MECHANISM OF SINGLET OXYGEN INTERACTION WITH SPIN TRAP α-PHENYL-*N-tert*-BUTYLNITRONE

ALEXANDER P. DARMANYAN

Institute of Chemical Physics, Academy of Sciences of the U.S.S.R., 117334 Moscow (U.S.S.R.)

GALINA MÓGER

Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Pusztaszeri út 59 - 67, 1525 Budapest (Hungary)

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Summary

The mechanism of singlet oxygen ($^1O_2$) quenching by α-phenyl-*N-tert*-butylnitrone was investigated by the laser flash photolysis technique using 1,3-diphenylisobenzofuran and rubrene as $^1O_2$ acceptors. It was found that the quenching is substantially a reversible electron transfer process with a rate constant of $(8.2 \pm 0.9) \times 10^6$ M^{-1} s^{-1} and that the rate constant for chemical reaction is equal to $(1.4 \pm 0.1) \times 10^5$ M^{-1} s^{-1} at 20 °C. From the triplet–triplet energy transfer method the position of the lowest triplet state of nitrone was estimated to be $16\,200 \pm 100$ cm^{-1}.
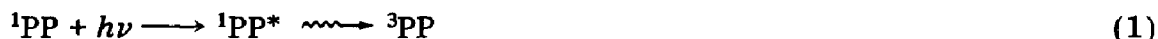
1. Introduction

A simple and convenient spin trap method was developed in the late 1960s for studying the nature of free radicals generated in the course of chemical reactions [1, 2]. As a rule, free radicals are short lived, *i.e.* their steady state concentrations are low and their direct detection by electron spin resonance (ESR) is impossible. The essence of the method consists in accepting the short-lived radicals with a spin trap, a nitroso compound or nitrone, specially added to the solution. This results in the formation of sufficiently stable nitroxyl radicals (spin adducts) which can easily be detected and have a typical ESR spectrum. By now, a wealth of information has been amassed concerning the nature and reactivities of short-lived radicals in different chemical reactions with this method (see for example refs. 3 - 5). The indirect spin trap method, however, has a disadvantage associated with the necessity to introduce into solution a large quantity (0.05 - 0.5 M) of a foreign compound, the radical acceptor. To be able to interpret the experimental data correctly it is necessary to know the mechanism of interaction between the spin trap and the various short-lived intermediates. In addition, it is of interest to investigate the possibility of

involvement of the spin adducts themselves as free radicals in the reaction under study [5].

Before ESR investigations of reactions involving singlet oxygen ($^1O_2$) are started, it is first necessary to establish the mechanism of $^1O_2$ interaction with spin traps. In this work we have used a laser photolysis technique to study the quenching of $^1O_2$ by a spin trap, α-phenyl-N-$tert$-butylnitrone (PBN), in benzene at 20 °C.

2. Experimental details

The absorption spectra and decay kinetics of short-lived intermediates were investigated by means of a nanosecond laser photolysis apparatus described elsewhere [6]. $^1O_2$ was obtained by exciting air-saturated proto-porphyrin (PP) solutions concentrated to 5×10^{-6} M with the second harmonic of an Nd^{3+} laser ($\lambda = 530$ nm; $\tau = 15$ ns; $E \lesssim 0.1$ J). This gives rise to the following reactions:

$$^1PP + h\nu \longrightarrow {}^1PP^* \rightsquigarrow {}^3PP \tag{1}$$

$$^3PP + O_2 \longrightarrow {}^1PP + {}^1O_2 \ ({}^1\Delta_g \text{ state}) \tag{2}$$

For porphyrins the energy splitting $\Delta E_{S_1-T} \approx 3500 - 4000$ cm^{-1} and the generation of $^1O_2$ may occur only in the course of quenching of the triplet state of molecules (reaction (2)) with a quantum yield close to unity [7]. The lifetime and reactivity of $^1O_2$ were determined from the rate of consumption of the effective $^1O_2$ acceptor, 1,3-diphenylisobenzofuran (DPBF) [8 - 11]. The total amount of DPBF consumed after the laser flash did not exceed 1% - 2% and the solution decolouration rate was exponential. The solutions were probed with an interference light filter at $\lambda = 435$ nm ($\Delta\lambda_{1/2} = 10$ nm). The experiments were carried out in a 1 cm quartz cell at 20 °C. The triplet energy donors (about 10^{-4} M) were excited by the second harmonic ($\lambda = 347$ nm) of a ruby laser.

