of an oxygen-saturated acetonitrile solution of DH (0.10 M; 1 M = 1 mol dm^{-3}) in the presence of DCA (4.0 × 10^{-4} M) with >340 nm light gave α-phenyl-*N*-benzylnitrone (PBN, isolated) and hydrogen peroxide (H_2O_2, iodometry) in quantitative yields (>95%) with quantitative recovery of the sensitizer. Control experiments reveal that the oxidation of DH takes place to a negligible extent without either DCA or oxygen and, in addition, even in the presence of H_2O_2, which is one of the oxidation products. The pronounced quenching of DCA (1.0 × 10^{-4} M) fluorescence by DH (1.5–20.0 × 10^{-3} M) in oxygen-free acetonitrile should be due to exothermic electron transfer ($\Delta G = -117$ kJ mol^{-1}) from DH [oxidation potential, $E_{ox} = +0.77$ V *vs.* SCE (saturated calomel electrode) in MeCN] to singlet DCA (reduction potential, $E_{red} = -0.97 + 2.91 = +1.94$ V *vs.* SCE in MeCN)[2c,5] but not due to endothermic energy transfer from singlet DCA (the first singlet excitation energy, $E_S = 280$ kJ mol^{-1})[5] to DH ($E_S \approx 350$ kJ mol^{-1}). The exothermicity ($\Delta G = -2.9$ kJ mol^{-1}) for electron transfer from DCA anion radical to oxygen[2c] suggests the involvement of $O_2^{\cdot-}$ in the sensitized oxidation process of DH as shown in Scheme 1.

By applying the steady-state approximation to this Scheme, we obtain the equation, $1/\Phi = (1 + k_d/k_t) + (k_{d'} + k_o[O_2])/(k_t[DH])$, showing the linear relationship between the reciprocal of quantum yield (Φ)† for the formation of PBN and the reciprocal of DH concentration. The observation of the linear plot (○) of $1/\Phi$ against 1/[DH] is consistent with the suggested Scheme 1 for the DCA-sensitized oxidation (Fig. 1). From an analysis of the lifetime ($k_{d'} = 6.25 \times 10^7$ s^{-1}),‡ O_2 quenching ($k_o[O_2] = 3.78 \times 10^7$ s^{-1}), and DH quenching ($k_t = 1.11 \times 10^{10}$ M^{-1} s^{-1}) of the DCA fluorescence, the value of $(k_{d'} + k_o[O_2])/k_t$ in the equation was determined to be 0.90 × 10^{-2} M, being in reasonable agreement with 1.3 × 10^{-2} M obtained as the slope of the linear plot (○) shown in Fig. 1. This finding provides a strong piece of evidence for the involvement of $O_2^{\cdot-}$ in the sensitized oxidation process.

The unexpected observation that the DCA (1.0 × 10^{-4} M)-sensitized photooxidation of DH (2.0–20.0 × 10^{-3} M) occurs even in a nonpolar solvent, CCl_4, suggests the operation of the $^1O_2$ mechanism instead of $O_2^{\cdot-}$ one as shown in Scheme 2. If so, then we expect the linear relationship between $1/\Phi$ and 1/[DH] also in this case because application of the steady-state approximation to Scheme 2 gives the equation, $1/\Phi = 1/\Phi_{isc}\,(1 + k_{d3}/k_{o3}[O_2])(1 + k_{d1}/k_{r1}\,[DH])$, where Φ_{isc} is the quantum yield of intersystem crossing. From the linear plot (◐) in Fig. 1, the ratio of intercept to slope (k_{r1}/k_{d1}) of 510 M^{-1} was obtained. A kinetic analysis of the oxidation of DH (1.5–7.0 × 10^{-3} M) sensitized by tetraphenylporphine (TPP, 2.0 × 10^{-5} M), which is known as an effective $^1O_2$ generator,[7] under the same irradiation conditions afforded the linear plot (●) with the ratio of intercept to slope of 460 M^{-1}. Thus, the finding that both the DCA- and TPP-sensitized oxidations in CCl_4 give the same k_{r1}/k_{d1} value within experimental error provides a strong piece of evidence for the participation of $^1O_2$ as the major oxidizing species. Because in addition to endothermicity (ΔG = 71 kJ mol^{-1}) of electron transfer from DH to $^1O_2$ ($E_{red} = +0.04$ V *vs.* SCE in MeCN)[2c] giving DH cation radical and $O_2^{\cdot-}$, these radicals in nonpolar solvents undergo no stabilization by solvation,[2c] a charge-transfer complex[8] formed between DH and $^1O_2$ may play a key role as the intermediate eventually yielding PBN and H_2O_2.

