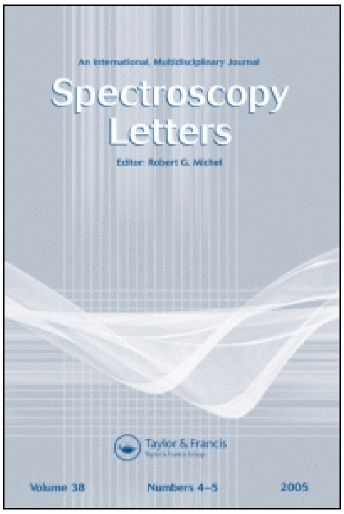

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B-type delayed fluorescence of rubreneperoxide in solution.

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B-type delayed fluorescence of rubreneperoxide in solution.

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Abstract

B-type of delayed fluorescence was observed for the first time for rubreneperoxide. Rubreneperoxide molecules were excited in a two step process. In the first step an excited singlet S_1 is created, which undergoes intersystem crossing to T_1; then T-T absorption creates an excited triplet rubreneperoxide molecule, which returns to the first excited singlet level by intersystem crossing. The recreated first excited singlet of rubreneperoxide decays back to the ground state by emitting B-type of delayed fluorescence.

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I. Introduction

Rubrence (5,6,11,12-tetraphenyltetracene, hereafter R) is widely used as singlet oxygen substrate to measure quantum yields of singlet oxygen production as well as the effectiveness of singlet oxygen quenchers [1-6]. This substrate reacts cleanly to form photoperoxides according to the following reaction scheme [7]:

$$ {}^1R + h\nu\,(UV - Vis) \rightarrow {}^1R^* $$

$$ {}^1R^* + O_2\left({}^3\Sigma_g^-\right) \rightarrow {}^3R^* + O_2\left({}^1\Delta_g\right) $$

$$ {}^3R^* + O_2\left({}^3\Sigma_g^-\right) \rightarrow {}^1R + O_2\left({}^1\Delta_g\right) $$

$$ {}^1R + O_2\left({}^1\Delta_g\right) \rightarrow RO_2 \text{ (stable)} $$

$$ {}^1RO_2 + h\nu \rightarrow {}^1RO_2^* \rightarrow {}^3RO_2^* $$

$$ {}^3RO_2^* + h\nu \rightarrow {}^3RO_2^{**} $$

$$ {}^3RO_2^{**} \rightarrow {}^1RO_2^* \rightarrow {}^1RO_2 + h\nu_{df} \text{ (B-type)} $$

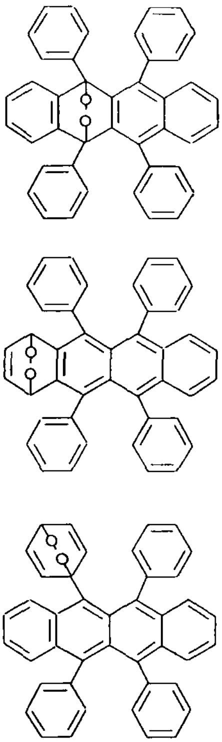
The bright red hydrocarbon rubrene forms three different oxides when irradiated by ultraviolet-visible light in the presence of molecular oxygen. The colorless substance obtained in this way is stable to have the structures I, II, and III as indicated in fig. 1 [8].

It is stable to heat, contains no active hydrogen and hydroxyl absorption in the IR. The direct photoxygenation of rubrene is studied by Bowen and Steadman [9]; they were mainly concerned with the formation of rubreneperoxide and absorption spectrum of it. Schumacher [10] confirmed the participation of two molecules of rubrene to form photoproducts with oxygen.

For many organic compounds the pattern of vibrational levels is more complex and all the transitions to the various levels of the first excited state appear as one broad absorption band, as it is seen in figure 2.

