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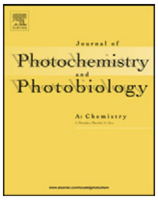

Phototransients of 2-ethylaminodiphenylborinate generated by direct photolysis and photosensitization☆

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ABSTRACT

Ground state interactions and excited states and transients formed after photolysis and photosensitization of 2-ethylaminodiphenylborinate (2APB) were studied by various techniques. The UV spectrum shows a large absorption band at 235 nm ($\varepsilon = 14{,}500\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$) with a shoulder at 260 nm. The fluorescence spectra show increasing emission intensity with maximum at 300 nm, which shifts to the red up to 10^{-3} M concentrations. At higher concentrations, the emission intensity decreases, probably due to the formation of aggregates. UV excitation in deareated solutions shows the formation of two transients at 300 and 360 nm. The latter has a lifetime of 5.7 μs in ethanol and is totally quenched in the presence of oxygen and assigned to the triplet state of 2APB. The 300 nm peak is not affected by oxygen, has a lifetime in the order of milliseconds, and corresponds to a boron-centered radical species originated from the singlet state. A boron radical can also be obtained by electron transfer from triplet Safranine to the borinate ($k_q = 9.7 \times 10^7\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$) forming the semioxidized form of the dye. EPR experiments using DMPO show that dye-sensitized and direct UV-photolysis of 2ABP renders initially arylboron-centered radicals.

1. Introduction

Photoinitiated polymerization is a tool that has been increasingly studied for a long time due to the special characteristics of better spatial precision and the possibility of performing the processes at low temperature [1,2]. Although dyes that absorb light in the visible region are the preferred photoinitiators, in recent years compounds absorbing in other wavelengths have been tested and used as initiators and/or co-initiators [1–3]. Between them, several boron compounds have been investigated [4,5].

Organoboron compounds can initiate polymerization of vinyl monomers in the presence of electron donors or acceptors [6,7]. Most of the current studies involved salts with anionic borane heterocyclic complexes, or complexes of BH_3 with electron donors [8,9]. In some cases, phenytrialkylborates have been used as counter-ions with cationic dyes [8,9]. In these cases, visible light is absorbed by the dye portion of the salt, and the borate ion acts as an intrinsic co-initiator [6,7]. Aliphatic alkyl boranes have also been used in free radical polymerizations in the presence of oxidants or reductants, although the low bond energy and high instability in oxygen, and their absorption at wavelengths under 220 nm hindered practical applications. [10,11].

2-Aminoethyldiphenylborinate (2APB) is a stable compound containing two phenyl rings and an aminoalkoxy group bound to the boron atom. It is largely used in biomedical applications to regulate the calcium storage in cells [12]. On the other hand, a new class of π-conjugated organoboron polymers [13,14] and borylene compounds [15] are examples of applications of boron compounds. Qualitative experiments proved that the addition of arylboron compounds to photopolymerizable formulations, in the presence of an appropriate dye, will accelerate the polymerization rate [5,8,9,16,17].

The photopolymerization initiated by the excitation of dyes in the presence of suitable co-initiators (electron donors or acceptors) has been studied in many cases and the reaction mechanism established as a function of the elemental reactions involved [1–3,16–18]. In the specific case of Safranine, these studies were done on systems involving the presence of an electron donor [1–3] and monomer [1,2,20]. Thus, in order to establish the overall reaction Scheme that leads to photopolymerization, all the reactions involving the excited states of the dye with the other components of the formulation (amines and monomers) were determined independently [1–3].

In this work we want to report features concerning the photophysics and photochemistry of the borinate compound and its interactions with the dye Safranine used as photosensitizer

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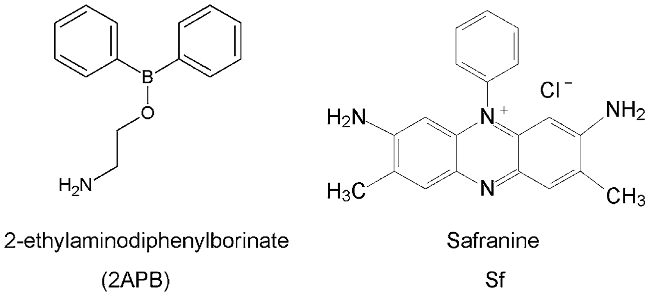

Scheme 1.

necessary to ascertain the role and pathway of the excited states and transients that initiate photopolymerization.

2. Experimental details

2-Ethylaminodiphenylborinate (2APB, 97%), Safranine O chloride (Sf, 97%) and 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) were from Aldrich and used without further purification. Scheme 1 shows the structure of the compounds used is this work. The solvents ethanol and dioxane were HPLC grade (Aldrich).

Absorption and fluorescence spectra were recorded on a Shimadzu UV 2550 and a Hitachi F-4500 spectrometers, respectively, using 1.0 cm pathlength quartz cells. For low temperature experiments the solutions were placed in NMR quartz tubes. The absorbance of the 2APB solutions was set at 0.1 for quantum yield determinations.