To estimate the extent to which $^1O_2$ mechanism contributes to the overall DCA-sensitized oxidation of DH in acetonitrile, solvent deuterium isotope effects on Φ were examined using deuteriated acetonitrile (CD_3CN) as solvent. Making the reasonable assumption that only the $^1O_2$ lifetime ($1/k_{d1}$ = 65 μs in MeCN and 600 μs in CD_3CN)[1] is subject to solvent deuterium isotope effects, the $\Phi(CD_3CN)/\Phi(MeCN)$ ratio is simplified to $\Phi(CD_3CN)/\Phi(MeCN) = (k_{d1}(MeCN) + k_{r1}[DH])/(k_{d1}(CD_3CN) + k_{r1}[DH])$. Taking into consideration that the reactivity of $^1O_2$ [k_{r1} = (460 M^{-1})k_{d1} = (460

$$\begin{aligned}
\mathrm{DCA} &\xrightarrow{h\nu} {}^1\mathrm{DCA}\\
{}^1\mathrm{DCA} &\xrightarrow{k_{d'}} \mathrm{DCA}\\
{}^1\mathrm{DCA} + \mathrm{O_2} &\xrightarrow{k_o} \mathrm{DCA} + \mathrm{O_2}\\
{}^1\mathrm{DCA} + \mathrm{DH} &\xrightarrow{k_d} \mathrm{DCA} + \mathrm{DH}\\
{}^1\mathrm{DCA} + \mathrm{DH} &\xrightarrow{k_t} \mathrm{DCA}^{\cdot-} + \mathrm{DH}^{+\cdot}\\
\mathrm{DCA}^{\cdot-} + \mathrm{O_2} &\xrightarrow{k_t'} \mathrm{DCA} + \mathrm{O_2}^{\cdot-}\\
\mathrm{DH}^{+\cdot} + \mathrm{O_2}^{\cdot-} &\xrightarrow{k_r} \mathrm{PBN} + \mathrm{H_2O_2}
\end{aligned}$$

Scheme 1 PBN = $PhCH_2N^+(-O^-)=CHPh$

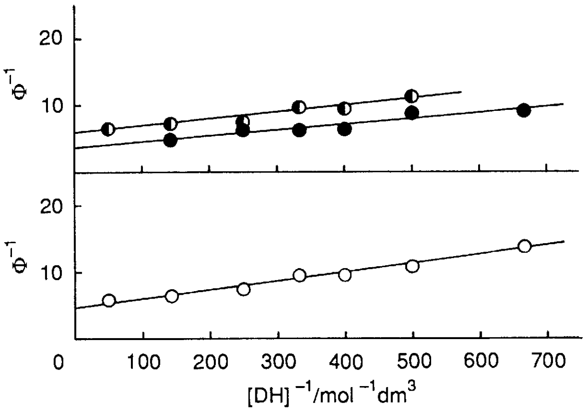

Fig. 1 Stern–Volmer plots of $1/\Phi$ *vs.* 1/[DH] for the DCA (◐,○)- and TPP (●)-sensitized photooxidations of DH with 366 nm light in oxygen-saturated acetonitrile (○) and CCl_4 (◐,●) at 24 ± 2 °C. [DCA] = 1.0 × 10^{-4} mol dm^{-3} and [TPP] = 2.0 × 10^{-5} mol dm^{-3} (TPP = 5, 10, 15, 20-tetraphenyl-21*H*, 23*H*-porphine).