2. Experimental

Rubrene was of Aldrich reagent grade, used as received. All other chemicals were also reagent grade. Rubrene reacted cleanly to form rubreneperoxides by



(I)

(II)

(III)

Fig. 1 Three different rubreneperoxides.

using singlet oxygen reaction scheme. Rubreneperoxide, at a concentration of 2.65 x 10^{-5} M, was in cyclohexane at room temperature. The steady state absorption spectra were measured in a Cary-219 spectrophotometer using a 1 nm bandpass. An SLM-8000-S fluorimeter was used to obtain steady state fluorescence and excitation spectra. Fluorescence lifetimes were determined with a PRA single photon counting nanosecond fluorescence spectrometer interfaced to a Terak 8510 graphic system for data analysis, storage, and display [8].

Three pulsed laser sources were used for laser flash photolysis: Lambda-Physik EMG-101 MSC excimer (XeCl, 308 nm, approximately, 10-100 mJ pulse^{-1}), Molectron UV-400 nitrogen (337.1 nm, approximately, 2-3 mJ pulse^{-1}), and Quanta-Ray DCR-1 Nd: YAG coupled with PDL-1 dye laser (266, 355, 485, and 532 nm, approximately, 10-100 mJ pulse^{-1}). The lasers were attenuated and/or adjusted properly or defocused so that their intensities as absorbed by the solutions were comparable when the three laser systems were used to generate excitation pulses at various wavelengths. A kinetic absorption spectrophotometer with nanosecond

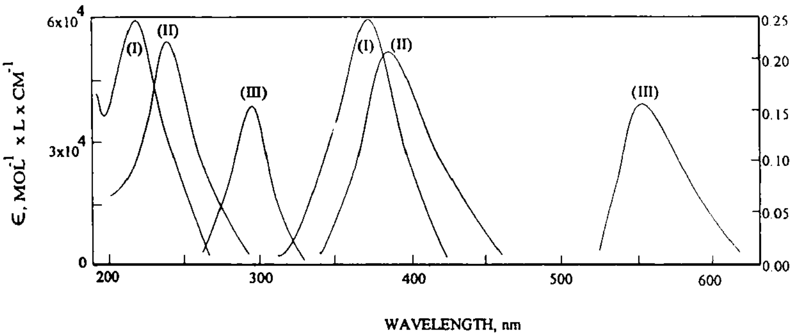


Fig. 2 The one-photon absorption and corrected fluorescence spectra of rubreneperoxides in cyclohexane at room temperature.

response (pulsed 500 W, Xenon lamp, Bausch and Lomb, UV-visible high intensity monochromator and RCA-4840 photomultiplier tube with output signal terminated into 93 Ω), a Tektronix 7912 digitizer and an LSI-11 microprocessor unit controlled the experiments and processed the data at the initial stage. The data from LSI-11 were finally transferred to a time shared PDP 11/55 computer system for storage and further analysis. The flash photolysis experiments were carried out on oxygen-free (degassed in vacuum line, background pressure = 10^{-7} Torr) solutions, contained in 1 x 0.2 cm^2 quartz cells, with the absorbed light passing along the 0.2 cm path length. The individual peroxides were separated and identified by the paper chromatography technique.

3. Results and discussion

All types of delayed fluorescence involve a metastable state which is first converted to an excited singlet state before emitting. It was deduced that E-type of delayed fluorescence was produced by thermal activation of molecules from the triplet level to the first excited singlet level.

P-type of delayed fluorescence is produced by triplet-triplet annihilation, and its decay time depends on the lifetime of the T_1 state.

Another type is the recombination delayed fluorescence which has been reported in rigid media. It requires ejection of an electron as a first step and would therefore be expected to occur preferentially by excitation with high energy quanta.

There is another mechanism which involves excitation of the triplet molecules by absorption of a second quantum of light [11-14]. The mechanism of B-type delayed fluorescence is described in detail [14].

