SINGLET OXYGEN QUENCHING BY STABLE NITROXY RADICALS

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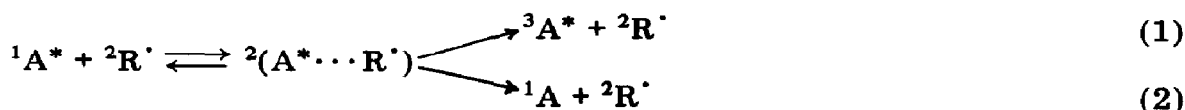
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Summary

The quenching mechanism of singlet oxygen luminescence at 1.27 μm by different aliphatic and aromatic nitroxy radicals has been studied. The $^1O_2$ was generated in solutions of anthracene or protoporphyrin IX by excitation with a 347 nm laser flash. The luminescence quenching rate constants have been found to be about 10^5 - 10^6 M^{-1} s^{-1} for aliphatic radicals and about 10^6 - 10^7 M^{-1} s^{-1} for aromatic radicals and are weakly dependent upon the nature of the solvent. The maximum value $k_q = 1.6 \times 10^7$ M^{-1} s^{-1} was obtained for di-*tert*-butyldiphenyl nitroxide which is characterized by a considerable delocalization of the unpaired electron over the molecular fragment and a lower steric screening of the $>$N—O$^{\cdot}$ centre in comparison with other radicals. From an analysis of the experimental data it has been concluded that $^1O_2$ quenching by radicals occurs exclusively via the electron exchange interaction in collision complexes.
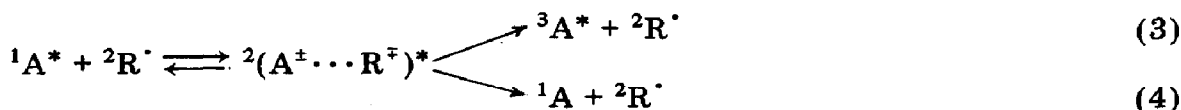
1. Introduction

Nitroxy radicals are known to be efficient quenchers of the excited triplet [1 - 8] and singlet [9 - 12] states of organic molecules and excimers [13]. It is well known that irrespective of the nature of the fluorophore the rate constants of fluorescence quenching by radicals in liquid solution are close to the diffusion limit ($k_q = 10^9$ - 10^{10} M^{-1} s^{-1}). The quenching of excited singlet states by stable radicals ($^2R^{\cdot}$) may occur via the following different mechanisms.

(1) Exchange interactions in a collision complex

$$^1A^* + {}^2R^{\cdot} \rightleftharpoons {}^2(A^* \cdots R^{\cdot}) \begin{cases} \nearrow {}^3A^* + {}^2R^{\cdot} \qquad (1) \\ \searrow {}^1A + {}^2R^{\cdot} \qquad (2) \end{cases}$$
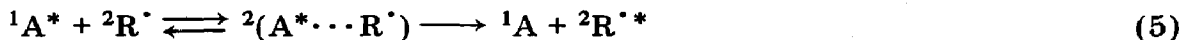
where the excited molecule ($^1A^*$) passes to the triplet state ($^3A^*$) or the ground state (^1A).

(2) Partial or complete reversible charge transfer (CT):

$$^1A^* + {}^2R^{\cdot} \rightleftharpoons {}^2(A^{\pm} \cdots R^{\mp})^* \begin{cases} \nearrow {}^3A^* + {}^2R^{\cdot} & \quad (3) \\ \searrow {}^1A + {}^2R^{\cdot} & \quad (4) \end{cases}$$

(3) The energy transfer mechanism

$$^1A^* + {}^2R^{\cdot} \rightleftharpoons {}^2(A^* \cdots R^{\cdot}) \longrightarrow {}^1A + {}^2R^{\cdot *} \qquad (5)$$

Reactions (1) - (5) are spin allowed. The fluorescence quenching of aromatic hydrocarbons occurs mainly via enhancement of intersystem crossing to the triplet state [11] and that of diphenyl polyenes occurs through enhancement of internal conversion [12]. However, the details of the quenching mechanisms are still not clear.

Aliphatic nitroxy radicals are characterized by a weak structureless absorption band at about 400 - 590 nm which is due to the spin-allowed n,π^* doublet–doublet transition [14]. In ref. 9 the energy of the lowest excited doublet state of di-*tert*-butyl nitroxide has been estimated as about $18\,200\ cm^{-1}$ and it has been concluded that energy transfer is impossible in the fluorescence quenching of Rhodamine B and rubrene by this radical. However, energy may be effectively transferred with rate constants close to the diffusion constant in the quenching of both high triplet states [6] and singlet states. At present the relative contributions of the three mechanisms to quenching of excited singlet states is a problem that is open to discussion. Further experiments with different classes of compounds are needed to support any theories on the excited state–radical interactions.

