AppliedChem

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Absolute Rate Constants for the Reaction of Benzil and 2,2′-Furil Triplet with Substituted Phenols in the Ionic Liquid 1-Butyl-3-methylimidazolium Hexafluorophosphate: A Nanosecond Laser Flash Photolysis Study

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Abstract: The triplet excited state reactivity towards phenolic hydrogen of the α-diketones benzil and 2,2′-furil in the ionic liquid 1-*n*-butyl-3-methyl imidazolium hexafluorophosphate [bmim.PF_6] was investigated employing the nanosecond laser flash photolysis technique. Irradiation (λ_{max} = 355 nm) of benzil yields its triplet excited state with λ_{max} at 480 nm and τ_T = 9.6 μs. Under the same conditions, 2,2′-furil shows a triplet-triplet absorption spectrum with bands at 380, 410, 450, and 650 nm and τ_T = 1.4 μs. Quenching rate constants (k_q) of the reaction between benzil triplet and substituted phenols ranged from 1.4×10^7 L mol^{-1} s^{-1} (*para*-chlorophenol) to 1.8×10^8 L mol^{-1} s^{-1} (*para*-methoxyphenol). A new transient was formed in all cases, assigned to the benzil ketyl. Similar results were obtained for the quenching of 2,2′-furil triplet by phenols, for which k_q ranged from 1.9×10^8 L mol^{-1} s^{-1} (*para*-chlorophenol) to 2.2×10^8 L mol^{-1} s^{-1} (*para*-methoxyphenol). The 2,2′-furil ketyl radical was also observed in all cases (λ_{max} = 380 nm). The quenching rate constants are almost independent of the substituent and diffusion-controlled ($k_q \sim 10^8$ L mol^{-1} s^{-1}). The proposed mechanism for the phenolic hydrogen abstraction by benzil and 2,2′-furil triplet may involve a proton-coupled electron transfer reaction, ultimately leading to the radical pair ketyl/aryloxyl.

Keywords: α-diketones; triplet excited state; ionic liquid; phenolic hydrogen abstraction; time resolved photolysis

Citation: Bertoti, A.R.; Netto-Ferreira, J.C. Absolute Rate Constants for the Reaction of Benzil and 2,2′-Furil Triplet with Substituted Phenols in the Ionic Liquid 1-Butyl-3-methylimidazolium Hexafluorophosphate: A Nanosecond Laser Flash Photolysis Study. *AppliedChem* **2024**, *4*, 224–235. https://doi.org/10.3390/appliedchem4030015

Academic Editor: Jason Love

Received: 15 April 2024
Revised: 7 June 2024
Accepted: 20 June 2024
Published: 26 June 2024

1. Introduction

The influence of the solvent on photochemical reactions is well established, and it is known that parameters such as polarity, viscosity, ability to donate hydrogen or electron, and the effect of heavy atoms control photochemical mechanisms.

Ionic liquids (IL) of the 1-alkyl-3-methylimidazolium class have been used in photochemical reactions involving energy, electron, and hydrogen transfer. The low solubility of oxygen and its reduced molecular diffusion in ionic liquids contribute strongly to obtaining a longer lifetime for triplet excited states [1,2].

Several studies on the photochemical behavior of triplet carbonyl compounds were reported in the literature. The quenching of the triplet excited state of benzophenone by naphthalene in various ionic liquids of the 1,3-dialkylimidazolium type revealed that the quenching rate constant is, in all cases, diffusion-controlled. Due to their high viscosity, the diffusion rate constant for ionic liquids is close to two orders of magnitude slower ($k_q \approx 10^8$ L mol^{-1} s^{-1}) than those observed for conventional organic solvents such as benzene, methanol, and acetonitrile [3]. Similarly, the triplet-triplet energy transfer between xanthone (donor) and naphthalene (acceptor) in the ionic liquid [bmim.PF_6] shows a rate constant k_q of about two orders of magnitude lower than that observed in conventional organic solvents. The hydrogen abstraction rate constant by the triplet excited state of xanthone also showed a dramatic decrease when the reaction was studied in the ionic liquid [bmim.PF_6]. In this ionic liquid, the triplet excited state of xanthone can react with phenols, yielding the corresponding xanthone ketyl radical, with quenching rate constants in the order of ~10^8 L mol^{-1} s^{-1} independently of the substituent [4].

