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Synthesis and Properties of a New Cationic Water-Soluble Trap of Singlet Molecular Oxygen

Véronique Nardello and Jean-Marie Aubry*

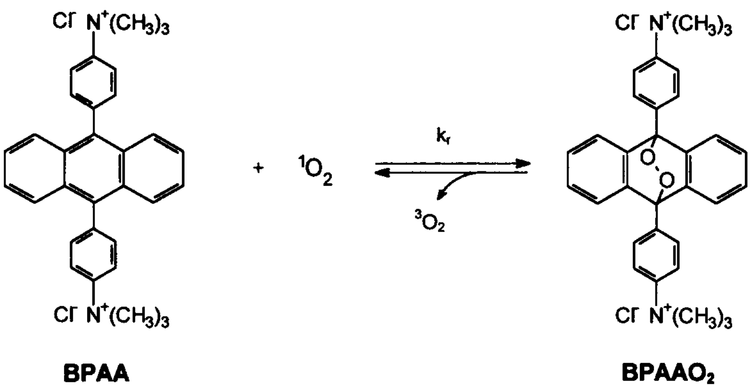
Equipe de Recherches sur les Radicaux Libres et l'Oxygène Singulet, associée au CNRS,
Faculté de Pharmacie de Lille, BP 83, F-59006 Lille, France

Abstract. A new cationic water-soluble trap of singlet oxygen ($^1O_2$, $^1\Delta_g$), the *bis*-9,10-anthracene-(4-trimethylphenylammonium) dichloride (BPAA), gives a specific endoperoxide $BPAAO_2$ as the sole product and allows the detection and the quantification of $^1O_2$ generated from cationic chemical or photochemical sources. © 1997 Elsevier Science Ltd.

Many processes involving excited singlet oxygen, $^1O_2$ ($^1\Delta_g$), (degradation of natural compounds under sunlight,[1] disproportionation of hydrogen peroxide by metal ions,[2,3] generation of $^1O_2$ by enzymes *in vivo*,[4] photodynamic effect[5]) occur in aqueous solutions. It is then required to resort to methods allowing the detection and the quantification of this excited species in such media. The most widely used and sensitive method is the chemical trapping.[6] However, most of the water-soluble traps described in the litterature bear anionic functions (COO^- and SO_3^-) which can interact with cationic chemical (e.g. the system $H_2O_2/Ca(OH)_2$[2]) or photochemical (e.g. methylene blue) sources of $^1O_2$. Accordingly, we undertook the synthesis of a cationic water-soluble trap, the *bis* 9,10-anthracene-(4-trimethylphenylammonium) dichloride (BPAA) and we report herein its spectroscopic features and a kinetic study of its reactivity with $^1O_2$.

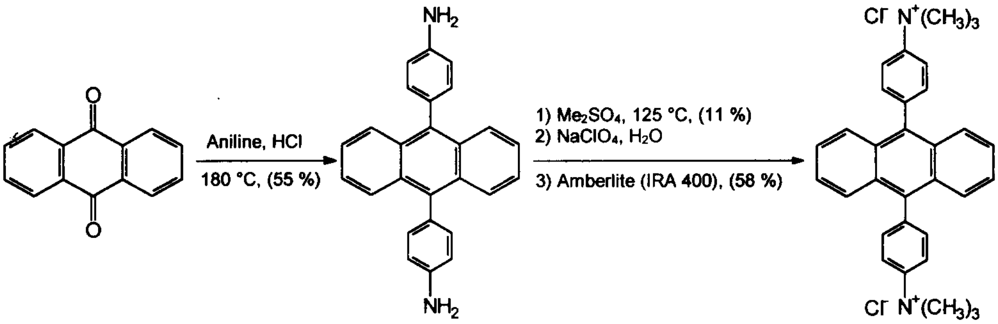
This new trap was designed on the basis of an anthracenic core which is well known to produce a stable and specific endoperoxide by reaction with $^1O_2$. In addition, the presence of two phenyl groups in the 9,10 positions enhances its reactivity towards $^1O_2$ and ensures a higher stability of this endoperoxide. The high water-solubility was obtained by grafting two quaternary ammonium functions which do not interfere with $^1O_2$ and which are resistant to usual oxidants. The plane of symmetry of the anthracenic core was kept in order to facilitate the structural determination of the products and to avoid a surfactant behavior of the trap in aqueous solution. This led to BPAA which reacts with $^1O_2$ giving as sole product the endoperoxide $BPAAO_2$ (Eq. 1).

