

## Nanosecond Laser Flash Photolysis Study of the Photochemistry of 2-Alkoxy Thioxanthenes

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Laser flash photolysis studies ( $\lambda = 355$  nm) on the characterization and reactivity for the triplet excited state of 2-methoxythioxanthone, 2-benzyloxythioxanthone, and 2-(*n*-propoxy) thioxanthone revealed that the transients generated in their excitation, in acetonitrile, have absorption bands with maxima at 310 and 620 nm. These transients decayed by a mixed 1<sup>st</sup> and 2<sup>nd</sup> order kinetics, with a lifetime of 5.3  $\mu$ s for 2-methoxythioxanthone and benzyloxythioxanthone and 3.9  $\mu$ s for 2-(*n*-propoxy) thioxanthone. In methanol, ethanol, and 2-propanol, a new absorption at 430–460 nm was observed, which was attributed to their corresponding ketyl radical (the second-order quenching rate constant ( $k_q$ ) is ca.  $10^5$  L mol<sup>-1</sup> s<sup>-1</sup>). The energy transfer rate constants for *trans*-stilbene, 1-methylnaphthalene, and 1,3-cyclohexadiene were diffusion-controlled, indicating a triplet energy for these alkoxy thioxanthenes higher than 61 kcal mol<sup>-1</sup>. The quenching rate constant observed for 1,4-cyclohexadiene (ca.  $10^9$  L mol<sup>-1</sup> s<sup>-1</sup>) suggests that the lowest energy triplet excited state for these thioxanthenes must have  $n\pi^*$  character. For phenols and indole ( $k_q$  ca.  $10^9$  L mol<sup>-1</sup> s<sup>-1</sup>), the reaction mechanism must involve the initial formation of a triplet exciplex, followed by a coupled electron/proton transfer. For triethylamine and 1,4-diazabicyclo[2.2.2]octane ( $k_q$  ca.  $10^9$  L mol<sup>-1</sup> s<sup>-1</sup>) it was observed the formation of the radical anion of the alkoxy thioxanthenes formed from electron transfer ( $\lambda = 410$  nm).

**Keywords:** laser flash photolysis, thioxanthenes, energy transfer, hydrogen transfer, electron transfer

### Introduction

The photophysical properties of many aromatic ketones are strongly influenced by the configuration of their electronically excited states. The initial study of the solvent effect in these cases aims to understand the reaction mechanisms in the ground and excited states of molecules.<sup>1-5</sup>

The nature of the excited state of thioxanthone (9*H*-thioxanton-9-one, TX) and its derivatives have been extensively studied. The energy for the triplet excited state of TX is approximately 65.5 kcal mol<sup>-1</sup>. The lowest energy singlet state has a  $\pi\pi^*$  configuration and, in hydroxylic solvents, shows intense fluorescence.<sup>6</sup> Thioxanthone can form free radicals in the triplet excited state and is often used as a photoinitiator for polymerization, a photosensitizer, and a photocatalyst.<sup>7-21</sup>

The efficient formation of the triplet excited state of thioxanthenes is attributed to the high value for the

intersystem crossing rate constant between systems involving the  $S_1$  ( $\pi\pi^*$ ) to  $T_2$  ( $n\pi^*$ ) states, followed by an internal conversion  $T_2$  ( $n\pi^*$ ) to  $T_1$  ( $\pi\pi^*$ ).<sup>22</sup> Intersystem crossing processes between systems that involve configuration changes are about three orders of magnitude more efficient than similar processes that involve  $S_1$  and  $T_n$  states with the same configuration.<sup>23,24</sup>

Early studies on the spectroscopy and kinetics of several alkoxy and halogen substituted thioxanthenes employing conventional flash photolysis showed that irradiation in the highly efficient hydrogen donor solvent 2-propanol leads to the formation of the corresponding ketyl radicals. Under this condition, the recorded transient absorption spectra showed absorption maxima between 340 and 420 nm for the 1-methoxy, 3-methoxy, and 2-methoxythioxanthone.<sup>25</sup> Similar results were reported for the photolysis of 2-benzyloxythioxanthone in tetrahydrofuran. In this case, a broad absorption band was observed with a maximum at 440 nm, associated with the ketyl radical derived from this thioxanthone.<sup>26</sup> In acetonitrile, the triplet excited state of these thioxanthenes presents an intense absorption in the 580–640 nm region.<sup>27</sup> Laser flash photolysis studies

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on 2-chlorothioxanthone in acetonitrile revealed that the T-T absorption generated upon 355 nm laser excitation has absorptions at 310 and 630 nm and depletion in the 350-400 nm region.<sup>28</sup>

In the presence of a tertiary amine, which acts as an electron donor, the triplet excited state of thioxanthone generates a pair of radical ions through the initial formation of an exciplex. These radical ions then decay to the alkylamino/ketyl radical pair, which has been used as the effective initiator in polymerization reactions.<sup>26</sup>

