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Photolysis of endoperoxides in the presence of nitroxides: a laser flash photolysis study with optical and ESR detection

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Time-resolved electron paramagnetic resonance spectroscopy, transient absorption, and phosphorescence spectroscopy were used to investigate the spin polarization of a nitroxide free radical induced by interaction with singlet oxygen (1O2). The latter was generated by photolysis of endoperoxides of two anthracene derivatives. Although both anthracene endoperoxides are structurally similar, opposite spin polarization of the nitroxide was observed. Photolysis of one endoperoxide leads to absorptive nitroxide spin polarization due to interaction with the generated 1O2. Photolysis of the other endoperoxide generated emissive nitroxide spin polarization, probably due to interaction of the endoperoxide triplet states with nitroxides.

1. Introduction

Spin polarization of stable radicals, such as nitroxides, generated upon deactivation of electronically excited singlet and triplet states, has been under investigation since its discovery in the 1980s. Initial investigations involving radicals interacting in solution with photoexcited organic species3–4 led to the development of the radical-triplet pair mechanism (RTPM) with Shushin making a significant contribution into the theory of RTPM.5–8 RTPM is discussed in detail for bimolecular collision complexes9–13 between photoexcited states and nitroxides, covalently linked systems,14 coordination complexes,15 and host–guest complexes.16 In general, in non-viscous solvents quenching of excited triplet states (in Boltzmann equilibrium) of organic molecules by a stable radical (nitroxide) leads to net emissive (E) polarization of the ESR signal of the nitroxide, whereas quenching of excited singlet states leads to net absorptive (A) polarization of nitroxide.1,19 Thus, there are two types of RTPM: QP-RTPM and DP-RTPM, which stand for quartet precursor of a pair and doublet precursor of a pair, respectively. Further details on the theory and practical implication can be found in the literature for QP-RTPM and DP-RTPM.20–24 In brief, QP-RTPM leads to the overpopulation of the doublet D±1/2 levels of the nitroxide and thus leads to net emissive transient ESR signals. It is independent of the sign of zero-field splitting in the triplet state. In order for this mechanism to operate, some magnetic interaction (e.g., zero-field splitting or hyperfine coupling) must be effective in mixing D±1/2 and Q±3/2 states in the collision complex, i.e., in the region of non-zero spin exchange interaction J between the excited triplet and the doublet (D) states. In addition, a negative sign of J and fast deactivation of the D±1/2 states of the encounter complex are assumed.

E or A polarization of nitroxide cannot only disappear during spin–lattice relaxation time (T1) of several microseconds but also change its sign, A → E or E → A. Therefore, nitroxides provide valuable information on temporal changes of the spin state of organic molecules in solution on a microsecond time scale.1,13,17,19

Obi et al.26 observed an unexpected result: quenching of photoexcited molecules in the triplet state in air-saturated solutions in the presence of nitroxides led to an A-pattern of polarization instead of the expected E-pattern. The authors reported that molecules in the triplet state quickly react with molecular oxygen O2(Σg+) or 3O2 to generate singlet oxygen, O2(Δg) or 1O2. Quenching of 1O2 by nitroxide leads to A-polarization of the latter.25,26 Our group77 has confirmed these results.25,26 In particular, we demonstrated that the decay time of nitroxide spin polarization correlates directly with the lifetime of 1O2 as measured by its phosphorescence.27

Only A-polarization was observed in these air-saturated solution studies.25–27 Under much higher concentration of nitroxide or under much lower concentration of 3O2, the quenching of triplet molecules by nitroxide will dominate the quenching by 3O2. Under such conditions only E-polarization of nitroxide...
is expected, assuming a rapid $S_1 \rightarrow T$ intersystem crossing as observed in the triplet sensitizer benzophenone.

To the best of our knowledge, in all reports to date on $^{1}O_{2}$ induced nitroxide spin polarization, $^{1}O_{2}$ was produced by triplet sensitization in a bimolecular reaction by quenching of triplet states of photoexcited sensitizers with $^{3}O_{2}$. This journal is © The Royal Society of Chemistry and Owner Societies 2014

In the current study, we generated $^{1}O_{2}$ in a monomolecular reaction by photolysis of two endoperoxides, 1,4-dimethoxy-9,10-diphenyl-1,4-peroxyanthracene (MOA-O$_2$) and 1,4-dimethyl-9,10-diphenyl-1,4-peroxyanthracene (MA-O$_2$) (Scheme 1), in the presence of nitroxide. To our surprise, opposite spin polarization of the nitroxide was observed when using the two structurally similar anthracene endoperoxides to generate $^{1}O_{2}$. The goal of this study is to understand mechanisms leading to opposite spin polarization. To elucidate the mechanisms, we used laser flash photolysis with optical transient detection and ESR detection.