A cationic polycyclic aromatic compound bearing water-solubilizing quaternary ammonium functions, the [2-(4-methyl-1-naphthyl)ethyl] trimethylammonium chloride (MNEA), had already been reported.[7] However, this naphthalenic derivative reacts slowly with $^1O_2$ and produces an unstable endoperoxide giving back the initial naphthalene and singlet oxygen even at room temperature.[8] Hence, this compound is more convenient as a $^1O_2$ carrier for biological systems rather than as a trap for the quantification of $^1O_2$ in aqueous media.[7]



Eq. 1

BPAA was prepared in four steps starting from anthraquinone. The synthesis of the diaminated precursor had already been described in the literature.[9] The action of pure methyl sulfate at 125 °C leads to the quaternary ammonium salt. Then, the $CH_3SO_4^-$ anion is successively replaced by ClO_4^- using sodium perchlorate and by Cl^- thanks to an ion exchange resin (Eq. 2).



Eq. 2

BPAA is highly soluble in water (> 10^{-2} M) but insoluble in apolar organic solvents. It is readily detectable by UV/visible spectrocopy in the spectral range 320-420 nm by three bands characteristic of its anthracenic core ($\varepsilon_{373\ nm} = 10330\ M^{-1}.cm^{-1}$). On the other hand, after reaction with $^1O_2$, only the absorption of substituted phenyl groups and of the peroxide bridge of the endoperoxide $BPAAO_2$ ($\varepsilon_{280\ nm} = 255\ M^{-1}.cm^{-1}$) remain (Figure 1, a and b). BPAA is the first trap allowing the quantification of $^1O_2$ generated by cationic chemical or photochemical sources. We showed that typical anionic traps such as potassium diphenylanthracene-2,3,6,7-tetracarboxylate (DPATC) and sodium diphenylanthracene-2,7-disulfonate (DPADS) interact with methylene blue modifying the absorption spectrum (Figure 1, c, d and e) and hence, its efficiency as a photosensitizer. In the same way, calcium ions 10^{-2} M, which catalyze the decomposition of hydrogen peroxide into $^1O_2$,[2] react with the ortho dicarboxylate groups of DPATC 10^{-4} M leading quantitatively to a precipitate and impeding the trapping of $^1O_2$.

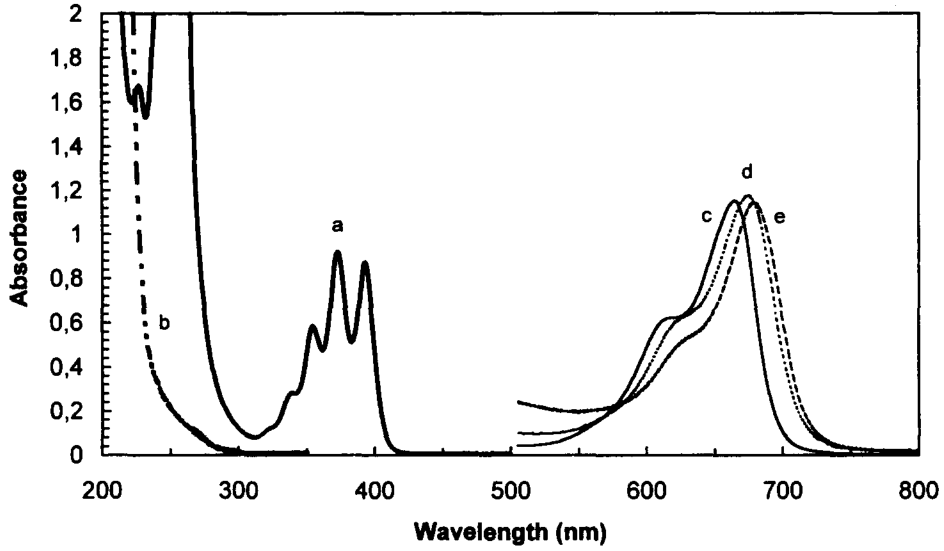


Figure 1. UV/visible spectra in H_2O of BPAA 10^{-4} M (a), $BPAAO_2$ 10^{-4} M (b), methylene blue 3×10^{-5} M alone (c) and in the presence of DPATC 10^{-2} M (d) or DPADS 10^{-2} M (e).

