Mechanism of the 9,10-Dicyanoanthracene-sensitized Photooxidation of *N,N*-Dibenzylhydroxylamine in Polar and Non-polar Solvents[1]

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The 9,10-dicyanoanthracene (DCA)-sensitized photooxidation of *N,N*-dibenzylhydroxylamine (DBH) gives α-phenyl-*N*-benzylnitrone (PBN) and hydrogen peroxide in quantitative yields at low conversions of the starting DBH both in oxygen-saturated polar solvents, acetonitrile and methanol, and in an oxygen-purged non-polar solvent, carbon tetrachloride. Thermodynamic and kinetic analyses of this sensitized oxidation in polar solvents indicate the involvement of superoxide ($O_2^{\cdot -}$) as the major oxidizing species in the process. Solvent deuterium isotope effects on the quantum yield for the appearance of PBN (Φ_{PBN}) provide supporting evidence for the preferential $O_2^{\cdot -}$ mechanism by which the sensitized reaction in acetonitrile and methanol proceeds. In addition, a higher sensitized-oxidation efficiency is obtained in methanol (limiting quantum yield, $\Phi_{PBN,lim} = 0.37$) than in acetonitrile ($\Phi_{PBN,lim} = 0.21$). This finding is explained in terms of the much slower rate of back electron transfer within the initially-formed solvent-separated radical ion pair in methanol as compared to that in acetonitrile. On the other hand, a comparison of the DBH concentration dependence of Φ_{PBN} for the DCA- and tetraphenylporphine-sensitized photooxidations in carbon tetrachloride establishes the exclusive operation of a singlet oxygen ($^1O_2$) mechanism in this non-polar solvent. The chemical deactivation of $^1O_2$ assisted by the hydroxylic hydrogen in DBH, taking place *via* a charge-transfer complex, is proposed to account for the efficient formation of PBN and hydrogen peroxide in carbon tetrachloride.

It is well-known that electron-deficient 9,10-dicyanoanthracene (DCA) sensitizes the photooxygenation of various types of electron-rich alkenes including aromatic compounds in oxygen (O_2)-saturated polar solvents.[2–4] In these DCA-sensitized photooxygenations superoxide ($O_2^{\cdot -}$)[2] or singlet oxygen ($^1O_2$)[3] or both[4] can be involved in the reactions as a crucial oxidizing species. The former is formed by one-electron reduction of O_2 with the DCA radical anion generated through electron transfer from an appropriate alkene to singlet DCA,[2,4] and the latter is produced by energy transfer from triplet DCA to O_2[3,4] which also enhances singlet ⟶ triplet intersystem crossing of DCA.[5] Many techniques have been developed to distinguish between $O_2^{\cdot -}$ and $^1O_2$, which take part in the reactions as key oxidizing species.[2–4] It has recently been suggested that the reactivity of alkenes toward $^1O_2$ determines the reaction course in DCA-sensitized photooxygenations.[6]

On the other hand, there are only a few studies concerning the photosensitized oxidations of hydroxylamines.[7–9] The 1,4-dicyanonaphthalene (DCN)-sensitized photooxidation of cyclic hydroxylamines in acetonitrile–water (4:1 v/v) was shown to give cyclic nitrones in high yields.[7] Electron transfer from the amines to singlet DCN was proposed to initiate these transformations. *N,N*-Diethylhydroxylamine (DEH) quenches $^1O_2$ efficiently by a chemical pathway eventually forming hydrogen peroxide (H_2O_2) through a possible intermediate, diethylnitroxide.[8] The photooxidation of DEH sensitized with Rose Bengal in MeCN was suggested to proceed by a $^1O_2$ mechanism, whereas a $O_2^{\cdot -}$ mechanism prevails in water.[9] The Rose Bengal–DEH system is not very effective for exploring systematically the mechanism of the sensitized oxidation of hydroxylamines, mainly because the final product, presumably nitrone, is not stable enough to permit a detailed kinetic analysis of the reaction course.

In order to obtain more insight into the oxidation mechanism of hydroxylamines, we undertook an investigation of the DCA-sensitized photooxidation of *N,N*-dibenzylhydroxylamine (DBH), being prepared as a model compound, in polar and non-polar solvents. In this paper we present results which demonstrate that one can choose either $^1O_2$ or $O_2^{\cdot -}$ as the major oxidizing species by controlling the polarity of solvent employed.