Photolysis of air-saturated PP solutions (3×10^{-5} M) in the presence of tetracene (1.5×10^{-4} M) and PBN (3.3×10^{-4} M) was carried out in a 2 mm cell under continuous illumination from a xenon lamp (120 W) passed through a light filter ($\lambda \geqslant 480$ nm). The rate of consumption of tetracene and PBN was determined near the maxima of the $S_0 \rightarrow S_1^*$ absorption band. The shape of the $S_0 \rightarrow S_1^*$ spectra did not change during the reaction.

The absorption spectra of the samples were recorded with a Specord UV−visible spectrophotometer, and the fluorescence and phosphorescence spectra with an Aminco−Bowman spectrofluorometer.

PBN (EGA−Chemie), DPBF (Fluka), benzophenone and duroquinone (AKZO Research Laboratories), 1,2,5,6-dibenzanthracene, 1,2-benzanthracene and phenazine (Gee Lawson Chemical Ltd.), anthracene, 9,10-dichloro-anthracene, rubrene and tetracene (Aldrich) and PP were used as supplied, without further purification. The solvent was twice-distilled "spectroscopic grade" benzene.
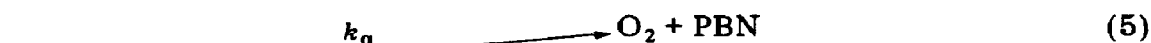
3. Results and discussion

In the presence of PBN a laser flash causes $^1O_2$ decay via radiationless energy transfer to solvent molecules:

$$^1O_2 \xrightarrow{k_d} O_2 \tag{3}$$

as a result of a chemical reaction with DPBF which yields the peroxide [12]:

$$^1O_2 + DPBF \xrightarrow{k_r^*} DPBF \cdot O_2 \tag{4}$$

or via the competing reactions with the spin trap molecules:

$$^1O_2 + PBN \begin{array}{c} \xrightarrow{k_q} O_2 + PBN \qquad (5) \\ \xrightarrow{k_r} products \qquad (6) \end{array}$$

Solution of the system of kinetic equations relating to reactions (3) - (6) gives the following formula for the $^1O_2$ decay rate:

$$[^1O_2] = [^1O_2]_0 \exp(-k_{eff}t) \tag{7}$$

where

$$k_{eff} = k_d + k_r^*[DPBF] + (k_r + k_q)[PBN] \tag{8}$$

The effective $^1O_2$ decay rate constants k_{eff} were determined from decolouration curves for DPBF solutions after a laser flash (see for example refs. 10 and 11). It was established experimentally that the fluorescence quantum yield of PP (about 0.15 [7]) and the triplet state lifetime (about 5×10^{-4} s) do not decrease in practice due to addition of PBN to solutions up to concentrations of 0.05 M, *i.e.* the quenching of the singlet and triplet states of PP by nitrone occurs at rate constants of less than 10^9 M^{-1} s^{-1} and 10^4 M^{-1} s^{-1} respectively. Thus, within the investigated PBN concentration range the PP triplet decays only via the reaction with oxygen (reaction (2)).

The sum $k_r + k_q$ was calculated from the k_{eff} *versus* [PBN] relationship for a constant DPBF concentration equal to 2.48×10^{-5} M. From the experimental data (Fig. 1) it was found that $k_r + k_q = (8.3 \pm 0.9) \times 10^6$ M^{-1} s^{-1}.
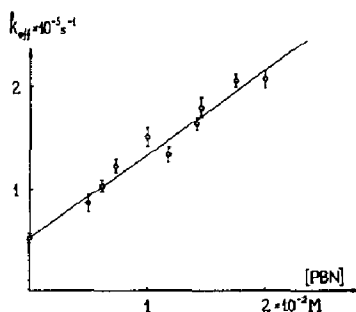

Fig. 1. Effective rate constant of $^1O_2$ decay as a function of the PBN concentration ([DPBF] = 2.48×10^{-5} M).