The photoreduction of benzophenone by amines in ionic liquids at room temperature through an electron transfer mechanism mainly provides benzhydrol, unlike what occurs with organic solvents, in which pinacolization or coupling between the ketyl radical derived from benzophenone and the α-aminyl radical occurs [5].

The triplet-triplet absorption spectrum for the carbonyl compounds thioxanthone and benzil in the ionic liquid [bmim.PF_6] is similar to those observed in organic solvents [6]. However, the lifetimes for the triplet excited state in both cases depend on the solvent type. Thus, thioxanthone has a triplet lifetime of 178 µs in [bmim.PF_6] and 14 µs in acetonitrile, whereas the lifetime obtained for benzil was 10 µs in [bmim.PF_6] and 3.8 µs in acetonitrile. It is worth noting that thioxanthone triplet lifetime varies dramatically depending on whether the solution is degassed, ranging from 178 µs in a deoxygenated [bmim.PF_6] solution to a surprising value of 500 ns in a non-deoxygenated solution. These triplet lifetime values unequivocally demonstrate the very low oxygen solubility in ionic liquids, as already reported [7].

α-Diketones are used in several applications in photochemical reactions, including photopolymerization by free radicals in the presence of hydrogen donors [8,9]. Due to their importance, many studies on the electronic and spectroscopic properties have been dedicated to α—diketones.

Several groups have demonstrated that the nπ* nature of the lowest energy excited state strongly depends on the dihedral angle between the carbonyl groups [10–12]. Benzil (E_T = 54.0 kcal/mol) is a α-dicarbonyl compound that presents different conformations due to the possible rotation of the $\sigma_{C\text{-}C}$ bond in the ground and excited state [13–16]. In the ground state, the angle between the two carbonyl groups in benzil is 72°, and, after excitation, the first triplet excited state acquires a *transoid* conformation in which the carbonyl groups are at 180° [15]. The lowest energy triplet excited state for benzil has an nπ* configuration, with a dipole moment equal to zero, which indicates an *s-trans* conformation for this triplet. On the other hand, ground state benzil has a dipole moment of 3.75 D, which is consistent with a *cisoid* conformation.

As the behavior of the benzil triplet excited state significantly depends on the structure and polarity of the medium, it has been used as an excellent probe to determine specific solute-solvent interactions both in isotropic solutions [13–16] and in organized systems [17,18].

Unlike benzil, 2,2′-furil (E_T = 54.5 kcal/mol) is more flexible since the aromatic five-membered furanyl rings allow a less hindered rotation along the $\sigma_{C\text{-}C}$ bond [19,20]. Furthermore, the presence of only one hydrogen in each furanyl ring results in the steric hydrogen/oxygen interaction of the carbonyl being much less important than that observed for benzil, in which two hydrogens carry out this interaction. Consequently, even in the ground state, the conformation of 2,2′-furil is almost *trans*-planar, with the torsion angle between the two carbonyl groups being 131° [21], whereas in the triplet excited state, only over long periods, a completely planar conformation is achieved.

The influence of the solvent on photochemical reactions is well established, and it is known that parameters such as polarity, viscosity, and its ability to donate hydrogen or electrons control photochemical mechanisms. Associated with this, there has recently been a significant interest in the use of ionic liquids as solvents due to their properties, including, among others, low melting point, extremely low vapor pressure, significant variation in their physicochemical properties as a function of their structure, forming a broad class of strongly polar solvents aiming at environmentally cleaner and more selective chemical processes, and having as one of the concerns the replacement of organic solvents, especially organohalogenated. Thus, in this work, kinetic and spectroscopic data are presented, using nanosecond laser flash photolysis, aimed to investigate the conformational effect on the reactivity of the triplet excited state reaction of benzil and 2,2′-furil (Figure 1) with phenols containing polar substituents, employing the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [bmim.PF_6] as a solvent.