Results and Discussion

Products Derived from the Sensitized Oxidation.—Irradiation of an O_2-saturated MeCN solution of DBH (0.10 mol dm^{-3}) containing DCA (4.0 × 10^{-4} mol dm^{-3}) with light of wavelengths longer than 340 nm gave α-phenyl-*N*-benzylnitrone (PBN)† in a nearly quantitative isolated yield based on consumed DBH (73% conversion). H_2O_2 was also found to be obtained in a quantitative yield by iodometry, while the sensitizer was recovered quantitatively (Scheme 1). As shown in Fig. 1, when the lower concentrations of DBH (1.0 × 10^{-2} mol dm^{-3}) was irradiated in the presence of DCA (4.0 × 10^{-4} mol dm^{-3}) under the same conditions as above, the undesirable decomposition of PBN took place at higher than 20% conversions. Control experiments revealed that the oxidation of DBH occurs to a negligible extent without either DCA or O_2 and, in addition, even in the presence of H_2O_2, which is one of the oxidation products. Similar results were also obtained in methanol (MeOH).

$$(PhCH_2)_2N\text{-}OH \xrightarrow[DCA]{h\nu,\,O_2} PhCH_2N^+(\text{-}O^-)\text{=}CHPh + H_2O_2$$

DBH PBN

Scheme 1

Irradiation of an O_2-purged MeCN solution of DBH (2.0 × 10^{-2} mol dm^{-3}) containing DCA (2.0 × 10^{-4} mol dm^{-3}) at 366 nm allowed us to determine the quantum yields for the disappearance of DBH (GLC) and for the appearance of PBN

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† IUPAC recommended name: *N*-benzylidenebenzylamine *N*-oxide.

(GLC) and H_2O_2 (iodometry) to be 0.19 ± 0.02, 0.18 ± 0.02, and 0.16 ± 0.02, respectively, at low conversions (7–8%) of the starting DBH. This finding is consistent with the observation that the sensitized oxidation of DBH gives PBN and H_2O_2 in a 1:1 stoichiometric ratio.

Kinetic Analysis in Polar Solvents.—The fluorescence of DCA (1.0×10^{-4} mol dm^{-3}; excitation wavelength = 366 nm) was quenched efficiently by DBH ($1.5–20.0 \times 10^{-3}$ mol dm^{-3}) according to the Stern–Volmer equation ($I_0/I = 1 + 177$ [DBH], where I and I_0 are the fluorescence intensities of DCA with and without DBH) in nitrogen-saturated MeCN at room temperature. Exciplex fluorescence was not observed under these experimental conditions. The DCA fluorescence was also quenched by oxygen in oxygen-saturated MeCN (I_{N_2}/I_{O_2} = 1.604) under the same conditions as above. The free energy change ΔG for electron transfer from DBH to singlet DCA was calculated to be -112 kJ mol^{-1} based on the simplified Weller equation:[10] ΔG (kJ mol^{-1}) = 96.5 ($E_{ox} - E_{red}$) $- E_S$, where E_{ox}, E_{red}, and E_S refer to the oxidation potential (+0.77 V *vs.* SCE in MeCN) of DBH, the reduction potential (-0.97 V *vs.* SCE in MeCN)[2c,11] of DCA, and the first singlet excitation energy (280 kJ mol^{-1})[11] of DCA, respectively. Thus the pronounced quenching of DCA fluorescence by DBH should be due to exothermic electron transfer but not due to endothermic singlet–singlet energy transfer from singlet DCA to DBH ($E_S \approx 350$ kJ mol^{-1}). The exothermicity ($\Delta G = -2.9$ kJ mol^{-1})[2c] for electron transfer from the DCA radical anion to O_2 suggests the involvement of $O_2^{\cdot -}$ in the oxidation process in a polar solvent, MeCN, as shown in Scheme 2 which includes a deactivation process by back electron transfer in the singlet cage $^1[DCA^{\cdot -}\ DBH^{\cdot +}]$ forming the starting DCA and DBH. By applying the steady-state approximation to this Scheme, we obtain eqn. (1):

$$\mathrm{DCA} \xrightarrow{h\nu} {}^1\mathrm{DCA}$$

$$^1\mathrm{DCA} \xrightarrow{k_d} \mathrm{DCA}$$

$$^1\mathrm{DCA} + \mathrm{O_2} \xrightarrow{k_o^1} \mathrm{FCA} + \mathrm{O_2}$$

