Interaction of Singlet Oxygen [$O_2(^1\Delta)$] with Aliphatic Amines and Hydroxylamines

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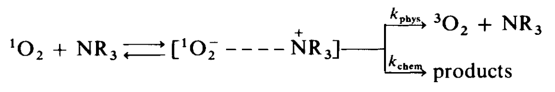
Singlet oxygen quenching rates for $O_2(^1\Delta)$ by triethylamine, diethylamine, and *N,N*-diethylhydroxylamine have been measured in several solvents. The data obtained for the amines are compatible with a charge-transfer quenching mechanism; quenching is faster in solvents of high capacity to stabilize charges and low capacity to donate a proton. Quenching by *N,N*-diethylhydroxylamine shows a different solvent dependence: the rate constant depends upon the availability of the hydroxylic hydrogen. This fact, together with the high yields of hydrogen peroxide produced in the singlet oxygen–diethylhydroxylamine reaction, implies a different quenching mechanism.

Amines are frequently employed as singlet oxygen quenchers; Bellus[1] has critically reviewed the data obtained up to 1976. Young *et al.*[2,3] and Monroe[4] found a good correlation between the quenching rate constant and the amine ionization potential for a series of amines. These results supported a previous suggestion that the quenching process is mediated by the formation of a charge-transfer intermediate[5]



$$^1O_2 + NR_3 \rightleftharpoons [^1O_2^{-} \cdots\cdots \overset{+}{N}R_3] \begin{cases} \xrightarrow{k_{phys}} {}^3O_2 + NR_3 \\ \xrightarrow{k_{chem}} \text{products} \end{cases}$$

Scheme 1.

The relationship between the physical quenching (k_{phys}) and the chemical process (k_{chem}) is determined by the amine characteristics (*e.g.* the presence of α-hydrogen atoms).

For a mechanism such as that depicted in Scheme 1, a substantial dependence of the total quenching rate constant (k_q) on the solvent might be expected. Quenching data reported by various groups for the deactivation of singlet oxygen by triethylamine seem to indicate a significant solvent dependence.[1,4] On the other hand, data reported for 1,4-diazabicyclo[2.2.2]octane (DABCO), one of the amines more widely investigated, show no evident solvent effect.[1,3]

The present paper aims to answer the following questions: (i) is there any significant solvent effect on the quenching of singlet oxygen by aliphatic amines? (ii) are hydroxylamines singlet oxygen quenchers? (iii) what is the mechanism of the process and what is the relevance of the chemical path in quenching by hydroxylamines? These last questions (iii) are considered of relevance in view of the known antioxidant capacity of hydroxylamine in chemical and in biological systems.[6]

Experimental

Rubrene, Rose Bengal, and 9,10-dimethylanthracene (DMA), (Aldrich) were used as received. Triethylamine (TEA) (Fluka), diethylamine (DEA) (Fluka), and *N,N*-diethylhydroxylamine (DEHA) (Aldrich) were distilled prior to use. *O,N*-Diethylhydroxylamine (OEHA) was obtained *via* synthesis of ethyl hydroxycarbamate, prepared according to the method of Jones,[7] followed by alkylation with ethyl iodide in basic medium. The product was distilled into dilute HCl and isolated under reduced pressure. *O,N,N*-Triethylhydroxylamine (TEHA) was obtained by treating OEHA with diethyl sulphate in KOH. Both products were identified by i.r. and n.m.r. spectroscopy; g.l.c. did not show any impurity (<0.1%).

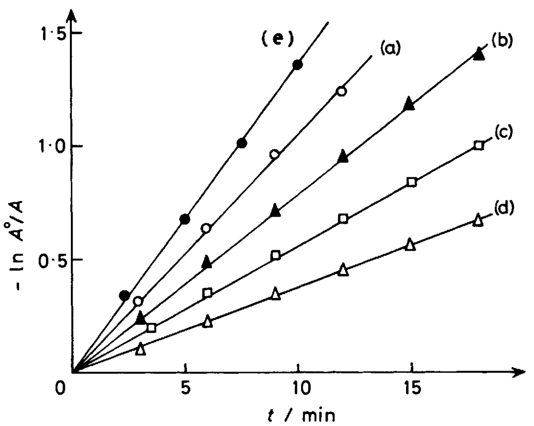


Figure 1. Photobleaching of DMA by DEHA; solvent acetonitrile; [DEHA] (a) 5.78×10^{-4}, (b) 1.16×10^{-3}, (c) 2.3×10^{-3}, (d) 4.57×10^{-3}M; (e) without added amine