2. Experimental

2.1. Materials

Toluene of spectrophotometric grade, methylcyclohexane, carbon tetrachloride, spin probe 4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl (OTEMPO) and 5,10,15,20-tetraphenylporphyrin were purchased from Aldrich. All purchased compounds were used as received. Endoperoxides of 1,4-dimethoxy-9,10-diphenyl-1,4-peroxyanthracene (MOA-O$_2$) and 1,4-dimethyl-9,10-diphenyl-1,4-peroxyanthracene (MA-O$_2$) were synthesized as described elsewhere.\textsuperscript{28} Chemical structures of endoperoxides and corresponding compounds after photolysis are depicted in Scheme 1.

2.2. Sample preparation

In a typical TR-ESR experiment, 0.6 mM of OTEMPO, and an amount of endoperoxide such that its absorbance (OD) at 308 nm through a 0.3 mm path length was approximately 0.2, were dissolved in 50 mL of toluene. Other compounds that were subjected to photoirradiation had OD $\sim$ 0.2. Solutions were deoxygenated when necessary by Ar bubbling for 10 min. The solution was pushed by a peristaltic syringe pump through the ESR cavity, typically at a flow rate of 0.5 mL min$^{-1}$, and discarded.

For determination of the $^{1}O_{2}$ quenching rate constants by MA and MOA, tetraphenylporphyrin solutions in toluene were prepared at a concentration such that the absorbance at 532 nm was $\sim$0.1 at a 1 cm path length.

2.3. Instrumentation and data acquisition

The 2D TR-ESR experiment was performed using a Bruker E-580 X-band spectrometer equipped with a cylindrical ER 4103TM cavity (Bruker) with optical access. Inside the cavity, the solution passed through a flat quartz cell (ER 160 FG-C from Bruker) for irradiation. Transient signals were generated by photoexcitation with pulses (308 nm) from a Lambda Physik excimer laser (CompEx). Pulse length was 10 ns, pulse frequency was 15 Hz and pulse energy was 60 mJ per pulse. The ESR signal at a specific magnetic field position was collected after the preamplifier (20 Hz – 400 kHz) with a digital oscilloscope (Le Croy 9450A operating at 300 MHz). Time resolution, controlled by the preamplifier, was on the order of 200 ns. Field advancement was coordinated with the oscilloscope acquisition by a pulse generator (DG535 from Stanford Research Systems) through a home-written program using Labview. Typically, the 2D acquisition had 256 field positions along one field axis and 400 points spanning 5 to 100 µs on the time axis. At each field position, an average of 80 transients were acquired. Finally, the matrix of data was subtracted by an average of 14 off-resonance transients signal (7 from low field and 7 from high field values) and elaborated using Matlab. The shown kinetic traces of nitroxide ESR are presented as averages of the three $^{14}$N components.

Transient absorption measurements employed the pulses from a Lambda Physik excimer laser (CompEx, 308 nm, 10 ns pulse length) and a computer-controlled system that has been described elsewhere.\textsuperscript{29}

Time-resolved $^{1}O_{2}$ phosphorescence measurements were performed on a Fluorolog-2 fluorometer (HORIBA Jobin Yvon) in conjunction with NIR-sensitive PMT (H9170-45, Hamamatsu). Additional details about signal amplification and storage have been reported elsewhere.\textsuperscript{27} Pulsed laser excitation was delivered by a Lambda Physik excimer laser (CompEx, 308 nm, 10 ns pulse length) or a Spectra Physics Nd:YAG laser (GCR-150-30, 532 nm, 7 ns pulse length).

3. Results and discussion

3.1. Spin polarization of OTEMPO under photolysis of MA-O$_2$

It is well-known that photolysis of endoperoxides leads to formation of $^{1}O_{2}$\textsuperscript{28,29} (Scheme 1). In addition, O–O cleavage can occur as side reaction upon photolysis, which forms rearrangement products of endoperoxides (not shown in Scheme 1). MA-O$_2$ was photolyzed inside the ESR cavity to produce $^{1}O_{2}$ (Scheme 1). In the presence of OTEMPO, polarized ESR spectra were observed (Fig. 1) during photolysis. During the early time scale an E-pattern of OTEMPO polarization was observed (Fig. 1b; 1.6 µs), followed by an A-pattern (Fig. 1b; 5.1 µs).
The ESR spectra displayed in Fig. 1b are characteristic for OTEMPO exhibiting the three $^{14}$N hyperfine components ($a_N = 15$ G).