In this work we have investigated the mechanism of quenching of singlet oxygen by different nitroxy radicals in liquid solution.

2. Experimental details

The investigations were carried out using laser flash photolysis apparatus described elsewhere [15]. Solutions of anthracene (1×10^{-4} M) and protoporphyrin IX (1×10^{-5} M) were used as $^1O_2$ sensitizers. The air-saturated solutions were excited in a 1 cm quartz cell with unfocused radiation from the second harmonic of a Q-switched ruby laser ($\lambda = 347$ nm; $\tau_{0.5} = 20$ ns; $E \leqslant 10$ mJ). The luminescence of $^1O_2$ at 1.27 μm was recorded using an FD-10 G germanium photodiode at an angle of 90° to the laser beam. The radiation from the $^1O_2$ was analysed with an interference light filter (transmission at 1.27 μm, 73%; $\Delta\lambda_{0.5} = 34$ nm) in combination with a silicon plate which cut off light with $\lambda < 960$ nm. The photodiode-detected signal was sent to a broad band amplifier with a gain factor of about 10^3 and then on to an oscilloscope. The time resolution of the entire recording system was better than 1 μs. A diffusion-scattering quartz plate was installed in front of the cell to reduce the laser radiation density. Under these conditions the $^1O_2$ luminescence decay kinetics followed an exponential law. All the experiments were carried out at 20 ± 1 °C.

The temperature dependence of the lifetime of $^1O_2$ in solutions with and without radicals was determined in an especially adapted cryostat in the range +20 to −30 °C. The absorption spectra of the solutions were recorded using a Specord UV−visible spectrophotometer.

Anthracene (Aldrich) and protoporphyrin IX dimethyl ester (see ref. 16) were used without further purification. The solvents were spectroscopic grade toluene and doubly distilled chloroform, acetonitrile and ethanol.

3. Results and discussion

The following nitroxy radicals were used.
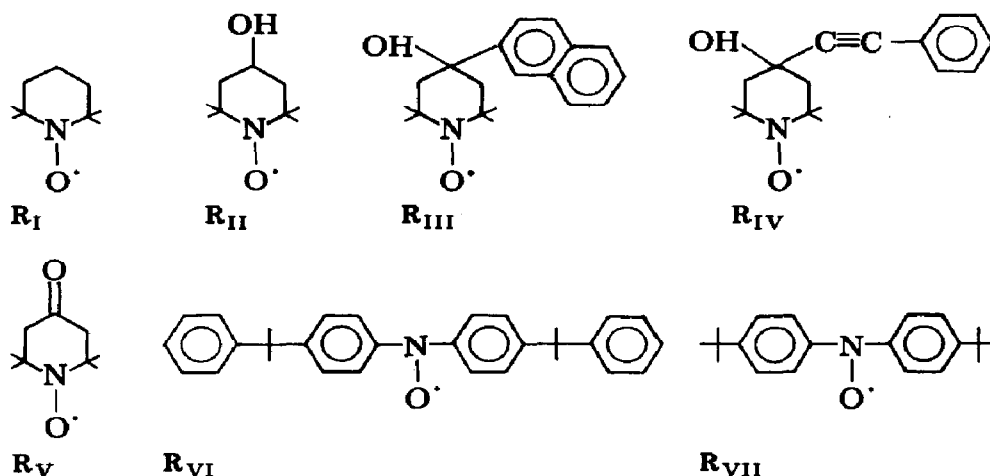
When radicals were added to the solutions (approximate concentration, 10^{-2} - (7×10^{-1}) M) the lifetime of the $^1O_2$ was observed to decrease. The luminescence decay rate constant k_{eff} was accurately described by the expression

$$k_{eff} = \tau_0^{-1}(^1\Delta_g) + k_q[R]$$

where $\tau_0(^1\Delta_g)$ is the lifetime of singlet oxygen in the pure solvent and k_q is the rate constant of luminescence quenching by the radical.