$$^1\mathrm{DCA} + \mathrm{DBH} \xrightarrow{k_{et}} {}^1[\mathrm{DCA^{\cdot -}\ DBH^{\cdot +}}]$$

$$^1[\mathrm{DCA^{\cdot -}\ DBH^{\cdot +}}] \xrightarrow{k_{-et}} \mathrm{DCA} + \mathrm{DBH}$$

$$^1[\mathrm{DCA^{\cdot -}\ DBH^{\cdot +}}] \xrightarrow{k_D} \mathrm{DCA^{\cdot -}} + \mathrm{DBH^{\cdot +}}$$

$$\mathrm{DCA^{\cdot -}} + \mathrm{O_2} \xrightarrow{k_{et'}} \mathrm{DCA} + \mathrm{O_2^{\cdot -}}$$

$$\mathrm{DBH^{\cdot +}} + \mathrm{O_2^{\cdot -}} \xrightarrow{k_r} \mathrm{PBN} + \mathrm{H_2O_2}$$

Scheme 2

$$1/\Phi_{PBN} = (1 + k_{-et}/k_D)\{1 + (k_d + k_o^1[O_2])/k_{et}[DBH]\}, \quad (1)$$

where Φ_{PBN} is the quantum yield for the formation of PBN.

The fortunate observation that PBN in MeCN exhibits strong UV absorption at 298 nm (molar absorption coefficient, $\varepsilon = 1.97 \times 10^4$ dm^3 mol^{-1} cm^{-1}) where DCA ($\varepsilon = 5.5 \times 10^2$ dm^3 mol^{-1} cm^{-1}) and DBH ($\varepsilon = 1.0$ dm^3 mol^{-1} cm^{-1}) show only weak absorption made it possible to determine Φ_{PBN} spectrophotometrically at considerably low conversions of DBH (≤1%). The same situation was also encountered in other solvents studied. The observation of the linear Stern–Volmer plots of $1/\Phi_{PBN}$ against the reciprocal of DBH concentration (1/[DBH]) in MeCN and MeOH is consistent with Scheme 2 proposed for the DCA-sensitized oxidation (Fig. 2). From the intercept and the ratio of the slope to intercept of these linear plots, we can estimate the limiting quantum yields for the appearance of PBN [$\Phi_{PBN,lim} = k_D/(k_{-et} + k_D)$] and the magnitude of $(k_d + k_o^1[O_2])/k_{et}$, respectively. Since the k_d, $k_o^1[O_2]$, and k_{et} values can be determined independently through an analysis of the lifetime ($1/k_d$), O_2 quenching ($k_o^1[O_2]$), and DBH quenching (k_{et}) of the DCA fluorescence, it is possible to compare the $(k_d + k_o^1[O_2])/k_{et}$ values obtained by two different procedures. These are collected in Table 1 which also includes the $\Phi_{PBN,lim}$, k_d, $k_o^1[O_2]$, and k_{et} values. Taking into account that the indirect and yet different procedures for the estimation of $(k_d + k_o^1[O_2])/k_{et}$ necessarily lead to a relatively large error, this value determined from the linear plot of $1/\Phi_{PBN}$ *vs.* 1/[DBH] in MeCN or MeOH is taken to be comparable to that calculated by using the DCA fluorescence-lifetime and -quenching parameters measured in each solvent. This finding, therefore, provides a strong piece of kinetic evidence for the involvement of $O_2^{\cdot -}$ as the major oxidizing species in the sensitized oxidation reactions in polar solvents, although there still remains the possibility of some contribution of the $^1O_2$ mechanism.

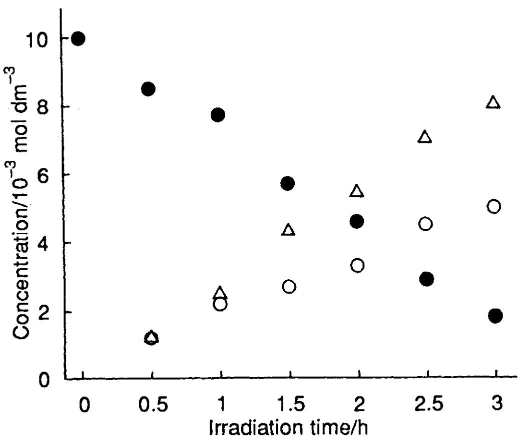


Fig. 1 Plots of reactant and product concentrations *vs.* irradiation time for the DCA (4.0×10^{-4} mol dm^{-3})-sensitized photooxidation of DBH (1.0×10^{-2} mol dm^{-3}) with light of wavelengths longer than 340 nm in O_2-purged acetonitrile at room temperature. ○, PBN; ●, DBH; △, H_2O_2.