Addition of DPBF to the system for $^1O_2$ detection may lead to deleterious side reactions. In addition, similar investigations were carried out with one compound, rubrene, which was both the sensitizer and the $^1O_2$ acceptor [10]. The value of $k_r + k_q$ was found to be the same, within experimental accuracy (about 10%), in both experiments.

No short-lived intermediates absorbing in the range 400 - 800 nm have been detected in laser-excited air-saturated PP plus PBN solutions for nitrone concentrations of up to about 0.05 M. To estimate the contribution of the chemical reaction (6) in the quenching of $^1O_2$ with nitrone we studied the consumption rate W of the standard compound, tetracene, as well as that of PBN under constant illumination. In these experiments, the losses of tetracene and PBN were independently monitored. In both experiments the concentration of PP was 3×10^{-5} M, i.e. the $^1O_2$ generation rate was the same. During illumination no PP was consumed. According to ref. 13 (T $\equiv$ tetracene)

$$\frac{k_r}{k_r^*} = \frac{\log([PBN]_f/[PBN]_0)}{\log([T]_f/[T]_0)} \tag{9}$$

Formula (9) gives k_r for PBN relative to k_r^* for tetracene. It was established experimentally that $W = 2.1 \times 10^{-7}$ M s^{-1} and $W = 5.2 \times 10^{-9}$ M s^{-1} for tetracene and PBN respectively. Therefore, the ratio k_r/k_r^* is equal to $(1.14 \pm 0.07) \times 10^{-2}$. Since in benzene $k_r^* = 1.2 \times 10^7$ M^{-1} s^{-1} [14], it can be found that, for PBN, $k_r = (1.4 \pm 0.1) \times 10^5$ M^{-1} s^{-1}. Reaction (6) yields a diamagnetic product [15], apparently an ene peroxide [16]. Hence, the $^1O_2$ quenching mainly follows route (5) with a rate constant k_q of 8.2×10^6 M^{-1} s^{-1}.

Reaction (5) may occur via either reversible electron transfer or energy transfer to the sufficiently low triplet state of PBN. To determine the reaction mechanism in this case the position of the triplet state of nitrone was determined. The long wavelength maximum of the absorption spectrum of PBN is near 33 200 cm^{-1} ($\epsilon = 1.6 \times 10^4$ M^{-1} cm^{-1}) and there was no fluorescence or phosphorescence (at 77 K), i.e. the quantum yields for the processes are both less than 5×10^{-4}. The energy of the PBN triplet state was determined by the method of triplet–triplet (T–T) energy transfer from different sensitizers, triplet energy donors (see for example ref. 17). Photoexcitation of the triplet energy donors gives rise to the following reactions (D $\equiv$ donor):

$$D(T) + PBN(S_0) \xrightarrow{k_Q} D(S_0) + PBN(T) \tag{10}$$

$$PBN(T) \xrightarrow{k_T} PBN(S_0) \tag{11}$$
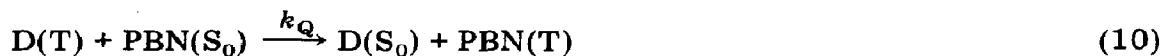
No T–T absorption of nitrone was observed during the sensitizer quenching. Neither was the T–T absorption observed during direct excitation of PBN (about 0.02 M) at the long wavelength extreme of the absorption band by radiation at 347 nm. Hence, for PBN, $k_T > 10^8$ s^{-1}. The short triplet state