A study of the solvent polarity variation on the triplet-triplet absorption spectrum of thioxanthone, as well as of thioxanthenes containing substituents on the aromatic ring, shows that the triplet-triplet absorption spectrum for these compounds presents three different bands in the regions between 305-330, 400-450 and 600-640 nm.<sup>7,25,29</sup> The absorption at 400-450 nm is usually attributed to the semi-reduced form of the ketone, resulting from hydrogen abstraction from the solvent by the triplet excited state of thioxanthone.<sup>25</sup>

Results from our group<sup>30</sup> on the photophysical and photochemical properties of thioxanthone using the laser flash photolysis technique show that its triplet excited state is easily obtained upon 355 nm irradiation. The triplet lifetime and the  $\lambda_{\text{max}}$  of the triplet-triplet absorption band of thioxanthone increase with the change from a non-polar to a polar solvent.<sup>30</sup> When hydrogen donor solvents such as methanol, ethanol, and 2-propanol were employed, it was possible to observe the appearance of a band at 410 nm in the transient absorption spectrum, which was attributed to the thioxanthone-derived ketyl radical.<sup>30,31</sup> Quenching rate constants for hydrogen-donor compounds ranged from  $1.7 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$  for toluene to ca.  $10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  for phenol and its derivatives containing polar substituents, and indole. The quenching rate constants employing electron donors such as 1,4-diazabicyclo[2.2.2]octane (DABCO) and triethylamine<sup>30</sup> were also on the order of  $10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ .

Several publications<sup>11,32-37</sup> from other groups deal with the study of the solvent effect on the photochemical and photophysical properties of thioxanthone, and its interaction with different compounds. Thioxanthone and its derivatives have been widely used as polymerization photoinitiators and photosensitizers for several decades.<sup>9,14,21,26,31,38-47</sup> However, nowadays, the study of the photophysics and

photochemistry of thioxanthenes remains a topic of great relevance, as demonstrated by recent review articles on the subject, which highlight both their ability to act as a potent photocatalyst for organic reactions as well as to promote photopolymerization processes and the 3D printing of photocurable resins under visible light.<sup>21,48</sup> In addition, they have also been used in the study of protein folding,<sup>49</sup> in the development of a new efficient photocaging system,<sup>50</sup> and as new drugs for the treatment of solid tumors.<sup>51-53</sup>

The present work aims to study the reactivity of the triplet excited state of 2-methoxythioxanthone (MeOTX), 2-benzyloxythioxanthone (BzOTX), and 2-(*n*-propoxy) thioxanthone (PrOTX) (Scheme 1) in the presence of different quenchers acting by energy, hydrogen, or electron transfer, employing the nanosecond laser flash photolysis technique.

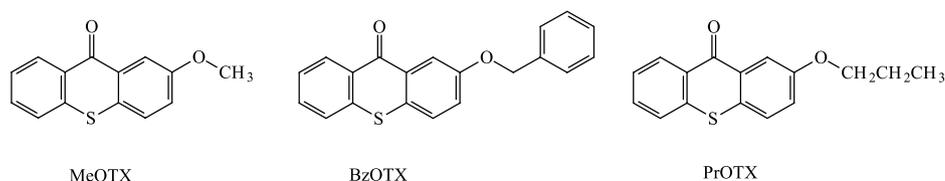
## Experimental

### Materials

Solvents (acetonitrile, methanol, ethanol, and 2-propanol, spectroscopic grade) were purchased from Sigma-Aldrich (São Paulo, Brazil). *trans*-Stilbene, 1-methylnaphthalene, 1,4-diazabicyclo[2.2.2] octane (DABCO), triethylamine, indole, and the phenols (H, 4-cyano, 3-cyano, 4-methyl, 3-methyl, 4-methoxy, 3-methoxy, 3-fluor, 3-chloro) were purchased from Sigma-Aldrich (São Paulo, Brazil) and used as received. 1,3-Cyclohexadiene (Sigma-Aldrich, São Paulo, Brazil) and 1,4-cyclohexadiene (Sigma-Aldrich, São Paulo, Brazil) were distilled bulb-to-bulb immediately before use.