From the experiments it has been found that $\tau_0(^1\Delta_g)$ is 14 ± 1.5 μs, 28 ± 2 μs, 65 ± 5 μs and 250 ± 20 μs is ethanol, toluene, acetonitrile and chloroform respectively. The values obtained for $\tau_0(^1\Delta_g)$ are in good agreement with the $^1O_2$ lifetime data obtained directly [17 - 19]. $\tau_0(^1\Delta_g)$ is only slightly dependent on the solvent temperature and, for example, in toluene it increases to 34 ± 2 μs as the temperature decreases to −60 °C. The temperature dependence of k_q has been determined from the temperature dependences of $\tau_0(^1\Delta_g)$ and k_{eff} (in the presence of about 0.2 - 0.5 M aliphatic radicals and about 0.01 M aromatic radicals). The k_q are found to follow closely the Arrhenius law $k_q = A \exp(-E_a/RT)$. The k_q, E_a and A obtained as well as the energy E_{CT} of the total CT states for the oxygen−

TABLE 1

Kinetic data of $^1O_2$ luminescence quenching by nitroxy radicals

Solvent	k_q $(M^{-1}\ s^{-1})$	E_a [a] $(kcal\ mol^{-1})$	$\log A$ [b]	E_{CT} [c] (cm^{-1})	ν_{max} (cm^{-1})
R_I					
Toluene	$(5.5 \pm 0.17) \times 10^5$	2.0	7.2		21000
Acetonitrile	$(4.3 \pm 0.27) \times 10^5$			11800	
Ethanol	$(2.5 \pm 0.1) \times 10^5$				22000
R_{II}					
Toluene	$(1.56 \pm 0.05) \times 10^5$	1.3	6.2		
Chloroform	$(1.14 \pm 0.04) \times 10^5$				
Acetonitrile	$(1.4 \pm 0.1) \times 10^5$			12200	
Ethanol	$(1.24 \pm 0.1) \times 10^5$				22000
R_{III}					
Chloroform	$(1.0 \pm 0.1) \times 10^5$	1.8	6.3		22500
R_{IV}					
Chloroform	$(7.5 \pm 0.8) \times 10^4$	0.32	5.1		23000
Ethanol	$(1.7 \pm 0.15) \times 10^5$				22500
R_V					
Toluene	$(1.2 \pm 0.1) \times 10^6$	1.6	7.3		
Acetonitrile	$(1.3 \pm 0.15) \times 10^6$			13500	
Ethanol	$(1.3 \pm 0.1) \times 10^6$				22800
R_{VI}					
Toluene	$(2.5 \pm 0.2) \times 10^6$	1.2	7.3	13200	17500[d]
R_{VII}					
Toluene	$(1.6 \pm 0.15) \times 10^7$	0.24	7.4		17500[d]
Acetonitrile	$(1.7 \pm 0.12) \times 10^7$				

[a] Error, ±10%.

[b] Error, ±0.15. A is in litres per mole per second.

[c] $E_{CT} = E_{1/2}^{ox}(R^{\cdot}/R^+) - E_{1/2}^{red}(O_2^-/O_2)$ where $E_{1/2}^{ox}(R^{\cdot}/R^+)$ is 0.64 V versus the standard calomel electrode (SCE), 0.69 V(SCE), 0.85 V(SCE) and 0.81 V(SCE) for R_I, R_{II}, R_V and R_{VI} respectively [20] in CH_3CN; $E_{1/2}^{red}(O_2^-/O_2) = -0.82$ V(SCE) in CH_3CN [21].

[d] Energy position of the long wavelength shoulder of the radical absorption spectrum.

radical systems and the positions ν_{max} of the long wavelength bands in the absorption spectra of the radicals are presented in Table 1.

From the experimental data it follows that aliphatic nitroxy radicals are weak quenchers of singlet oxygen with $k_q \approx 10^5$ - 10^6 M^{-1} s^{-1}. Thus the hypothesis that a nitroxy radical such as R_{II} is as effective a quencher of $^1O_2$ as 1,4-diazabicyclo[2.2.2]octane, advanced in ref. 22 on the basis of indirect evidence, is not corroborated by the data of the present study.

No short-lived products of reactions between $^1O_2$ and $^2R^{\cdot}$ were observed in the laser photolysis of solutions containing about 0.2 - 0.5 M aliphatic radicals or about 0.01 M aromatic radicals. With the aim of determining the contribution of the chemical reaction to the quenching process we first studied the rate of consumption of a standard compound (as in ref. 16), *i.e.* anthracene, in reaction with $^1O_2$ under continuous irradiation at 350 - 380 nm. No radical consumption was observed in a similar experiment using toluene containing a large concentration of radicals where practically all the $^1O_2$ molecules decayed through reaction with $^2R^{\cdot}$. Hence the $^1O_2$ luminescence quenching occurs via a physical mechanism and the rate constant of the chemical reaction does not exceed 10^3 M^{-1} s^{-1}.

The energy transfer mechanism cannot be responsible for the quenching of the $^1\Delta_g$ state of oxygen (7882 cm^{-1}) by radicals since the lowest excited doublet states of $^2R^{\cdot}$ are too high (*cf.* Table 1). CT interactions cannot play any significant role either. The CT levels of $(O_2^{-}\cdots R^{+})$ are much higher than the $^1\Delta_g$ state of oxygen and, besides, the rate constants k_q do not increase sharply with solvent polarity. The very small variations in k_q are apparently due to the different degree of solvation of the radicals in the solvents investigated.