The longer-lived absorptive signal decayed with a lifetime of $\tau_{1/e} \sim 25 \mu$s, which is similar to the $^{1}$O$_2$ life time in toluene ($\tau_{1/e} \sim 29 \mu$s). The rate constant of $^{1}$O$_2$ quenching by nitroxide in toluene is relatively low, $k_q \sim 5 \times 10^5$ M$^{-1}$ s$^{-1}$. Therefore, considering a OTEMPO concentration of 0.6 mM, quenching by OTEMPO practically does not accelerate the $^{1}$O$_2$ decay with $\tau_{1/e} \sim 25 \mu$s. Thus, OTEMPO polarization follows the $^{1}$O$_2$ decay. This A-signal (Fig. 1) can be ascribed with confidence to DP-RTPM under quenching of $^{1}$O$_2$ by OTEMPO.

The origin of E-polarization (Fig. 1b) at the initial observation time (1.6 µs) is less clear. Endoperoxides decompose slowly at room temperature into their parent compound and $^{1}$O$_2$, and possibly other products. We suppose that MA, formed at a low concentration at room temperature, produces triplet states ($^{3}$MA*) under photoexcitation. The latter is quenched efficiently by OTEMPO with creation of E-polarization (Fig. 1b). Overall, photolysis of MA-O$_2$ (with inevitable products of its decomposition) leads to an E $\rightarrow$ A change of polarization pattern (Fig. 1).

### 3.2. Spin polarization of OTEMPO under photolysis of MOA-O$_2$

Photolysis of MOA-O$_2$ leads to even more complex observations than photolysis of MA-O$_2$. Fig. 2a shows the 2D TR-ESR surface of spin polarized OTEMPO signal obtained under photoexcitation of MOA-O$_2$ in the presence of OTEMPO. A strong E-signal of OTEMPO is observed, the time dependence of which is depicted in Fig. 2b. The emissive OTEMPO polarization decayed with a lifetime of $\tau_{1/e} = 0.9 \pm 0.1$ µs. Fig. 2c shows spectra observed at different times after the laser pulse.

Thus, the polarization patterns of OTEMPO under photoexcitation of MOA-O$_2$ (Fig. 1) and MOA-O$_2$ (Fig. 2) are very different. The most probable cause of E-polarization of OTEMPO (Fig. 2) is attributed to QD-RTPM in the interaction of triplet MOA-O$_2$ and OTEMPO. Lack of A-polarization (Fig. 2) can be related to a low concentration of $^{1}$O$_2$ in the solvent bulk. We will provide arguments below supporting these two statements.

In addition, MOA-O$_2$ decomposes at room temperature into MOA (Scheme 1) and $^{1}$O$_2$. A lifetime of $\tau_{1/e} = 69$ min at 325 K for MOA-O$_2$ has been reported previously. Some MOA is unavoidably present during measurements performed at room temperature. Therefore, we studied TR-ESR under photolysis of MOA in the presence of OTEMPO as an alternative mechanism for the observed E-polarization in Fig. 2.

### 3.3. Spin polarization of OTEMPO under photolysis of MOA

Fig. 3 presents TR-ESR observations during MOA photolysis in the presence of OTEMPO.

In the case of MOA we observed A $\rightarrow$ E change of the polarization pattern. We assume that polarization is induced by two separate RTPM mechanisms. First, DP-RTPM generated by the
radical-enhanced intersystem crossing from the excited singlet to the excited triplet state of MOA produces an A-signal. After consumption of the singlet excited states of MOA, triplet excited states interact with OTEMPO by QP-RTPM to produce an E-signal. A similar A→E polarization pattern of nitroxide has been reported for coronene, fluoranthene, and naphthalene.13

Since the time evolution of the polarized ESR signal is different for MOA (A→E polarization pattern, Fig. 3a) compared to the observed E-signal for MOA-O2 (Fig. 2b), we conclude that small amounts of impurity of MOA in MOA-O2 can only be a minor contributor to the observed ESR signal for MOA-O2 photolysis. Therefore, the emissive signal of Fig. 2 is apparently QP-RTPM, which should originate from the interaction of triplet MOA-O2 and OTEMPO.

### 3.4. Kinetic studies by transient absorption and 1O2 phosphorescence

Transient absorption experiments were performed to identify the triplet state of MOA-O2. Laser excitation of argon-saturated toluene solutions of MOA-O2 at 308 nm generated transient absorption at 420 nm, which is typical for triplet state absorption of naphthalene and anthracene derivatives.32 The transient decayed with a lifetime of 23 µs (Fig. 4, left). The interaction of these MOA-O2 triplet states with OTEMPO (QP-RTPM) is most likely responsible for the observed E-signal (Fig. 2). The MOA-O2 quenching rate constant by OTEMPO ($k_q = 3.2 \times 10^7 \text{ M}^{-1} \text{s}^{-1}$) was determined from the transient absorption decays at 420 nm at various OTEMPO concentrations, and was extracted from the slope of the plot shown in Fig. 4, right.