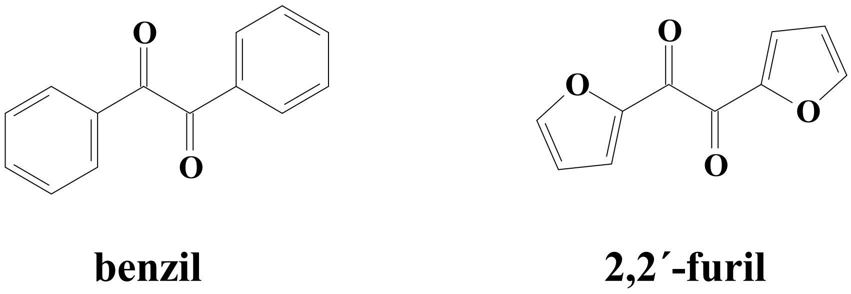


Figure 1. Structures for benzil and 2,2′-furil.

2. Materials and Methods

Materials. HPLC-grade acetonitrile was purchased from J. T. Baker (Phillipsburg, NJ, USA). 1-*n*-Butyl-3-methylimidazolium hexafluorophosphate [bmim.PF_6] was purchased from Fundação Universidade Federal do Rio Grande do Sul (Porto Alegre, Brazil), and used as received. Benzil and 2,2′-furil from Aldrich (São Paulo, Brazil) were purified by recrystallization from aqueous ethanol. Phenol, *para*-methoxyphenol, *para-tert*-butylphenol, *para*-phenylphenol, *para*-methylphenol, *para*-chlorophenol, *para*-fluorophenol, and *trans*-stilbene were purchased from Sigma-Aldrich (São Paulo, Brazil) and used as received.

Methods. Spectra in the ultraviolet-visible region were recorded on a Hewlett Packard 8453 (Palo Alto, CA, USA) spectrophotometer equipped with a diode array detector and interfaced with a PC containing Windows Workstation 4.0 software.

Nanosecond laser flash photolysis experiments were performed using a Luzchem model mlfp 112 system (Gloucester, ON, Canada) employing a 175 W CERMAX xenon lamp (Gloucester, ON, Canada), a CUI laser Corporation Digikröm CM 110 monochromator (Putnam, CT, USA), a Hamamatsu photomultiplier (h), and a Tektronix model TDS 2012 oscilloscope (Beaverton, OR, USA) where the photomultiplier signals are digitized. The oscilloscope can make acquisitions every two nanoseconds and its memory can store up to 15,000 points. The data read by the oscilloscope are transmitted to a personal computer through a GPIB interface. The computer controls the acquisition, processing, and the frequency of the laser pulse and the shutters through the Kinetic Processor program, which uses the Labview software (2004 Version) manufactured by National Instruments. The software allows successive shots to be made with the laser, after which it takes an average of the signals for noise minimization. The number of shots used for each analysis depends on the intensity of the signal obtained. The samples were irradiated with the third harmonic (λ = 355 nm, 10 ns pulse, ~40 mJ/pulse) of a Surelite II model, Continuum Nd/YAG laser (Milpitas, CA, USA). The beam is concentrated, but not focused, into the sample compartment by a set of fiber optics. The laser is pulsed continuously at a frequency of 1 Hz, adjusted by the instrument's control program, to make reproducible the beam energy.

The benzil and 2,2′-furil concentration was chosen to have a 0.2 absorbance at the excitation wavelength (355 nm). As a response from the computerized laser system, a plot of the decay of the transient signal, measured by the variation in optical density as a function of time is obtained. The semi-logarithmic representation provides the order of the kinetic trace, its rate constant, the transient lifetime, and the optical density at absorption maximum. The absorption spectrum of transients is made by selecting time intervals after the laser pulse at a specific wavelength.