The use of $\Phi_{PBN,lim}$ makes it possible to discuss solvent effects on the behaviour of the singlet radical ion pair $^1[DCA^{\cdot -}$ $DBH^{\cdot +}$] without a consideration of the $^1O_2$ mechanism. An inspection of the relation, $1/\Phi_{PBN,lim} = 1 + k_{-et}/k_D$, demonstrates that the relative rate (k_{-et}/k_D) of back electron transfer (k_{-et}) to diffusive separation (k_D) of paired radical ions determines the oxidation efficiency of DBH. From steady-state product analysis[12] and magnetic field dependence of the geminate recombination[13] of similar types of radical ion pairs, the k_D has been determined to be 5×10^8 s^{-1} in MeCN[12,13] and 2.5×10^8 s^{-1} in MeOH[13] at room temperature. Based on these k_D values we estimated the rate of return electron transfer as $k_{-et} = 1.9 \times 10^9$ s^{-1} in MeCN and 4.3×10^8 s^{-1} in MeOH. Thus the greater reactivity in MeOH ($\Phi_{PBN,lim} = 0.37$) than in MeCN ($\Phi_{PBN,lim} = 0.21$) is attributed to the much slower rate (a factor of *ca.* 5) of reverse electron transfer in the MeOH cage. This solvent effect on k_{-et} also provides strong evidence for the existence of the solvent-separated radical ion pair, which must be stabilized to some extent not only by electrostatic interaction

Table 1 Limiting quantum yields and physical parameters of the lifetime, O_2 quenching, and DBH quenching of the DCA fluorescence

Solvent	$\Phi_{PBN,lim}$ [a]	$k_d/10^7\ s^{-1}$	$k_o^1[O_2]/10^7\ s^{-1}$	$k_{et}/10^{10}\ dm^3\ mol^{-1}\ s^{-1}$	$(k_d + k_o^1[O_2])/k_{et}$ [b]$/10^{-3}\ mol\ dm^{-3}$	$(k_d + k_o^1[O_2])/k_{et}$ [c]$/10^{-3}\ mol\ dm^{-3}$
MeCN	0.21	6.3	3.8	1.11	9	3
MeOH	0.37	6.4	5.6	0.81	15	26

[a] Quantum yield estimated by the extrapolation of the linear $1/\Phi_{PBN}$ *vs.* 1/[DBH] plot to the intercept. [b] Calculated by using the independently determined parameters k_d, $k_o^1[O_2]$, and k_{et}. [c] Determined from the ratio of slope to intercept of the linear $1/\Phi_{PBN}$ *vs.* 1/[DBH] plot.

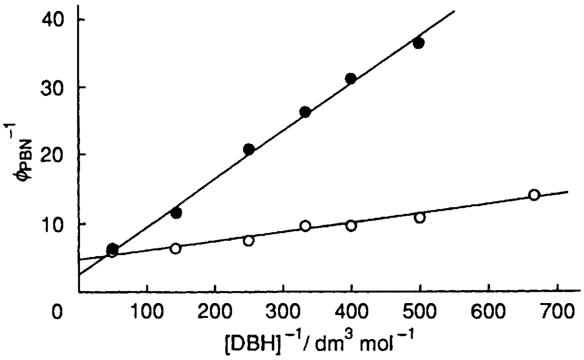


Fig. 2 Stern–Volmer plots of $1/\Phi_{PBN}$ *vs.* 1/[DBH] for the DCA (1.0×10^{-4} mol dm^{-3})-sensitized photooxidation of DBH with 366 nm light in O_2-saturated acetonitrile (○) and methanol (●) at 24 ± 2 °C