### Synthesis of substituted thioxanthenes

The 2-methoxy-, 2-benzyloxy-, and 2-(*n*-propoxy) thioxanthenes used in this work were kindly provided by Prof Dr Miguel Neumann (University of São Paulo, São Carlos). The synthesis of substituted thioxanthenes consisted of a simple alkylation reaction between 2-hydroxythioxanthone and the corresponding alkyl halide (methyl iodide, benzyl chloride, or 1-propyl chloride). Briefly, 1.2 g of 2-hydroxythioxanthone (ca. 5 mM) was dissolved in *N,N*-dimethylformamide (10.0 mL), and then



**Scheme 1.** Structure for the 2-alkoxy thioxanthenes investigated in the present work.

the corresponding alkyl halide (5 mM) was added to the reaction medium, maintaining a constant temperature of 60 °C throughout the procedure. Then, 2 mL of an aqueous potassium hydroxide solution (5% m/v) were slowly added to the medium to form a red-colored precipitate (2-hydroxythioxanthone phenoxide). After the reaction, filtration was carried out, and the resulting solid was recrystallized from dioxane/water, yielding a yellow-colored product.<sup>25-27,31</sup> The spectroscopic and spectrometric data for the 2-alkoxythioxanthenes obtained agree with the proposed structures.

#### Laser flash photolysis

The nanosecond laser flash photolysis experiments were performed using a Luzchem model mlfp 112 system (Gloucester, Canada) employing a 175 W ceramic xenon lamp, a CUI Laser Corporation Digikröm CM 110 monochromator, a Hamamatsu photomultiplier, a Tektronix oscilloscope TDS 2012 model, with the entire system being controlled by a personal computer containing a National Instruments Labview software.<sup>54</sup> The samples were irradiated with a continuum Nd/YAG laser, model Surelite II, using the third harmonic ( $\lambda = 355$  nm, 10 ns pulse, ca. 40 mJ *per* pulse).

Kinetic and spectroscopic data about the excited state of the thioxanthenes used, as well as the reaction rate constants between these transients and a quencher, were obtained using the nanosecond laser flash photolysis technique implemented in the Photochemistry Laboratory of the Instituto de Química at the Universidade Federal do Rio de Janeiro-Brazil, in the Lablaser of the Instituto de Química at the Universidade Federal da Bahia-Brazil, and at the Photochemistry Laboratory at the Universidade de São Paulo-São Carlos-Brazil and also using a Luzchem model mlfp 112 system.

For the quenching experiments, ca.  $10^{-4}$  mol L<sup>-1</sup> solutions of MeOTX, BzOTX, and PrOTX in acetonitrile (absorbance ca. 0.3 at 355 nm, measured in a Varian DMS-80 UV-Vis spectrophotometer, Palo Alto, California, USA) were prepared. Solutions of quenchers were also prepared in varying concentrations using acetonitrile as a solvent so that there was no change in the reaction medium while quencher solutions were added. All experiments used a 10 × 10 mm<sup>2</sup> static quartz cell containing 3.0 mL of the thioxanthone solution sealed with a rubber septum. The samples used in the laser flash photolysis experiments were degassed immediately before irradiation by passing a stream of oxygen-free nitrogen for 30 min. In the quenching experiments, aliquots of the different quencher solutions were gradually added with a microliter syringe.

Second-order quenching rate constants for the triplet excited state of MeOTX, BzOTX, and PrOTX were obtained from Stern-Volmer plots (equation 1),<sup>55</sup> and, in all cases, linear plots were obtained, showing very good correlation coefficients.

$$k_{\text{obs}} = k_0 + k_q[Q] \quad (1)$$

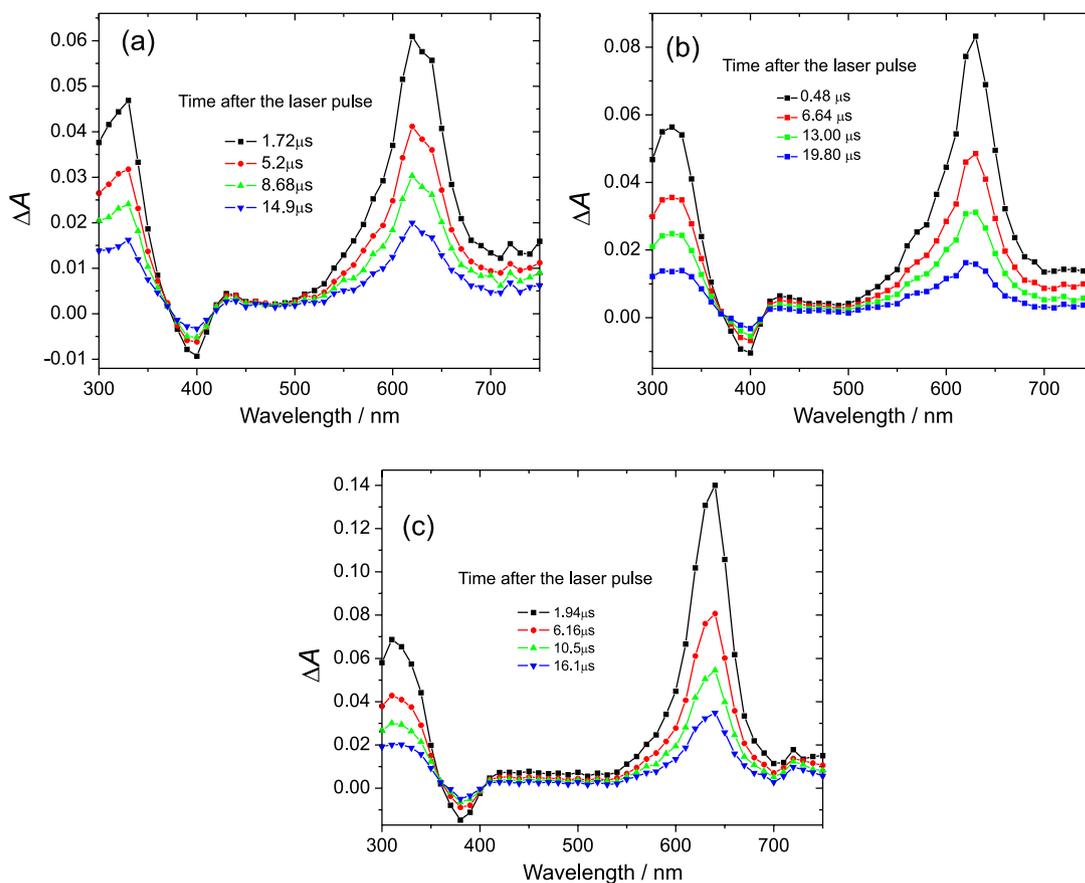
where  $k_{\text{obs}}$  is the triplet decay rate constant in the presence of the quencher;  $k_0$  is the triplet decay rate constant in the absence of the quencher Q;  $k_q$  is the second-order quenching rate constant, expressed in L mol<sup>-1</sup> s<sup>-1</sup>; and [Q] is the quencher concentration in mol L<sup>-1</sup>.