In all experiments, a static quartz cell 10 mm × 10 mm was used that contained 1 mL of ketone solution in the ionic liquid 1-*n*-butyl-3-methyl imidazolium hexafluorophosphate [bmim.PF], deaerated for 30 min with Argon as the presence of oxygen can quench the triplet formation. Quenching experiments were carried out using stock solutions of the quencher so that it was only necessary to add volumes of the order of microliters to the cell to obtain adequate concentrations of the quencher. The rate constants for the phenolic hydrogen abstraction by the benzil and 2,2′-furil were obtained from Stern-Volmer plots according to Equation (1) [22].

$$k_{obs} = k_o + k_q[Q] \tag{1}$$

where k_{obs} is the experimentally observed rate constant, k_o is the decay rate constant of the triplet excited state in the absence of the quencher, k_q is the decay rate constant of the triplet excited state in the presence of the quencher, and $[Q]$ is the concentration of the quencher in mol L^{-1}.

3. Results and Discussion

The absorption spectrum for the transient generated by the irradiation of benzil in [bmim.PF_6] shows maximum absorption at 480 nm (Figure 2), with a lifetime of 10 µs, in a similar way to what was previously described by our group [6]. The triplet characteristic of this transient was confirmed by quenching studies using *trans*-stilbene (E_T = 49 kcal/mol) as a quencher [23]. In this case, a quenching rate constant identical to the diffusion-controlled rate constant (k_{diff}) for [bmim.PF_6] was obtained, which was calculated as 1.0×10^8 L mol^{-1} s^{-1} employing the Smoluchowski–Stokes–Einstein equation [23]. The decay for this triplet is purely first order (Figure 3), which indicates that, in this solvent, the deactivation of benzil triplet by a triplet-triplet annihilation process is highly inefficient, a consequence of the low diffusion rate constant for [bmim.PF_6].

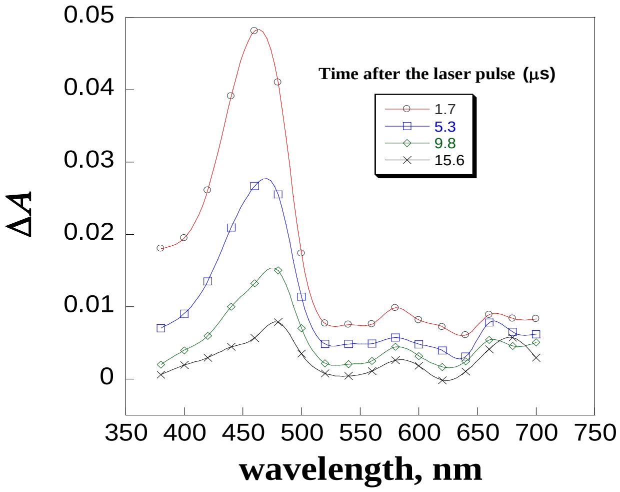


Figure 2. Absorption spectra for the transient generated in the photolysis (λ = 355 nm) of benzil in [bmim.PF_6].

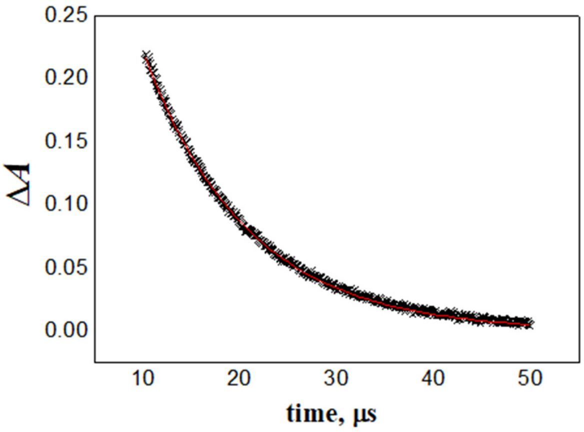


Figure 3. Kinetic decay trace for benzil in [bmim.PF_6], monitored at 480 nm.