$$\begin{aligned}
\mathrm{DCA} &\xrightarrow{h\nu} {}^1\mathrm{DCA} \xrightarrow{\Phi_{isc}} {}^3\mathrm{DCA}\\
{}^3\mathrm{DCA} &\xrightarrow{k_{d3}} \mathrm{DCA}\\
{}^3\mathrm{DCA} + \mathrm{O_2} &\xrightarrow{k_{o3}} \mathrm{DCA} + {}^1\mathrm{O_2}\\
{}^1\mathrm{O_2} &\xrightarrow{k_{d1}} \mathrm{O_2}\\
\mathrm{DH} + {}^1\mathrm{O_2} &\xrightarrow{k_{r1}} \mathrm{PBN} + \mathrm{H_2O_2}
\end{aligned}$$

Scheme 2

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† The quantum yields for appearance of PBN were determined by using a potassium trioxalatoferrate(III) actinometer[6] at low conversions (<1%) of the starting DH at 24 ± 2 °C. The quantitative analysis of PBN formed by 366 nm light irradiation in acetonitrile was carried out spectrophotometrically at 298 nm where molar extinction coefficients of PBN, DCA and DH were 2.0 × 10^4, 5.5 × 10^2, and 1.0 M^{-1} cm^{-1}, respectively. All the quantum yields are average values from more than five determinations.

‡ The DCA-fluorescence lifetimes ($1/k_{d'}$ = 16.0 ns in MeCN and 15.4 ns in CD_3CN) were measured under nitrogen at 26 °C with a time-correlated single-photon counting apparatus (Horiba NAES-700).

$M^{-1})(39 \times 10^{-3}\ s)^{-1} = 1.2 \times 10^4\ M^{-1}\ s^{-1}]$[9] undergoes only very small solvent polarity effects,[1] this quantum yield ratio was calculated to be 8.2 at $[DH] = 2.0 \times 10^{-2}$ M, being much larger than the observed isotope effect of 1.2 ± 0.1. This result, therefore, presents additional evidence in support of the $O_2^{\cdot -}$ mechanism by which the DCA-sensitized oxidation in acetonitrile proceeds.

The present results demonstrate that one can choose either $^1O_2$ or $O_2^{\cdot -}$ by controlling the polarity of solvent used in the DCA-sensitized photooxidation of hydroxylamines which have high reactivity toward these two oxidizing species.

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References

1 Y. Araki, D. C. Dobrowolski, T. E. Goyne, D. C. Hanson, Z. Q. Jiang, K. J. Lee and C. S. Foote, *J. Am. Chem. Soc.*, 1984, **106**, 4570.

2 (*a*) J. Eriksen, C. S. Foote and T. L. Parker, *J. Am. Chem. Soc.*, 1977, **99**, 6455; (*b*) A. P. Schaap, K. A. Zaklika, B. Kaskar and L. W.-M. Fung, *J. Am. Chem. Soc.*, 1980, **102**, 389; (*c*) J. Eriksen and C. S. Foote, *J. Am. Chem. Soc.*, 1980, **102**, 6083; (*d*) D. S. Steichen and C. S. Foote, *J. Am. Chem. Soc.*, 1981, **103**, 1855.

3 J. Santamaria, *Tetrahedron Lett.*, 1981, **22**, 4511.

4 G. Pandey, G. Kumaraswamy and A. Krishna, *Tetrahedron Lett.*, 1987, **28**, 2649.

5 J. Eriksen and C. S. Foote, *J. Phys. Chem.*, 1978, **82**, 2659.

6 C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, 1956, **235**, 518.

7 A. A. Krasnovsky, Jr., *Chem. Phys. Lett.*, 1981, **81**, 443; U. Opriel, K. Seikel, R. Schmidt and H.-D. Brauer, *J. Photochem. Photobiol., A: Chem.*, 1989, **49**, 299; B.-M. Kwon, C. S. Foote and S. I. Khan, *J. Org. Chem.*, 1989, **54**, 3378.

8 C. S. Foote, in *Singlet Oxygen*, eds. H. H. Wasserman and R. W. Murray, Academic Press, London, 1979, ch. 5; E. L. Clennan, L. J. Noe, T. Wen and E. Szneler, *J. Org. Chem.*, 1989, **54**, 3581 and references cited therein.

9 R. Schmidt and H.-D. Brauer, *J. Am. Chem. Soc.*, 1987, **109**, 6976.