## Results and Discussion

Laser flash photolysis ( $\lambda = 355$  nm) of nitrogen degassed acetonitrile solutions of 2-methoxythioxanthone (MeOTx), 2-benzyloxythioxanthone (BzOTX), or 2-(*n*-propoxy) thioxanthone (PrOTX) led to the formation of readily detectable transients with absorptions in the 309 and 620 nm regions and a depletion in the 350-400 nm region (Figure 1). In a previously published work, it was reported that in ethyl acetoacetate the transient generated in the laser excitation of these alkoxyxanthenes showed absorptions at 310 and 640 nm.<sup>29</sup>

The decay associated with these absorptions showed mixed first and second-order kinetic, a usual behavior for long-lived triplets (Figure 1). The contribution of 2<sup>nd</sup> order decay in triplet aromatic ketones is usually associated with a deactivation process by triplet-triplet annihilation.<sup>56</sup> As a consequence, the decay for these transients is concentration dependent, and for acetonitrile as a solvent, the following self-quenching rate constants were measured:  $(3.9 \pm 0.2) \times 10^7$  L mol<sup>-1</sup> s<sup>-1</sup> for MeOTX;  $(2.0 \pm 0.2) \times 10^7$  L mol<sup>-1</sup> s<sup>-1</sup> for BzOTX, and  $(3.1 \pm 0.1) \times 10^7$  L mol<sup>-1</sup> s<sup>-1</sup> for PrOTX. From the decays in acetonitrile, a triplet lifetime of  $5.3 \pm 0.2$   $\mu$ s was obtained for MeOTX and BzOTX, and  $3.9 \pm 0.2$   $\mu$ s for PrOTX.

The transients obtained on laser irradiation of MeOTX, BzOTX, and PrOTX were assigned to their corresponding triplet excited state because they were quenched at a diffusion-controlled rate constant ( $k_{\text{diff}}$  for acetonitrile was calculated as  $1.68 \times 10^{10}$  L mol<sup>-1</sup> s<sup>-1</sup> by employing the Smoluchowski-Stokes-Einstein theory)<sup>57</sup> with *trans*-stilbene (triplet energy ( $E_T$ ) = 49 kcal mol<sup>-1</sup>), 1,3-cyclohexadiene ( $E_T$  = 53 kcal mol<sup>-1</sup>). For 1-methylnaphthalene ( $E_T$  = 61 kcal mol<sup>-1</sup>) (Table 1),<sup>57</sup> the energy transfer rate constant was one order of magnitude slower than for *trans*-stilbene and 1,3-cyclohexadiene, i.e., ca.  $10^9$  L mol<sup>-1</sup> s<sup>-1</sup>. Such difference in behavior suggests



**Figure 1.** Triplet-triplet absorption spectra ( $\lambda_{exc} = 355$  nm) in acetonitrile (ca.  $1 \times 10^{-4}$  mol L<sup>-1</sup>), recorded at different times after the laser pulse, for: (a) 2-methoxythioxanthone; (b) 2-benzyloxythioxanthone; (c) 2-(*n*-propoxy) thioxanthone.