A previous publication from our group showed the different kinetic behavior for the decay of benzil triplet in [bmim.PF_6] and acetonitrile. In the latter case, it was clearly demonstrated that the decay in acetonitrile does not follow a clear first-order kinetic, with the second-order component of the decay being assigned to a triplet-triplet annihilation process [4].

Quenching of benzil triplet by substituted phenols (phenol, *para*-methoxyphenol, *para-tert*-butylphenol, *para*-phenylphenol, *para*-methylphenol, *para*-chlorophenol, and *para*-fluorophenol) in [bmim.PF_6] following the Stern–Volmer equation (Equation (1)) resulted in linear plots from which it was possible to calculate the 2nd-order rate constants for this quenching process as shown in Table 1. This table indicates that the quenching rate constants of benzil triplet by the phenols used in this work in [bmim.PF_6] is almost independent of the substituent, being very close to the diffusion rate constant in this solvent (k_{diff} = 10^8 L mol^{-1} s^{-1}). Representative plots of the quenching of benzil triplet by different phenols are shown in Figure 4.

Table 1. Second-order quenching rate constants for the reaction of the triplet excited state of benzil by phenols containing polar substituents, [bmim.PF_6].

Quencher	k_q, L mol^{-1} s^{-1}	R^2
phenol	$(8.4 \pm 0.3) \times 10^7$	0.9904
para-methoxyphenol	$(1.8 \pm 0.1) \times 10^8$	0.9889
para-terc-butylphenol	$(7.3 \pm 0.2) \times 10^7$	0.9823
para-phenylphenol	$(6.7 \pm 0.5) \times 10^7$	0.9761
para-methylphenol	$(5.4 \pm 0.3) \times 10^7$	0.9946
para-chlorophenol	$(1.4 \pm 0.1) \times 10^7$	0.9867
para-fluorophenol	$(1.8 \pm 0.1) \times 10^7$	0.9892

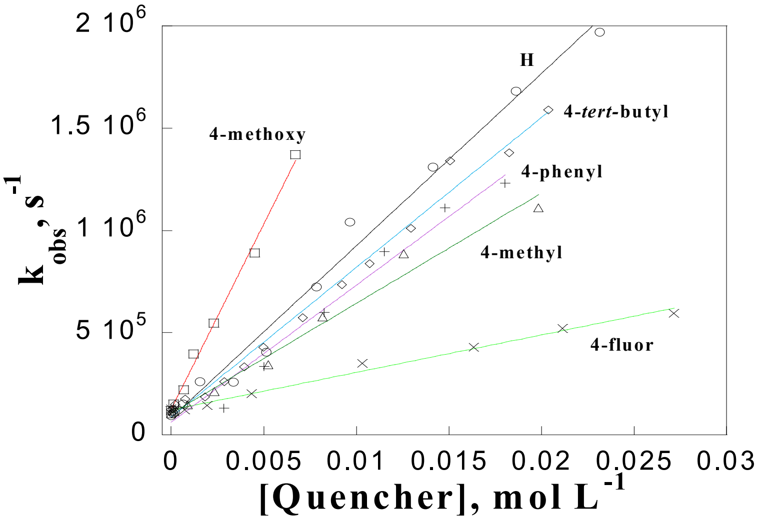


Figure 4. Stern–Volmer plots for the quenching of benzil triplet by several phenols in [bmim.PF_6].

Photolysis (λ_{exc} = 355 nm) of a [bmim.PF_6] solution of benzil in the presence of a phenol substituted by a polar group resulted in a new intense absorption band with a maximum of below 360 nm and a less intense broad band with a maximum of 550 nm. These two bands correspond to the benzil ketyl radical, as previously reported in the literature [18,24,25].