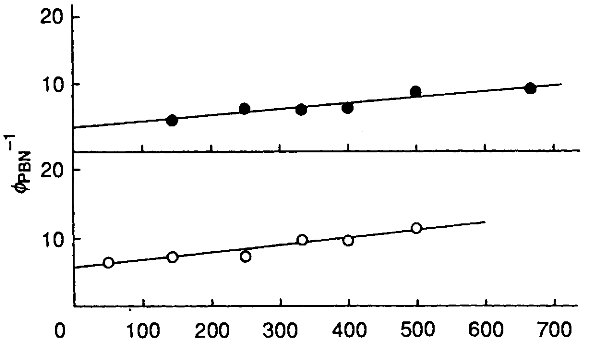
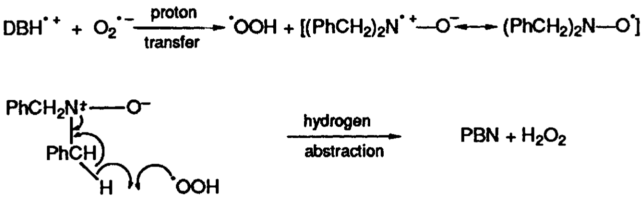


Fig. 3 Stern–Volmer plots of $1/\Phi_{PBN}$ *vs.* 1/[DBH] for the DCA (○, 1.0×10^{-4} mol dm^{-3})- and TPP (●, 2.0×10^{-5} mol dm^{-3})-sensitized photooxidations of DBH with 366 nm light in O_2-saturated carbon tetrachloride at 24 ± 2 °C

but also by hydrogen-bonding between radical ions and solvent molecules broken into the cage. Since MeOH (relative permittivity, $\varepsilon_{25\,°C} = 32.7$)[14] has solvent polarity comparable to that of MeCN ($\varepsilon_{25\,°C} = 35.9$),[14] this additional stabilization due to the hydrogen bonding should retard charge recombination to result in the higher reactivity of DBH in MeOH.

Special salt effects on the sensitized reactions have been known to provide a useful tool for exploring the behaviour of radical ion pair intermediates.[15,16] Therefore, we used the relatively low concentration of lithium perchlorate (LPC) as a salt to protect our system from substantial ionic strength effects and measured the DBH (1.5–20.0 × 10^{-3} mol dm^{-3}) concentration dependence of Φ_{PBN} in the presence of LPC (2.0 × 10^{-2} mol dm^{-3}) in MeCN. From the intercept of the linear Stern–Volmer plot, we obtained $\Phi_{PBN,lim} = 0.26$, showing only a slight increase in $\Phi_{PBN,lim}$ (= 0.21 at [LPC] = 0 mol dm^{-3}). This finding suggests that the rate of back electron transfer in the solvent-separated radical ion pair should be much greater than that of the exchange reaction between the lithium ion (Li^+) and DBH radical cation. If we could assume that the exchange rate k_{ex} between Li^+ and $DBH^{\bullet +}$ has a comparable magnitude to that ($k_{ex} = 1.5 \times 10^8$ dm^3 mol^{-1} s^{-1}) between Li^+ and aromatic amine radical cation,[15] we may calculate the pseudo-first-order rate constant k_{ex}' for the exchange in MeCN to be $k_{ex}' = k_{ex}[LPC] = (1.5 \times 10^8\ dm^3\ mol^{-1}\ s^{-1})(2.0 \times 10^{-2}\ mol\ dm^{-3}) = 3 \times 10^6\ s^{-1}$, which is much smaller than $k_{-et} = 1.9 \times 10^9\ s^{-1}$. This consideration supports our suggestion mentioned above.

In the Rose Bengal-sensitized oxidation of DEH diethylnitroxide has been proposed as a key intermediate.[9] Although we did not attempt to detect a dibenzylnitroxide intermediate, it is likely that rapid proton transfer from acidic DBH radical cation to basic $O_2^{\bullet -}$ [17] may yield dibenzylnitroxide and hydroperoxyl radical, with hydrogen abstraction from the former intermediate producing the final products PBN and H_2O_2 as shown in Scheme 3.



Scheme 3

Kinetic Analysis in Non-polar Solvents.—Since non-polar solvents have no ability to stabilize dissociated free radical ions by solvation, the singlet cage $^1[DCA^{\bullet -}\ DBH^{\bullet +}]$ must be deactivated exclusively through reverse electron transfer.[2,3] Thus the participation of $O_2^{\bullet -}$ in the sensitized oxidation process is very unlikely in non-polar solvents, allowing us to expect negligible formation of PBN and H_2O_2, when the DCA-sensitized oxidation of DBH is conducted in a non-polar solvent, carbon tetrachloride (CCl_4). Contrary to our expectation, the DCA (2.0 × 10^{-4} mol dm^{-3})-sensitized photooxidation of DBH (2.0 × 10^{-2} mol dm^{-3}) with 366 nm light in O_2-saturated CCl_4 proceeded efficiently giving PBN (GLC) and H_2O_2 (iodometry) in a 1:1 stoichiometric ratio at low conversions (6–8%). This result strongly suggests the operation of the $^1O_2$ mechanism as depicted in Scheme 4 which allows us to derive eqn. (2) using the steady-state approximation where