that the triplet energy for the alkoxy thioxanthenes studied in this work must be at least isoenergetic to that of 1-methylnaphthalene. This result is fully in accord with literature data on the triplet energy for thioxanthenes.<sup>6</sup>

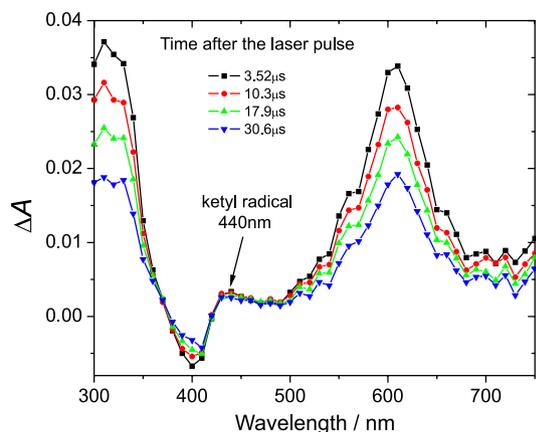
In addition to the absorptions observed at 310 and 620 nm for triplet MeOTX, BzOTX, and PrOTX, transient

absorption spectra for these thioxanthenes in hydroxylic solvents such as methanol, ethanol, or 2-propanol revealed the presence of a new absorption in the 420–440 nm region. Figure 2 shows a representative transient spectrum for PrOTX in 2-propanol. As these solvents are known as hydrogen donating species,<sup>29,58,59</sup> this new absorption can be assigned to the ketyl radical resulting from a hydrogen

**Table 1.** Second-order rate constants ( $k_q$ ) for the quenching of 2-methoxythioxanthone, 2-benzyloxythioxanthone, and 2-(*n*-propoxy) thioxanthone in acetonitrile by energy, hydrogen, and electron transfer

Quencher	$k_q / (\text{L mol}^{-1} \text{s}^{-1})$		
	MeOTX	BzOTX	PrOTX
<i>trans</i> -Stilbene	$(1.1 \pm 0.1) \times 10^{10}$	$(1.1 \pm 0.1) \times 10^{10}$	$(1.2 \pm 0.1) \times 10^{10}$
1,3-Cyclohexadiene	$(1.1 \pm 0.1) \times 10^{10}$	$(1.1 \pm 0.1) \times 10^{10}$	$(1.0 \pm 0.1) \times 10^{10}$
1-Methylnaphthalene	$(2.6 \pm 0.1) \times 10^9$	$(3.3 \pm 0.1) \times 10^9$	$(3.4 \pm 0.1) \times 10^9$
Methanol	$(1.1 \pm 0.1) \times 10^5$	$(1.3 \pm 0.1) \times 10^5$	$(6.4 \pm 0.2) \times 10^4$
Ethanol	$(1.8 \pm 0.1) \times 10^5$	$(2.1 \pm 0.1) \times 10^5$	$(1.2 \pm 0.1) \times 10^5$
2-Propanol	$(2.2 \pm 0.1) \times 10^5$	$(2.6 \pm 0.1) \times 10^5$	$(1.8 \pm 0.1) \times 10^5$
1,4-Cyclohexadiene	$(4.1 \pm 0.1) \times 10^9$	$(2.4 \pm 0.1) \times 10^9$	$(3.0 \pm 0.1) \times 10^9$
DABCO	$(6.5 \pm 0.1) \times 10^9$	$(6.1 \pm 0.2) \times 10^9$	$(6.6 \pm 0.1) \times 10^9$
Triethylamine	$(2.9 \pm 0.1) \times 10^9$	$(3.5 \pm 0.2) \times 10^9$	$(3.4 \pm 0.1) \times 10^9$

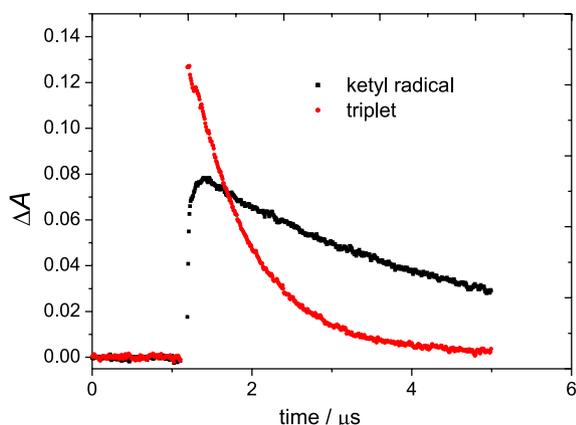
DABCO: 1,4-diazabicyclo[2.2.2]octane; MeOTX: 2-methoxythioxanthone; BzOTX: 2-benzyloxythioxanthone; PrOTX: 2-(*n*-propoxy) thioxanthone.