Two different methods were employed to determine the quenching rate constants. In benzene and hexane solutions the effect of amine concentration upon the sensitized photo-oxidation of rubrene was measured.[8] In polar solvents, Rose Bengal was employed as sensitizer and the amine quenching rate constant was evaluated from the inhibition of DMA bleaching. Both methods were employed in methanol, giving identical results. Hydrogen peroxide was measured by iodide titration.[9]

All the solutions were saturated with oxygen and irradiated with 527 nm light. The bleaching of DMA or rubrene as a function of time in the presence and in the absence of the quencher was recorded with a Carl Zeiss spectrophotometer.

Results and Discussion

The photobleaching of DMA by $^1O_2$ (sensitized by Rose Bengal) was inhibited by amines and hydroxylamines. The bleaching followed first-order kinetics; typical plots are shown in Figure 1. The ratio between the slope at zero amine (Y^0) and the slope at a given amine concentration (Y) allowed the determination of $k_q\tau(^1O_2)$ according to equation (i), where k_q

$$Y^0/Y = 1 + k_q\tau(^1O_2)[Q] \qquad \text{(i)}$$

is the quenching rate constant of the process $^1O_2 + Q \longrightarrow$ quenching. Plots of this type are shown in Figure 2.

When rubrene was employed as sensitizer (non-polar solvents) the singlet oxygen concentration was monitored by

Table. Rate constants for the quenching of $^1O_2$ by amines and hydroxylamines

	Solvatochromic parameters			10^7k_q/dm^3 mol^{-1} s^{-1} ^{a}				
Solvent	α	π^*	β	TEA	DEA	DEHA	TEHA	OEHA
n-Hexane	0.00	−0.08	0.04	4.75	0.48	2.5	0.06	0.003
Benzene	0.00	0.59	0.1	17.6	4.6	2.7		
Acetone	0.06	0.71	0.48	30.5	10.1	2.5		
Acetonitrile	0.19	0.75	0.31	19.5	8.6	1.8	0.21	0.08
Methanol	0.93	0.6	(0.62)	1.3 (1.5)^b	0.22 (0.3)^b	0.3		
Formamide	0.71	0.97		0.79	0.23	1.0		
Chloroform	0.44	0.58	0.00	7.4 (6.5)^a	1.15 (1.5)^a	1.2		

[a] Lifetimes taken from P. B. Merkel and D. R. Kearns, *J. Am. Chem. Soc.*, 1972, **94**, 7244; D. R. Adams and F. Wilkinson, *J. Chem. Soc., Faraday Trans. 2*, 1972, **68**, 586. [b] Data from ref. 4.

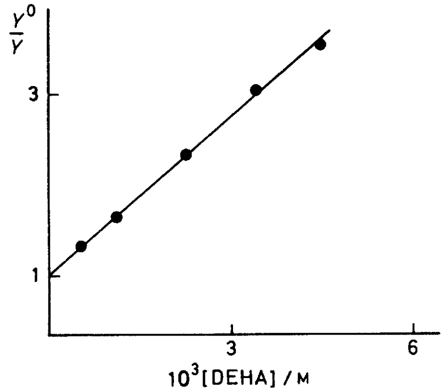


Figure 2. Y^0/Y according to equation (i) as a function of DEHA concentration; solvent acetonitrile

following the rate of rubrene autoxidation. For this system, the kinetics are not first-order and the rate constants were obtained from the initial rates of rubrene consumption,[10] according to equation (ii) where k_{ox} is the rate constant for the $^1O_2$ oxidation

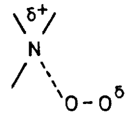
$$k_q = \frac{k_{ox}[\mathrm{Ru}]_0 + [\tau(^1O_2)]^{-1}}{[Q]}\left[\frac{(d[\mathrm{Ru}]/dt)^0}{(d[\mathrm{Ru}]/dt)_0^Q} - 1\right] \qquad \text{(ii)}$$

of rubrene,[8b] $(d[\mathrm{Ru}]/dt)_0$ is the initial rate of rubrene loss, and superscripts Q and 0 indicate the presence or absence of quencher.