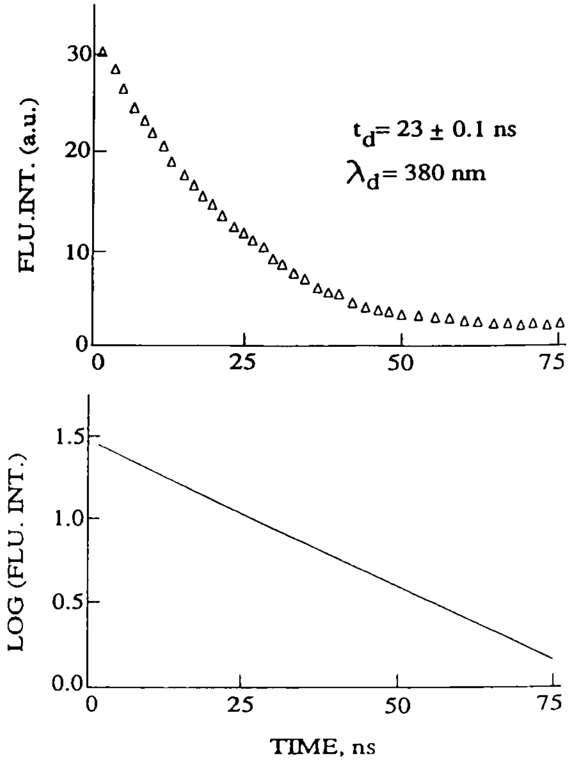


Fig. 3 B-type of delayed fluorescence decay of rubreneperoxide (I), in cyclohexane at room temperature, (Decay of T_2 state via S_1 state).

Rubreneperoxide molecules were excited in a two step process involving the $S_0 \rightarrow S_1$ and $T_1 \rightarrow T_2$ transitions. The rubreneperoxide molecules in the T_2 state returned to the first excited singlet state, $^1M^*(S_1)$ by intersystem crossing from the excited triplet T_2. The recreated electronically excited S_1 state decayed back to the ground state ^1M (S_0) by emitting B-type of delayed fluorescence.

The lifetime of B-type delayed fluorescence will be the lifetime of T_2 state, instead of T_1, because the T_2 state is responsible for repopulating the S_1 state of the molecule.

Figure 2 shows the absorption spectra and power corrected fluorescence spectra, figure 3, the decays of B-type delayed fluorescence of rubreneperoxide (I) in cyclohexane at room temperature and Table 1 the singlet and triplet parameters.

Table I

Molecule in cyclohexane	Decay of S_1 Prompt (Normal) Fluorescence (ns)	Decay of T_1 Disappearance of T_1 state (ns)	Decay of T_1, via S_1 P-type delayed Fluorescence (ns)	Decay of T_2, via S_1, B-type delayed Fluorescence (ns)
Rubreneperoxide (I)	$t_d = 0.707 \pm 0.027$* $\lambda_d = 380$ nm	$t_d = 2559 \pm 10$* $\lambda_d = 450$ nm	$t_d = 263 \pm 5$* $\lambda_d = 380$ nm	23±0.1
Rubreneperoxide (II)	$t_d = 4.455 \pm 0.115$* $\lambda_d = 390$ nm	$t_d = 2765 \pm 10$* $\lambda_d = 430$ nm	$t_d = 280 \pm 5$ $\lambda_d = 390$ nm	25±0.1
Rubreneperoxide (III)	$t_d = 7.192 \pm 0.089$* $\lambda_d = 555$ nm	$t_d = 2147 \pm 10$* $\lambda_d = 390$ nm	$t_d = 235 \pm 5$ $\lambda_d = 555$ nm	26±0.1

*The values are taken from reference 8, with the permission of F. Bayrakçeken.

Rubrebeperoxide is a colorless substance and can be used as a laser dye at 380 nm, [8], therefore the main goal was, to examine all kinds of fluorescence emissions of rubreneperoxide, to make a non-fading laser dye which will have many applications in quantum electronics devices, such as chemically sensitive electronic circuits.

Acknowledgments

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Abbreviations:

R = Rubrene

RO_2 = Rubreneperoxide

${}^3\Sigma_g^-$ = Ground State of oxygen molecule (Triplet State)

${}^1\Delta_g$ = Excited State of oxygen molecule (Singlet State)

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