No evidence was found for forming the aryloxyl radical derived from phenol, which usually exhibits absorption in the 400 nm region. The non-observation of the aryloxyl radical may be due to the low phenolic hydrogen abstraction rate constant by the benzil triplet (k_q ~ 10^7 mol L^{-1} s^{-1}, Table 1), associated with its low molar absorption coefficient when compared to that of the benzyl ketyl radical. Figure 5 shows representative spectra of the formation of the benzil ketyl radical, using as an example its photolysis in the presence of *para*-fluorophenol in the ionic liquid [bmim.PF_6].

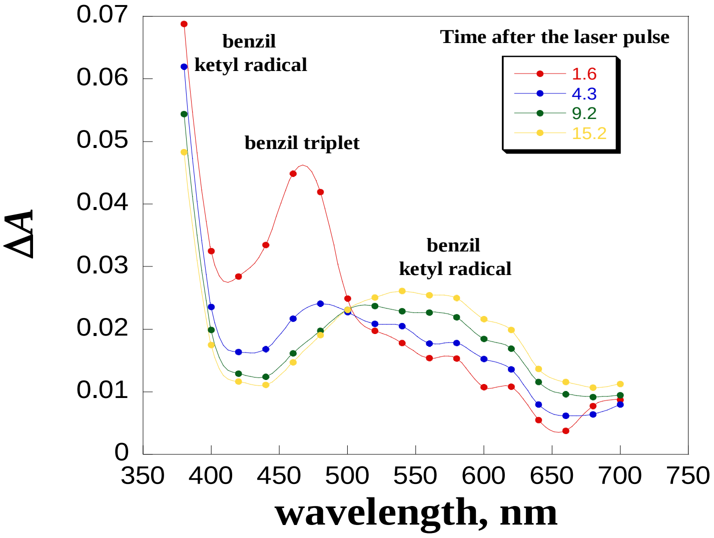


Figure 5. Transient absorption spectra for the photolysis (l = 355 nm) of benzil in the presence of excess *para*-fluorophenol in [bmim.PF_6].

The absorption spectrum for the transient generated upon irradiation (λ_{exc} = 355 nm) of 2,2′-furil in [bmim.PF_6] is much more complex than that recorded for benzil. As can be seen in Figure 6, this spectrum presents maximum absorptions with narrow bands at 380 and 410 and broad bands at 450 and 650 nm, like that described in the literature employing acetonitrile as the solvent [19]. The lifetime for this transient monitored at these maxima was 1.4 μs. The purely first-order decay obtained for this transient (Figure 7) indicates that its deactivation does not involve a triplet-triplet annihilation process. Its characterization as the triplet excited state of 2,2′-furil was confirmed by quenching studies using *trans*-stilbene (E_T = 49 kcal/mol) (Figure 8), for which an energy transfer rate constant was measured as (2.42 ± 0.06) × 10^8 L mol^{-1} s^{-1} (R^2 = 0.9973).

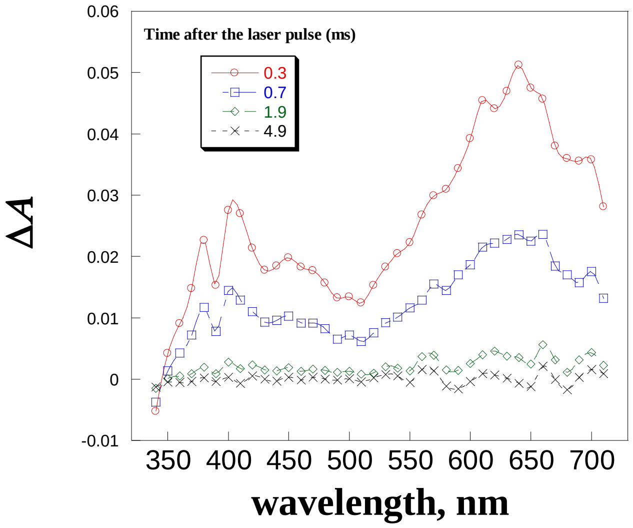


Figure 6. Absorption spectra for the transient generated in the photolysis (λ = 355 nm) of 2,2′-furil in [bmim.PF_6].