$$\mathrm{DCA} \xrightarrow{h\nu} {}^1\mathrm{DCA} \xrightarrow[\mathrm{O_2}]{\Phi_{isc}} {}^3\mathrm{DCA}$$

$${}^3\mathrm{DCA} \xrightarrow{k_d^3} \mathrm{DCA}$$

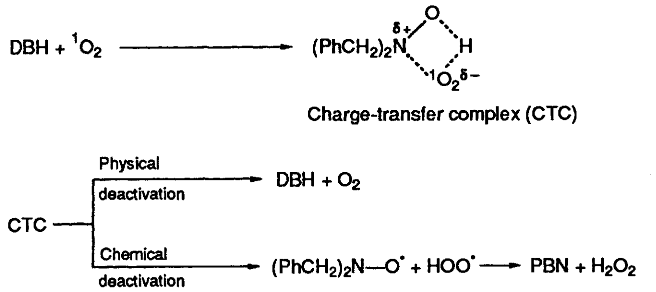
$${}^3\mathrm{DCA} + \mathrm{O_2} \xrightarrow{k_o^3} \mathrm{DCA} + {}^1\mathrm{O_2}$$

$${}^1\mathrm{O_2} \xrightarrow{k_d^1} \mathrm{O_2}$$

$$\mathrm{DBH} + {}^1\mathrm{O_2} \xrightarrow{k_r^1} \mathrm{PBN} + \mathrm{H_2O_2}$$

Scheme 4

$$1/\Phi_{PBN} = 1/\Phi_{isc}(1 + k_d^3/k_o^3[O_2])(1 + k_d^1/k_r^1[DBH]) \quad (2)$$



Scheme 5

Φ_{isc} is the quantum yield of intersystem crossing. The quantum yields (Φ_{PBN}) for the DCA (1.0×10^{-4} mol dm^{-3})-sensitized oxidation of DBH ($2.0–20.0 \times 10^{-3}$ mol dm^{-3}) in CCl_4 were determined at conversions of less than 1% in the same manner as in polar solvents. The linear relationship between $1/\Phi_{PBN}$ and 1/[DBH] shown in Fig. 3 not only agrees with the $^1O_2$ mechanism but also gives $\Phi_{PBN.lim} = 0.18$ and $k_r^1/k_d^1 = 510$ dm^3 mol^{-1}, which were estimated from the intercept and the ratio of intercept to slope of the observed linear plot, respectively. The oxidation of DBH ($1.5–7.0 \times 10^{-3}$ mol dm^{-3}) sensitized with 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine (TPP, 2.0×10^{-5} mol dm^{-3}), which is known as an effective $^1O_2$ generator,[18] under the same irradiation conditions was also found to afford the linear Stern–Volmer plot with $\Phi_{PBN.lim} = 0.27$ and $k_r^1/k_d^1 = 460$ dm^3 mol^{-1} (Fig. 3). Thus the finding that both the DCA- and TPP-sensitized oxidations in CCl_4 give almost the same k_r^1/k_d^1 value provides strong evidence for the involvement of $^1O_2$ in the DCA-sensitized oxidation process. By using the $^1O_2$ lifetime of 39 ms measured in CCl_4 with TPP (2.0×10^{-5} mol dm^{-3}) as a sensitizer,[19] we calculate the total rate constant (k_r^1) for the reaction of DBH with $^1O_2$ to be $k_r^1 = (460$ dm^3 mol$^{-1})k_d^1 = (460$ dm^3 mol$^{-1}) (39 \times 10^{-3}$ s$)^{-1} = 1.2 \times 10^4$ dm^3 mol^{-1} s^{-1}.