Triplet quenching and transient absorption spectra were carried out using a LFP-112 Luzchem model nanosecond laser flash photolysis spectrometer. Excitation was performed using the second (532 nm) and fourth (266 nm) harmonics of a Brilliant B Nd-YAG laser, with 5.2 ns pulses. Kinetic analysis was done with the Luzchem software.

Fluorescence lifetime measurements were performed with an Optical Building Blocks Corp. fluorometer. The excitation and emission wavelengths were $\lambda = 280$ and 310 nm, respectively. Fluorescence decay times were fitted with a monoexponential function, optimizing Chi square, residuals, and standard deviation parameters. All solutions were deaerated by bubbling oxygen-free nitrogen.

2APB radicals were generated by UV irradiation and in quartz capillaries and identified by the EPR spin trapping technique using DMPO. The same procedure was used for the 2APB radicals produced by photosensitization by Safranine.

The EPR X-band/9.5 GHz (Bruker ELEXSYS E580) measurements were carried at 298 K in a rectangular cavity with 100 kHz magnetic field modulation. The solutions of 2APB $1 \times 10^{-4}\,M^{-1}$ in ethanol or dioxane contained 50 mM DMPO. Irradiation of the boron compound was carried out by a UV lamp at 254 nm and for the solutions containing Safranine by a green led emitting in the 520 nm range. Measurements were performed at different times during the irradiation of an unique sample.

3. Results and discussion

3.1. Ground-state and singlet-state process

In order to evaluate the possibility of polymerization photoinitiation by 2APB alone or in the presence of Safranine in the presence of, it is necessary to identify all the photoreactions of 2APB and the interactions between the borinate and Sf in the ground and excited states.

The absorption spectrum of 2APB in ethanol presents a maximum around 235 nm and a smaller shoulder around 260 nm (Fig. 1a). The extinction coefficient at the larger maximum (235 nm) was found to be 14,500 $M^{-1}\,cm^{-1}$. The fluorescence at low concentrations has a maximum around 300 nm, which gradually shifts to longer wavelengths at increasing concentrations, reaching the limit of 310 nm at 1×10^{-3} M. Above this concentration, the wavelength of the emission maximum remains constant, but the fluorescence intensity starts to decrease (Fig. 1b). Light scattering at 310 nm of 2APB solutions remains constant up to 1×10^{-3} M, increasing afterwards, as can be seen in Fig. 2, where it is plotted together with the emission intensity as a function of concentration. The fluorescence emission starts to decrease at the same concentration where the scattering increases. This behavior, which is similar to that observed for various aromatic compounds, can be ascribed to the aggregation of 2APB. This is confirmed by experiments in dioxane, where the change in slope can be observed around 4×10^{-4} M.

Fig. 3 shows the total emission spectrum and the phosphorescence emission of 2APB at 77 K. The decay of the phosphorescence emission is shown in Fig. 3b and can be calculated to be 2.5 s, compatible with the decay time of 2.1 s reported for triphenylborane [13]. The fluorescence quantum yield at 293 K was obtained by

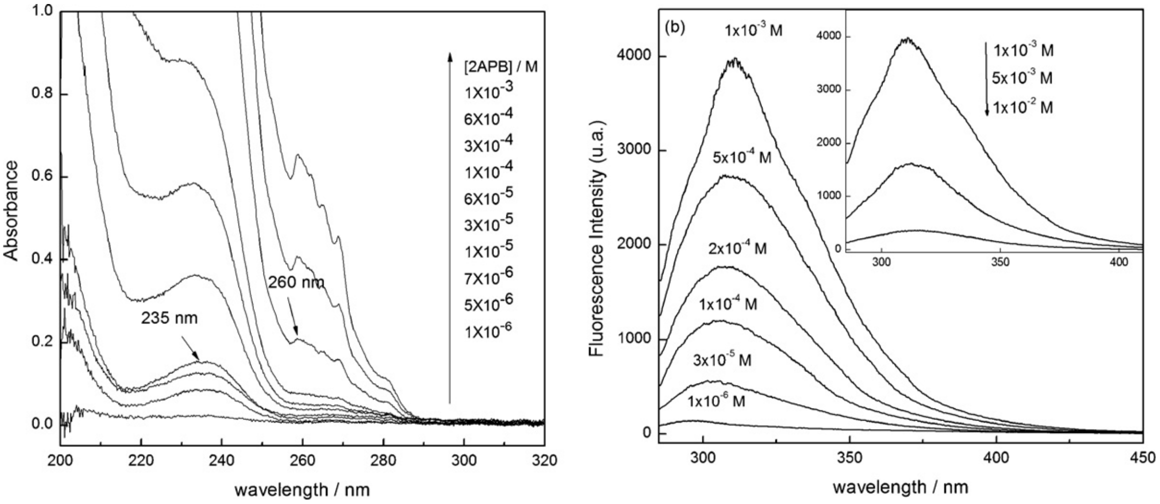

Fig. 1. (a) Absorption spectra of 2APB and (b) fluorescence spectra ($\lambda_{exc} = 260$ nm) at low and high concentrations (inset).