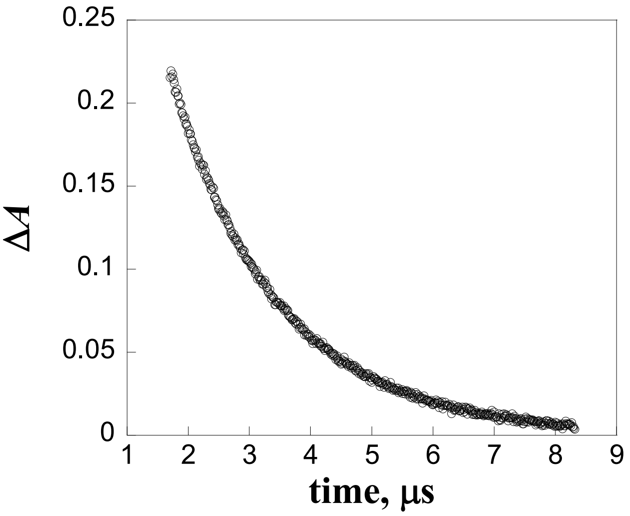


Figure 7. Decay for the transient generated in the photolysis (λ = 355 nm) of 2,2′-furil in [bmim.PF$_6$], monitored at 650 nm.

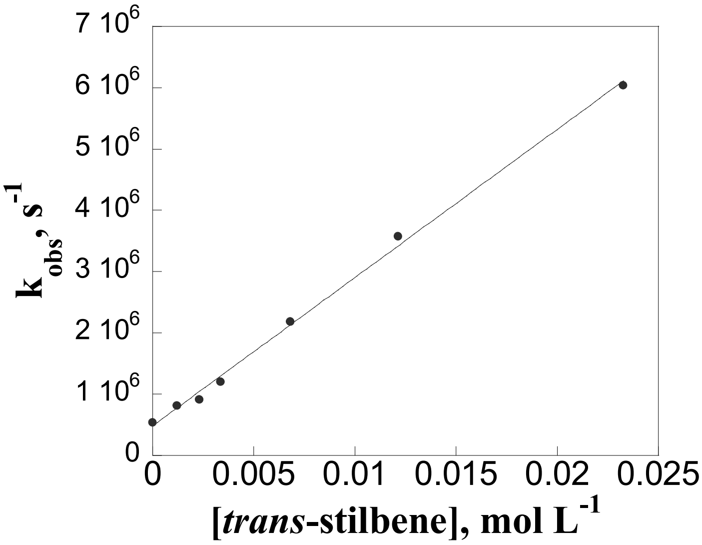


Figure 8. Stern–Volmer plot for the quenching of 2,2′-furil triplet by *trans*-stilbene in [bmim.PF$_6$].

Representative plots for 4-fluorophenol, 4-methoxyphenol, and 4-methylphenol are shown in Figure 9, from which it was possible to calculate the second-order quenching rate constants for this process (Table 2). This table indicates that in [bmim.PF$_6$] the quenching of 2,2′-furil triplet by these phenols is independent of the substituent, with the quenching rate constants being identical to the diffusion rate constant in this ionic liquid (k_{diff} = 10^8 L mol^{-1}s^{-1}).

Table 2. Second order rate constants for quenching of the triplet excited state of 2,2′-furil by phenols containing polar substituents, in [bmim.PF$_6$].