In addition to the fact that free radical ions are not subject to any stabilization in non-polar solvents,[2,3] endothermicity ($\Delta G = 71$ kJ mol^{-1}) of electron transfer from DBH to $^1O_2$ ($E_{red} = +0.04$ V *vs.* SCE in MeCN)[2c] giving $DBH^{\cdot +}$ and $O_2^{\cdot -}$ should eliminate the possibility that $O_2^{\cdot -}$ formed through quenching of $^1O_2$ by DBH becomes the key oxidizing species in CCl_4. Recently both amines and hydroxylamines have been shown to quench $^1O_2$ physically or chemically by way of a charge-transfer complex.[8,20] From a different solvent dependence of the rate constants for the $^1O_2$ quenching by these amines, Encinas and co-workers suggested that the quenching of $^1O_2$ by hydroxylamines takes place by a mechanism different from that for secondary and tertiary amines.[8] They proposed that the hydroxylic hydrogen atom in DEH promotes chemical deactivation to a substantial extent giving the final product H_2O_2. As judged by the relatively large dissociation energy (*ca.* 290 kJ mol^{-1})[21] of the O–H bond, direct hydrogen-atom transfer from DEH to $^1O_2$ is unlikely to occur efficiently in the quenching process. The fact that DBH has an oxidation potential comparable to that ($E_{ox} = +0.78$ V *vs.* SCE in MeCN)[22] of triethylamine makes it reasonable to assume that the $^1O_2$ quenching by DBH proceeds by the hydroxylic hydrogen-assisted charge-transfer mechanism shown in Scheme 5. The formation of the charge-transfer complex[8,20] may enhance both the acidity of the hydroxy group in DBH and the basicity of $^1O_2$ to result in an accelerated chemical-deactivation process through which PBN and H_2O_2 are eventually obtained.

Solvent Deuterium Isotope Effects.—Since the possibility of the $^1O_2$ mechanism in MeCN and MeOH still remains, we examined solvent deuterium isotope effects on Φ_{PBN} using deuteriated acetonitrile (CD_3CN) and methanol (MeOD) as solvents in order to estimate the extent to which the $^1O_2$ mechanism contributes to the overall DCA-sensitized oxidation of DBH in these polar solvents. Making the reasonable assumption that only the $^1O_2$ lifetime ($1/k_d^1 = 65$ µs in MeCN,[3] 600 µs in CD_3CN,[3] 9.5 µs in MeOH,[18a] and 37 µs in MeOD[23] at room temperature) is subject to solvent deuterium isotope effects, the ratio of $\Phi_{PBN}(D)$ to $\Phi_{PBN}(H)$ is simplified to eqn. (3) where D and H in parentheses indicate deuteriated and

$$\Phi_{PBN}(D)/\Phi_{PBN}(H) = \{k_d^1(H) + k_r^1[DBH]\}/\{k_d^1(D) + k_r^1[DBH]\}, \quad (3)$$

protiated solvents, respectively. On the other hand, the $O_2^{\cdot -}$ mechanism should not be expected to exhibit a solvent deuterium isotope effect because the DCA-fluorescence lifetimes in N_2-purged MeCN (16.0 ns) and MeOH (15.6 ns) are consistent with those in CD_3CN (15.4 ns) and MeOD (15.8 ns), respectively, within experimental error. Thus the extent of contribution of the $^1O_2$ mechanism can be established qualitatively based on the $\Phi_{PBN}(D)/\Phi_{PBN}(H)$ ratio. Taking into consideration that the reactivity of $^1O_2$ toward some alkenes[24] and DEH[8] undergoes only small solvent polarity effects, we may utilize the value of 1.2×10^4 dm^3 mol^{-1} s^{-1} obtained in CCl_4 as k_r^1 for this calculation. From eqn. (3) the quantum-yield ratio $\Phi_{PBN}(D)/\Phi_{PBN}(H)$ was calculated to be 8.2 for CD_3CN/MeCN and 3.9 for MeOD/MeOH at [DBH] = 2.0×10^{-2} mol dm^{-3}. A comparison of these calculated isotope effects with the observed ones of 1.2 ± 0.1 for CD_3CN/MeCN and 0.9 ± 0.1 for MeOD/MeOH establishes that the $^1O_2$ mechanism makes only very little contribution to our sensitized oxidation in MeCN and MeOH, providing additional evidence in support of the preferential $O_2^{\cdot -}$ mechanism by which the DCA-sensitized reactions of DBH in these two polar solvents proceed.