**Figure 2.** Transient absorption spectra ( $\lambda_{\text{exc}} = 355 \text{ nm}$ ) for 2-(*n*-propoxy) thioxanthone in 2-propanol as solvent.

abstraction reaction from the solvent by the triplet excited state of MeOTX, BzOTX, and PrOTX.<sup>30</sup>

This absorption can be associated with the ketyl radical derived from BzOTX, MeOTX, or PrOTX, not only because the formation of this transient had previously been reported for triplet thioxanthone,<sup>29,30</sup> but mainly because it presents a much slower decay than their corresponding triplet excited state. Figure 3 shows a comparison between the decay of PrOTX triplet in acetonitrile, monitored at 610 nm, and that of its respective ketyl radical in 2-propanol, monitored at 440 nm. It is important to note that besides the difference in the decay rate constants, the trace corresponding to the ketyl radical clearly indicates a growth kinetics for this transient. This suggests the ketyl radical formation from the triplet excited state of alkoxythioxanthone through a hydrogen abstraction mechanism, with the solvent 2-propanol being the hydrogen donor.



**Figure 3.** Decay trace for the triplet excited state of 2-(*n*-propoxy) thioxanthone (PrOTX) in acetonitrile, monitored at 610 nm (red); in black, growth and decay for the transient generate upon laser photolysis of PrOTX in 2-propanol ( $\lambda_{\text{mon}} = 440 \text{ nm}$ ).

Alcohols (methanol, ethanol, 2-propanol), 1,4-cyclohexadiene, phenols, and indole were used as

quenchers in the study of the triplet reactivity of MeOTX, BzOTX, and PrOTX in processes involving the hydrogen abstraction reaction, whereas tertiary amines (DABCO and triethylamine) were employed in the electron transfer quenching process. All reactions were performed in acetonitrile as solvent.

The rate constants obtained for the quenching of MeOTX, BzOTX, and PrOTX by methanol, ethanol, and 2-propanol are shown in Table 1. From these results, dependence of the quenching rate constant of the thioxanthenes with the structure of the alcohol used as a quencher is indicated. Thus, the highest hydrogen abstraction rate constant value corresponds to the alcohol having the weakest H–COH bond. In other words, the most stable ketyl radical derived from the alcohol is formed, with hydrogen abstraction rate constants being in the order  $k_{2\text{-PrOH}} > k_{\text{EtOH}} > k_{\text{MeOH}}$  for all alkoxy thioxanthenes under study. It is worth noting that ketyl radicals derived from these alcohols cannot be detected spectroscopically with our experimental setup.

The second-order quenching rate constants obtained for reactions of MeOTX, BzOTX, and PrOTX with methanol, ethanol, and 2-propanol suggest that their reactive triplet excited state has  $n\pi^*$  character (Table 1). Time-dependent density functional theory calculations indicated the  $T_1$  states for thioxanthenes have  $\pi\pi^*$  character, regardless of solvent polarity.<sup>60</sup> Even though there are examples where the  $\pi\pi^*$  triplet state shows some reactivity,<sup>58</sup> based on the quenching rate constants observed in the current study, we may neglect its contribution to the thioxanthenes reactivity, at least for hydrogen abstraction reactions from alcohols and 1,4-cyclohexadiene. Since these rate constants have the same order of magnitude as those obtained for a typical aromatic carbonyl compound with a triplet excited state which is known to behave as a pure  $n\pi^*$  triplet state, such as benzophenone, it is reasonable to assume that the reactive triplet states for MeOTX, BzOTX, and PrOTX have the same configuration.<sup>61</sup> For comparison only, benzophenone reacts with methanol, ethanol, and 2-propanol with rate constants of  $3 \times 10^5$ ,  $6 \times 10^5$ , and  $1 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ , respectively.<sup>62</sup>

To further confirm the  $n\pi^*$  character of the reactive triplet states for MeOTX, BzOTX, and PrOTX, hydrogen abstraction rate constants were measured employing the excellent hydrogen donor 1,4-cyclohexadiene as a quencher.<sup>63</sup> The high  $k_q$  values obtained, close to the diffusion-controlled rate constant for acetonitrile, confirm that the  $n\pi^*$  triplet is the state responsible for these thioxanthenes reactivity. For comparison, the triplet state of typical  $n\pi^*$  aromatic ketones, such as 10,10-dimethylanthrone and benzophenone, reacts with