TABLE 1

Triplet energies and triplet quenching rate constants of the sensitizers
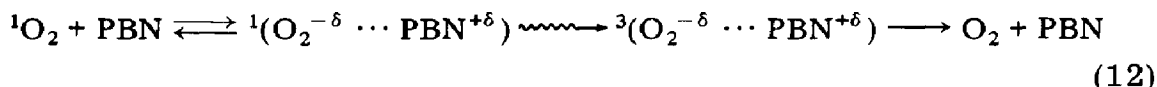
Sensitizer	E_T [a] (cm^{-1})	k_Q $(M^{-1} s^{-1})$
Benzophenone	24400	$(2.6 \pm 0.2) \times 10^9$
Duroquinone	19300	$(2.0 \pm 0.08) \times 10^9$
1,2,5,6-dibenzanthracene	18300	$(3.2 \pm 0.08) \times 10^9$
1,2-benzanthracene	16500	$(1.7 \pm 0.07) \times 10^9$
Phenazine	15400	$(1.7 \pm 0.1) \times 10^8$
Anthracene	14700	$(2.0 \pm 0.05) \times 10^7$
9,10-dichloroanthracene	14000	$(4.9 \pm 0.2) \times 10^5$
Tetracene	10250	$< 1 \times 10^4$

[a]See refs. 18 and 19.
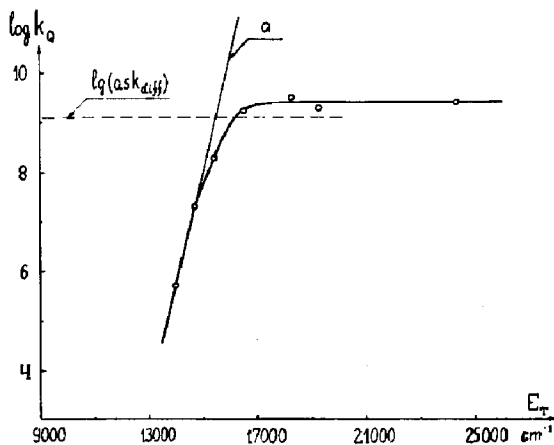
Fig. 2. Sensitizer triplet quenching rate constant as a function of the lowest triplet state energies: line a, the theoretical $\Delta(\log k_Q)$ vs. $\Delta E_T/2.303RT$ relationship.

lifetime is apparently due to the great contribution of the charge transfer state in the nitrone triplet structure.

The relationship between the quenching rate constant k_Q and the triplet state energy E_T of the sensitizers was determined experimentally (Table 1 and Fig. 2). The slope of the experimental log k_Q versus E_T relationship coincides with the theoretical value $(2.303RT)^{-1}$ expected for quenching occurring exclusively via the energy transfer mechanism [20]. For benzophenone, duroquinone and 1,2,5,6-dibenzanthracene, k_Q is limited by molecular diffusion. Since the spin is not affected in reaction (10), the averaged diffusion constant $k_{diff} = 2.6 \times 10^9$ M^{-1} s^{-1}. According to ref. 21 the sensitizer and PBN triplet states are isoenergetic when $k_Q = 0.5k_{diff}$. From Fig. 2 it follows that the energy E_T of the lowest PBN triplet state is $16\,200 \pm 100$ cm^{-1}. Therefore, $^1O_2$ quenching by nitrone via the energy transfer mechanism is substantially endothermic and its rate constant cannot be greater than 10^3 M^{-1} s^{-1}.

It may be concluded that reaction (5) takes the reversible electron transfer route, as assumed in ref. 16 for nitrones. Oxygen, to say nothing of $^1O_2$, is a stronger electron acceptor than PBN. According to the literature, the reduction potentials $E_{1/2}$ in dimethylformamide are -0.87 V [22] and -2.21 V [23] (measured with respect to a saturated calomel electrode) for oxygen and PBN respectively. It appears that reaction (5) involves formation of a short-lived charge transfer complex in the excited state in which PBN plays the role of an electron donor:

$$^1O_2 + PBN \rightleftharpoons {}^1(O_2^{-\delta} \cdots PBN^{+\delta}) \leadsto {}^3(O_2^{-\delta} \cdots PBN^{+\delta}) \longrightarrow O_2 + PBN$$

$$(12)$$

Thus PBN is a strong enough $^1O_2$ deactivator ($k_r + k_q = 8.3 \times 10^6$ M^{-1} s^{-1}). The $^1O_2$ quenching by nitrone is mainly a reversible electron transfer process (reaction (12)). In photochemical experiments the presence in the system of PBN with a sufficiently low triplet (16 200 cm^{-1}) may be responsible for the effective sensitizer triplet quenching by the energy transfer mechanism.

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