When $^1O_2$ is generated in an aqueous solution of BPAA, it can disappear according to three main pathways (Eq. 1, 3 and 4). The second one (Eq. 3) is the deactivation of $^1O_2$ by water ($k_d = 22.7 \times 10^4$ s^{-1} in H_2O and 1.5×10^4 s^{-1} in D_2O).[10] The two others are the chemical (Eq. 1) and the physical (Eq. 4) quenchings of $^1O_2$ by BPAA.

$$^1O_2 + \text{solvent} \xrightarrow{k_d} {}^3O_2 \qquad \text{Eq. 3}$$

$$^1O_2 + \text{BPAA} \xrightarrow{k_q} {}^3O_2 + \text{BPAA} \qquad \text{Eq. 4}$$

The overall rate constant $k_r + k_q$ was measured by flash photolysis which consists in monitoring the time-resolved decay of the singlet oxygen luminescence at 1270 nm in aqueous solutions (D_2O) containing increasing concentrations of BPAA.[11] This method led to a value of 2.0×10^7 M^{-1}.s^{-1}. The ratio $k_r / (k_r + k_q)$ was determined by submitting an aqueous solution (D_2O) of BPAA 10^{-2} M to a known amount of $^1O_2$ chemically generated by thermolysis (40 °C/ 3 h) of the naphthalenic endoperoxide $MNEAO_2$.[12] Under these conditions, the quenching of $^1O_2$ by D_2O (Eq. 3) is negligible and only equations 1 and 4 compete. Therefore, the percentage of trapped $^1O_2$ (= $[BPAAO_2]/[^1O_2]_{cumulative}$) is simply equal to the ratio $k_r / (k_r + k_q)$ which was found to be 70 %. Thus, when an unknown source of $^1O_2$ can operate in D_2O, the above experimental conditions may be applied and the $^1O_2$ yield may be readily determined from the disappearance of BPAA and the formation of $BPAAO_2$ monitored by ^1H NMR. When the quantification of $^1O_2$ must be carried out in ordinary water, the excited species can be trapped with a more dilute solution of BPAA (10^{-4} M) according to the procedure previously described for another trap.[6]

The disappearance of BPAA is then easily monitored by UV spectroscopy (Figure 1) and the involvement of $^1O_2$ is proved by the regeneration of BPAA by thermolysis of the endoperoxide (4 h/ 100 °C). At 100 °C, the decomposition of $BPAAO_2$ occurs according to a first order kinetics with a rate constant k equal to 1.2×10^{-2} min^{-1} ($t_{1/2}$ = 58 min). The chemical cycloreversion yield is very good (92.5 %) and shows that neither the presence of quaternary ammonium functions nor the aqueous medium disturb the process since for the parent hydrocarbon, diphenylanthracene (DPA), the cycloreversion yield is equal to 95 %.[13]

BPAA: *^{1}H NMR.* δ (D_2O): 3.70 (s, 18H); 7.42 (m, 4H); 7.5 (m, 4H); 7.57 (m, 4H); 8.0 (m, 4H). *^{13}C NMR.* δ (D_2O): 60.08 (CH_3); 122.9 (=CH); 129.1 (=CH); 132.04 (=CH); 135.89 (=CH); 138.01 (=C); 143.44 (=C); 149.07 (=C). **$BPAAO_2$:** *^{1}H NMR.* δ (D_2O): 3.79 (s, 18H); 7.50 (m, 4H); 8.0 (m, 4H); 7.45 (m, 4H); 7.55 (m, 4H). *^{13}C NMR.* δ (D_2O): 60.02 (CH_3); 88.0 (C-O); 123.35 (=CH); 126.42 (=CH); 131.63 (=CH); 132.21 (=CH); 137.0 (=C); 141.21 (=C); 150.0 (=C). Elementary analyses were satisfactory for both compounds.

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