Experimental

Materials and Solvents.—*N,N*-Dibenzylhydroxylamine (DBH) was prepared by treatment of benzyl chloride with hydroxylamine according to the method of Jones and Sneed.[25] The crude DBH was purified by recrystallization from aqueous ethanol and then from hexane–EtOAc to give colourless needles, m.p. 123–124 °C (lit.,[25] 123 °C). The oxidation of DBH with yellow mercury(II) oxide in diethyl ether gave crude α-phenyl-*N*-benzylnitrone (PBN) repeated recrystallization of which from hexane–acetone afforded analytically pure PBN, m.p. 82–84 °C (lit.,[26] 81.5–83.5 °C). The structure of DBH and PBN was also established by IR and ^1H NMR spectroscopy. 9,10-Dicyanoanthracene (DCA) was recrystallized twice from benzene. Commercially available hydrogen peroxide (31wt% aqueous solution) and 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine of high purity were used as received.

Carbon tetrachloride was of spectroscopic grade and was used without further purification along with [$^2H_3$]acetonitrile (CD_3CN, 99.5 atom%) and [O-^{2}H]methanol (MeOD, 99.5 atom%). MeCN and MeOH were carefully purified according to standard methods.[14]

Measurements.—IR and ^1H NMR spectra were taken with a Hitachi 270–30 infrared spectrometer and a JEOL FX-200 spectrometer, respectively. UV and fluorescence spectra were recorded on a Shimadzu UV-210A spectrophotometer and a Shimadzu RF-5000 spectrofluorimeter, respectively. GLC analysis was carried out on a Shimadzu GC-8AP gas chromatograph equipped with flame ionization detector, using a 3.0 × 3000 mm glass column packed with 10% silicone SE-30 on Chromosorb W (60–80 mesh). Fluorescence lifetimes were measured under N_2 at 26 °C with a time-correlated single-photon counting apparatus (Horiba NAES-700; excitation wavelength = 366 nm; cut-off wavelength = 410 nm).

A potassium trioxalatoferrate(III) actinometer[27] was employed to determine quantum yields for the DCA-sensitized photooxidation of DBH at low conversions ($\leqslant 1\%$ for UV analysis and 6–8% for GLC analysis) of the starting DBH in order to avoid the undesirable decomposition of PBN formed. A 500 W high-pressure Hg lamp was used as the light source from which 366 nm light was selected with Corning 0-52, Corning 7-60, and Toshiba IRA-25S glass filters. Quantitative GLC (DBH and PBN) and iodometric (H_2O_2) analyses of the photolysate were carried out by utilizing linear calibration curves for each compound, made under the same analytical conditions. Molar absorption coefficients (ε_{max}) of PBN at its first UV absorption-maximum wavelength ($\varepsilon_{max} = 1.97 \times 10^4$ dm^3 mol^{-1} cm^{-1} at 298 nm in MeCN, 2.02×10^4 dm^3 mol^{-1} cm^{-1} at 295 nm in MeOH, and 2.04×10^4 dm^3 mol^{-1} cm^{-1} at 303 nm in CCl_4) were employed to quantify the formation of PBN spectrophotometrically. All the quantum yields are an average of more than five determinations. The Φ_{PBN} values determined independently in MeCN at [DBH] = 2.0×10^{-2} mol dm^{-3} were consistent with each other [Φ_{PBN} = 0.18 ± 0.02 (GLC) and 0.17 ± 0.01 (UV)].

The half-wave oxidation potential of DBH was measured in MeCN by cyclic voltammetry on a Hokuto HAB-151 potentiostat/galvanostat connected to a Yokokawa XY recorder. The electrode system comprised a platinum working electrode, a platinum auxiliary electrode, and a saturated calomel reference electrode (SCE). A solution containing DBH at 10^{-3} mol dm^{-3} was prepared in dry, degassed MeCN with 0.1 mol dm^{-3} tetrabutylammonium perchlorate as a supporting electrolyte. The scanning voltage was 50 mV s^{-1} and the current 5 μA cm^{-1}.

For the purpose of isolating the photoproducts, an MeCN solution (80 cm^3) of DBH (0.10 mol dm^{-3}) containing DCA (4.0×10^{-4} mol dm^{-3}), placed in a Pyrex vessel, was irradiated for 40 h under dry O_2 at room temperature with light of wavelengths longer than 340 nm (Corning 0-52 glass filter) from a 500 W high-pressure Hg lamp. A 5 cm^3 aliquot of the solution was pipetted off and then subjected to iodometric analysis of the H_2O_2 produced. The remaining solution was concentrated to dryness on a rotary evaporator, and the resulting residue was chromatographed on silica gel (70–230 mesh, Merck) eluting with chloroform to give DCA, DBH and PBN. Physical properties of each compound agreed with those of commercially available (DCA) or independently prepared authentic (DBH and PBN) samples.

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