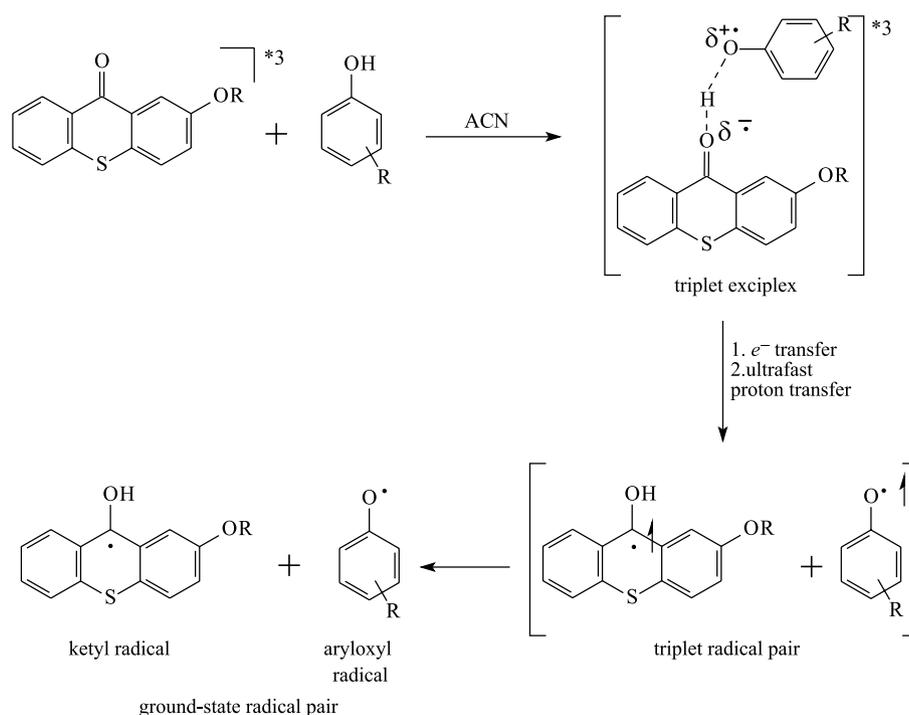
**Table 2.** Second-order rate constants ( $k_q$ ) for the quenching of 2-methoxythioxanthone (MeOTX), 2-benzyloxythioxanthone (BzOTX), and 2-(*n*-propoxy) thioxanthenes (PrOTX) by phenols containing polar substituents, and indole

Quencher	$k_q / (\text{L mol}^{-1} \text{s}^{-1})$		
	MeOTX	BzOTX	PrOTX
Phenol	$(5.0 \pm 0.2) \times 10^9$	$(5.0 \pm 0.2) \times 10^9$	$(4.1 \pm 0.1) \times 10^9$
4-Methoxyphenol	$(7.0 \pm 0.1) \times 10^9$	$(5.5 \pm 0.3) \times 10^9$	$(3.7 \pm 0.1) \times 10^9$
3-Methoxyphenol	$(3.3 \pm 0.1) \times 10^9$	$(4.0 \pm 0.1) \times 10^9$	$(4.5 \pm 0.1) \times 10^9$
3-Chlorophenol	$(3.6 \pm 0.1) \times 10^9$	$(3.7 \pm 0.2) \times 10^9$	$(4.8 \pm 0.2) \times 10^9$
3-Fluorophenol	$(3.4 \pm 0.1) \times 10^9$	–	$(4.9 \pm 0.2) \times 10^9$
4-Methylphenol	$(3.3 \pm 0.1) \times 10^9$	$(3.4 \pm 0.1) \times 10^9$	$(6.6 \pm 0.2) \times 10^9$
3-Methylphenol	$(4.0 \pm 0.1) \times 10^9$	$(2.8 \pm 0.1) \times 10^9$	$(2.9 \pm 0.1) \times 10^9$
4-Cyanophenol	$(2.4 \pm 0.1) \times 10^9$	$(1.8 \pm 0.2) \times 10^9$	$(6.6 \pm 0.1) \times 10^9$
3-Cyanophenol	$(2.0 \pm 0.1) \times 10^9$	–	$(4.0 \pm 0.1) \times 10^9$
Indole	$(2.3 \pm 0.1) \times 10^8$	$(4.8 \pm 0.1) \times 10^8$	$(2.2 \pm 0.1) \times 10^9$

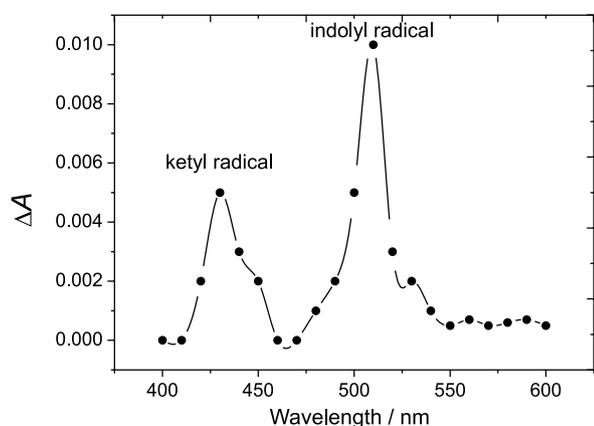
the ketyl radical from MeOTX, respectively. Similar results were found in the quenching process of triplet MeOTX, BzOTX, and PrOTX by the several phenols employed in this work.