Thus only the electron-exchange interactions leading to enhanced intersystem crossing can be responsible for $^1O_2$ luminescence quenching by radicals:

$$^1O_2 + {}^2R^{\cdot} \rightleftharpoons {}^2(O_2\cdots R^{\cdot})^* \rightsquigarrow {}^2(O_2\cdots R^{\cdot}) \longrightarrow {}^3O_2 + {}^2R^{\cdot} \qquad (6)$$
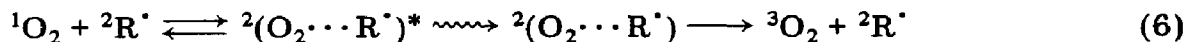
The rate constants k_q of singlet oxygen quenching (about 10^5 - 10^7 M^{-1} s^{-1}) are somewhat smaller than those for the quenching of the lowest triplet states of anthracene, perylene and tetracene by different nitroxy radicals ($k_q \approx 10^6$ - 10^8 M^{-1} s^{-1} [2, 6, 7]). It is believed that for these aromatic hydrocarbons the quenching also occurs via exchange interactions [7, 11]. This may be due to the fact that the final state density and the Franck–Condon factor for the radiationless transition are smaller in the system ($^1O_2\cdots{}^2R^{\cdot}$) than in (^{3}hydrocarbon$\cdots{}^2R^{\cdot}$).

In the aliphatic radicals R_I - R_V the unpaired electron is almost localized on the paramagnetic $>N\!-\!O^{\cdot}$ centre [14] and the low k_q are probably due to the strong screening of this centre by methyl groups. In the aromatic radicals R_{VI} and R_{VII} the spin density is characteristically more delocalized over the molecular fragments and the steric hindrance about the $>N\!-\!O^{\cdot}$ centre is lower [14]. It is therefore completely reasonable that the k_q should be higher for radicals R_{VI} and R_{VII} than for R_I - R_V. It is interesting to note that the increase in the quenching rate constants is mainly due to the decrease in activation energy E_a of reaction (6). Of the radicals R_I - R_V, R_V has a somewhat higher k_q. This may be due to the fact that the radicals R_I - R_{IV} have an "armchair" configuration while that of R_V is "twisted" [14]. In the latter configuration the $>N\!-\!O^{\cdot}$ centre cannot be as strongly screened by methyl groups as in the former configuration.

Thus the quenching of the $^1\Delta_g$ state of oxygen and the lowest triplet states (T_1) of hydrocarbons by radicals takes place with low rate constants

(about 10^5 - 10^8 M^{-1} s^{-1}) via the enhanced intersystem crossing mechanism on account of exchange interaction. It is known that the singlet states (S_1^*) of hydrocarbons are also quenched by the enhanced intersystem crossing mechanism but with rate constants close to the diffusion constant k_{diff} [11]. Such a sharp difference cannot be explained solely by quenching via the exchange mechanism involving a transition of the hydrocarbon to the second triplet level (T_2), i.e. by the considerable decrease in the energy gap of the transition ($\Delta E(S_1^*-T_2) \ll \Delta E(S_1^*-T_1)$). For most aromatic hydrocarbons the T_2 level is below the S_1^* state, but for pyrene and 1,2-benzanthracene it is above it [23]; nevertheless $k_q \approx k_{diff}$ in all cases [9, 10]. The estimates for the energies of the CT complexes of tetramethylpiperidine-N-oxide (R_I) [7], di-*tert*-butyl nitroxide and 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxide (R_{II}) with aromatic hydrocarbons show that the CT levels are below the S_1^* state but above the T_1 state. Hence, the CT interactions must be the main contributor to the fluorescence quenching and irrespective of the solvent polarity the quenching rate constant must be close to k_{diff}. Furthermore, there is experimental evidence indicating that the CT interactions as a rule result in enhancement of intersystem crossing in the excited hydrocarbon [24 - 26].

The most pressing problem today is to find organic compounds for which the conditions $E(S_1^*) < E_{CT}$ and $E(S_1^*) < E(^2R^{\cdot *})$ are satisfied, i.e. for which the CT and energy transfer processes can be neglected. For these compounds the fluorescence quenching will occur only through electron-exchange interactions in collision complexes. This will make possible a comparison of the fluorescence quenching effectiveness of these compounds and of $^1O_2$ luminescence by the enhanced intersystem crossing exchange mechanism and will probably give an estimate of the contribution of CT interactions in the quenching of aromatic hydrocarbons.

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