It has been shown, that the products of endoperoxide photolysis participate in the [4 + 2] cycloreversion affecting the yield of generated $^1$O2.38,29,33 After photolysis of endoperoxides, the anthracene derivatives MA and MOA are formed, potentially trapping $^1$O2 generated during endoperoxide formation. The efficiency of this reaction is controlled by the quenching rate constant of $^1$O2 by MA and MOA. These quenching rate constants were determined by time-resolved $^1$O2 phosphorescence quenching experiments. $^1$O2 was generated by sensitization with tetraphenylporphyrin and pulsed laser excitation (532 nm). Tetraphenylporphyrin triplet states are efficiently quenched by dissolved $^3$O2, generating $^1$O2 which shows a characteristic phosphorescence at 1270 nm. The $^1$O2 phosphorescence lifetime was measured in the presence of various concentrations of MA and MOA. The bimolecular quenching rate constants were obtained by plotting the inverse of the $^1$O2 lifetime vs. the concentration of MA or MOA. $^1$O2 was generated by sensitization with tetraphenylporphyrin with pulsed laser excitation (532 nm) in toluene at 23 °C.

![Fig. 4](image)

**Left:** Transient absorption trace monitored at 420 nm following pulsed laser excitation (308 nm) of argon-saturated acetonitrile solutions of MOA-O2 at 23 °C. **Right:** Plot of the first-order decay rate constant ($k_{obs}$) at 420 nm in the presence of different OTEMPO concentrations. The bimolecular quenching rate constant ($k_q$) was obtained from the slope.

![Fig. 5](image)

**Determination of the $^1$O2 quenching rate constant ($k_q$) by MOA and MA.** The plot shows dependence of the inverse of $^1$O2 phosphorescence lifetime ($k_{obs}$) monitored at 1270 nm vs. the concentration of MA or MOA. $^1$O2 was generated by sensitization with tetraphenylporphyrin with pulsed laser excitation (532 nm) in toluene at 23 °C.

![Fig. 6](image)

**Phosphorescence of $^1$O2 monitored at 1270 nm generated by pulsed laser excitation (308 nm) of MA-O2 (red line) and MOA-O2 (blue line) in argon-saturated toluene solutions at 23 °C.** [MA-O2] = [MOA-O2] = 2 mM, [OTEMPO] = 4 mM, 0.3 nm optical path length.
that of MA-O$_2$. In addition, the $^{1}$O$_2$ lifetime when generated by photolysis of MOA-O$_2$ is only one half of the lifetime generated from MA-O$_2$ (Fig. 6). Therefore, the amount of $^{1}$O$_2$ available for interaction with OTEMPO to generate polarization is approximately six times lower for MOA-O$_2$ compared to MA-O$_2$. The photolysis conditions in these $^{1}$O$_2$ phosphorescence experiments (0.3 mm flow cell, pulsed laser excitation at 308 nm, and concentrations described above) are almost identical to the TR-ESR experiments.

On the other hand, photolysis of MA-O$_2$ leads to a relatively high concentration of $^{1}$O$_2$ in the solvent bulk. $^{1}$O$_2$ forms an encounter pair with OTEMPO, which leads to A-polarization by the DP-RTPM (Fig. 1a).

4. Conclusions

Spin polarization induced by interaction of $^{1}$O$_2$ with OTEMPO was studied, in the case where $^{1}$O$_2$ was produced by photodecomposition of two structurally similar endoperoxides (Scheme 1). However, very different polarization patterns were observed. Under photolysis of MA-O$_2$ in the presence of OTEMPO we observed the expected A-pattern of polarization during $^{1}$O$_2$ quenching by OTEMPO. In contrast, during photolysis of MOA-O$_2$, we observed strong E-pattern of OTEMPO polarization. The opposite polarization signs for the two endoperoxides are likely caused by the higher (up to 27 times) $^{1}$O$_2$ quenching rate constants by MOA compared to MA, where $^{1}$O$_2$ released from MOA-O$_2$ excited states is quickly quenched by the reaction product MOA. Consequently, the concentration of $^{1}$O$_2$ is not sufficient for frequent encounters with OTEMPO to generate A-polarization.

In general, our TR-ESR, transient absorption and $^{1}$O$_2$ phosphorescence experiments demonstrate that photolysis of the studied endoperoxides is a rather complex process. In particular, we demonstrated that photoexcitation of MOA-O$_2$ leads to the formation of a triplet state, which generates E-polarization of OTEMPO (QP-RTPM). The kinetics of these processes are summarized in Scheme 2.

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References