Phenols and indole quench the triplet excited state of MeOTX, BzOTX, and PrOTX by hydrogen abstraction with the quenching rate constants measured for these reactions being close to the diffusion-control in all cases (Table 2). As can be seen by inspecting Tables 1 and 2, the quenching rate constants for phenols are higher than those observed for alcohols because the hydrogen abstraction reaction occurs by different mechanisms in these two cases. In reactions

involving the triplet excited state of carbonyls and alcohols, saturated aliphatic hydrocarbons (such as cyclohexane), and dienes (such as 1,4-cyclohexadiene) a mechanism called a “pure” alkoxy hydrogen abstraction, due to the similarity between the reaction of carbonyl triplets and alkoxy radicals, such as the *tert*-butoxy radical, is operating.<sup>69,70</sup> On the other hand, hydrogen abstraction reaction from phenols is usually described by a mechanism in which, after the initial formation of a triplet exciplex, the electron transfer process is followed by an ultra-rapid proton transfer, ultimately resulting in the aryloxy-ketyl radical pair (Scheme 4).<sup>71-80</sup>

**Scheme 4.** Mechanistic proposal for the phenolic hydrogen abstraction by the triplet excited state of 2-methoxythioxanthone, 2-benzyloxythioxanthone, and 2-(*n*-propoxy) thioxanthone in acetonitrile.

Indole reacts with carbonyl compounds through the very same mechanism proposed for phenols (Scheme 4) involving formation of a triplet exciplex intermediate, followed by an electron transfer coupled with an ultra-fast proton transfer (Table 2). The proposed mechanism for the reactions of MeOTX, BzOTX, and PrOTX with indole results in the formation of the indolyl radical, which has absorption around 500 nm,<sup>81-84</sup> and the ketyl radical derived from the thioxanthenes. A representative spectrum is shown in Figure 6 for the reaction of triplet MeOTX with indole, in which it was possible to observe the presence of the indolyl radical at 510 nm and the ketyl radical from the alkoxyxanthone with maximum absorption at 430 nm.



**Figure 6.** Transient absorption spectrum generated on the excitation ( $\lambda = 355$  nm) of 2-methoxythioxanthone in presence of large excess of indole solution, in acetonitrile, and recorded 6.0  $\mu$ s after the laser pulse.

In conclusion, it was demonstrated that the spectroscopic and kinetic properties of MeOTX, BzOTX, and PrOTX, as well as their photochemical reactivity towards hydrogen and electron transfer reactions, are independent of the structure of the substituent. These results agree with those reported in the literature for the photochemistry of thioxanthenes.<sup>20,25,27,29-31</sup>

## Conclusions

The absorption spectra of transients generated in the excitation ( $\lambda = 355$  nm) of MeOTX, BzOTX, and PrOTX show absorption at 309 and 620 nm and a depletion in the 350-400 nm region. In 2-propanol a new absorption in the 419-469 nm region could be observed, which corresponds to the respective ketyl radicals derived from the alkoxy thioxanthenes and generated by a hydrogen transfer process from the solvent. Confirmation of the transient formed in the irradiation of these thioxanthenes as their triplet excited state was made by energy transfer quenching studies, from

which one can conclude that the triplet energy for these alkoxy thioxanthenes is close to 61 kcal mol<sup>-1</sup>. For electron transfer reactions with DABCO and triethylamine, it was possible to observe absorption bands in the region of 460 and 500 nm (MeOTX) assigned to the formation of the corresponding anion radical. The hydrogen abstraction rate constants by these triplets varied from 10<sup>5</sup> L mol<sup>-1</sup> s<sup>-1</sup>, for alcohols, to 10<sup>9</sup> L mol<sup>-1</sup> s<sup>-1</sup>, for 1,4-cyclohexadiene (1,4-CHD). The high value of  $k_q$  for 1,4-CHD indicates that the reactive triplet excited state for MeOTX, BzOTX, and PrOTX must have a  $n\pi^*$  character. The high value for the quenching rate constants for phenols (10<sup>9</sup> L mol<sup>-1</sup> s<sup>-1</sup>) suggest a mechanism in which there is the initial formation of a triplet exciplex, followed by a coupled electron/proton transfer. For indole, the same mechanism that was previously proposed for phenol reaction must be operating. In this case, the measured quenching rate constants were  $(2.3 \pm 0.1) \times 10^8$  (MeOTX),  $(4.8 \pm 0.1) \times 10^8$  (BzOTX), and  $(2.2 \pm 0.1) \times 10^9$  L mol<sup>-1</sup> s<sup>-1</sup> (PrOTX).

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## Author Contributions

J.C.N.-F. was responsible for conceptualization; J.F.R. for spectroscopic and kinetics analyses, writing, revision, and editing; F.A.S. for formal analysis, investigation, writing-original draft preparation.

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