These methods require that the amines do not quench the sensitizer singlets or triplets under the experimental conditions employed.[11] We can disregard this possibility for the following reasons: (i) k_q values were found to be independent of DMA concentration; (ii) k_q values were found to be independent of oxygen pressure; (iii) linear Stern–Volmer-type plots were obtained over a wide range of quencher concentrations; (iv) data obtained in double-quenching experiments (using sodium azide) were compatible with those expected from a competition for $^1O_2$; (v) the amine concentrations employed were relatively low (below 0.05M) and no significant singlet dye quenching was observed.

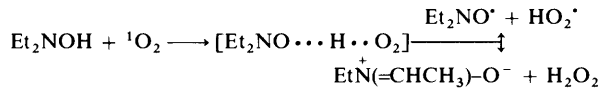
The values of k_q obtained are summarized in the Table, which also includes some results previously reported. The similarity between our data and those reported in the literature lends further support to the methods employed in the present work.

These data show that k_q values for TEA and DEA are strongly solvent-dependent. Nevertheless, the values of k_q are not simply related to macroscopic parameters of the solvent such as dielectric constant. The Table also gives the solvatochromic parameters α, β, and π^* of the solvents employed.[12] The data indicate that high k_q values are obtained in solvents of high π^* and low α. Since the π^* scale is a measure of the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect, and the α scale describes the ability of the solvent to donate a proton in a solvent-to-solute hydrogen bond,[12] the results are compatible with a mechanism involving the formation of a charge-transfer complex such as (A). Solvents with large π^* stabilize the complex and solvents with high α values preclude its formation by protecting the nitrogen lone pair. Similar results have been reported for the quenching of excited anthracene derivatives by aliphatic amines,[13] a process that is also mediated by a charge-transfer complex between the amine and the excited aromatic compound.



(A)

The data obtained with DEHA show that this compound is an efficient singlet oxygen scavenger. Nevertheless, the dependence of the quenching rate constant on the solvent is noticeably different from that observed when an amine (*e.g.* DEA) is employed as quencher. In particular (i) k_{DEHA} is similar in n-hexane, benzene, acetone, and acetonitrile, (ii) in solvents of low π^* (n-hexane) and high α values (formamide), $k_{\mathrm{DEHA}} > k_{\mathrm{DEA}}$, while in solvents of high π^* and low α values $k_{\mathrm{DEA}} > k_{\mathrm{DEHA}}$. These data could imply a different quenching mechanism and that structures such as (A) are much less relevant for DEHA than for DEA. The data can be explained if a simple 'free-radical-like' process such as shown in Scheme 2 is contributing to the total rate of the interaction. The occurrence of this process, promoted by the lability of the hydroxylic hydrogen in hydroxylamines,[14] is also supported by the low reactivity observed for TEHA and OEHA (see Table). Furthermore, the fact that the lower k_{DEHA} values are obtained in solvents of rather large α values is also compatible with the participation of the hydroxylic hydrogen in the rate-determining step.



$$\mathrm{Et_2NOH} + {}^1\mathrm{O_2} \longrightarrow [\mathrm{Et_2NO}\cdots\mathrm{H}\cdot\cdot\mathrm{O_2}] \longrightarrow \begin{cases} \mathrm{Et_2NO^{\bullet}} + \mathrm{HO_2^{\bullet}} \\ \mathrm{Et\overset{+}{N}({=}CHCH_3){-}O^-} + \mathrm{H_2O_2} \end{cases}$$

Scheme 2.

The occurrence of either of the processes is Scheme 2 followed by $\mathrm{HO_2^{\bullet}} + \mathrm{Et_2NOH} \longrightarrow \mathrm{HOOH} + \mathrm{Et_2NO^{\bullet}}$ would require a high yield in HOOH formation. The hydrogen peroxide yield was evaluated in methanol employing diphenylbenzofuran as actinometer, giving $\varphi_{\mathrm{H_2O_2}}$ *ca.* 0.85. Furthermore, $(\varphi_{\mathrm{H_2O_2}})_{\mathrm{DEHA}}/(\varphi_{\mathrm{H_2O_2}})_{\mathrm{TEA}}$ was 4.1. These results show that a chemical path such as that in Scheme 2 is dominating the interaction between $^1O_2$ and DEHA.

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