Quencher	k_q, L mol^{-1} s^{-1}	R^2
phenol	$(2.2 \pm 0.4) \times 10^8$	0.9794
para-methoxyphenol	$(2.9 \pm 0.2) \times 10^8$	0.9769
para-methylphenol	$(3.5 \pm 0.2) \times 10^8$	0.9840
para-chlorophenol	$(1.9 \pm 0.2) \times 10^8$	0.9939
para-fluorophenol	$(2.1 \pm 0.2) \times 10^8$	0.9764

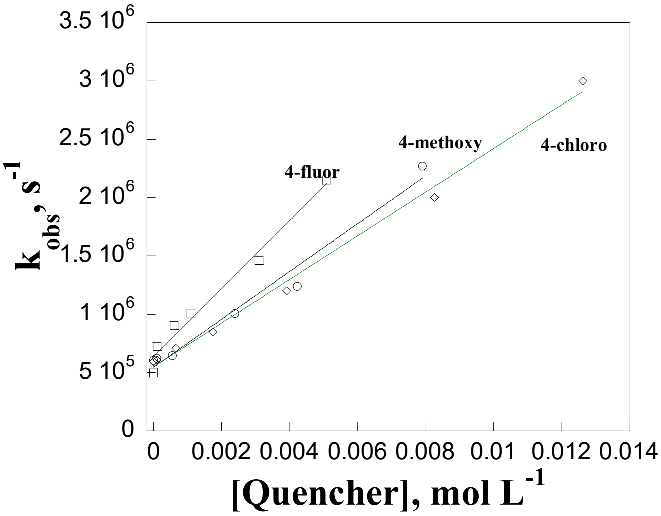


Figure 9. Representative Stern–Volmer plots for the quenching of 2,2′-furil triplet by several phenols (4-fluor-; 4-methoxy-; 4-chloro-) in [bmim.PF$_6$].

The photolysis of 2,2′-furil in the presence of phenol and its derivatives containing polar substituents in [bmim.PF$_6$] resulted, in all cases, in the formation of a new transient with maximum absorption at 380 nm (Figure 10), which can be associated with the 2,2′-furil ketyl radical according to previous literature results [19]. This transient decays with a lifetime over 25 ms when data acquisition was set at a 10 ms timescale (Figure 11A), whereas at a shorter timescale (200 ns), the kinetic profile for formation of this new transient reveals that the 2,2′-furil ketyl radical grows-in with first order kinetics (Figure 11B).

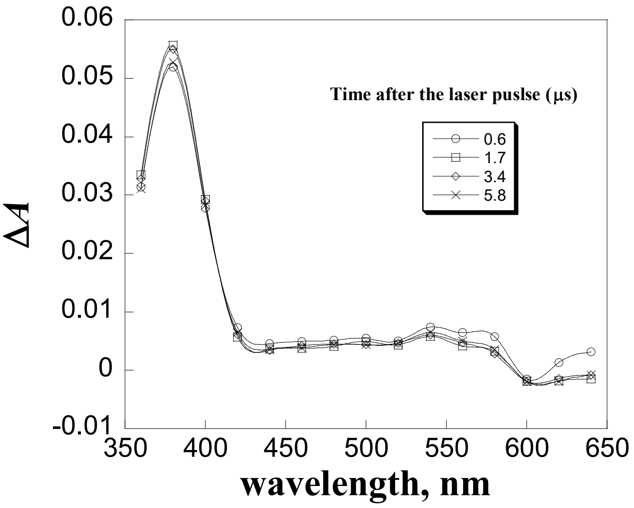


Figure 10. Transient absorption spectra for the photolysis (l = 355 nm) of 2,2′-furil in the presence of excess *para*-chlorophenol in [bmim.PF$_6$].

Phenolic hydrogen abstraction reaction is a well known process in the photochemistry of the triplet excited state of carbonyl compounds [26–33]. This reaction is usually described by a proton-coupled electron transfer (PCET) mechanism [34–40] involving the initial formation of a hydrogen bond stabilized triplet exciplex through a partial electron transfer. The transition state involved in the triplet exciplex formation has a small activation energy barrier, according to previous work from our group [41], with the triplet exciplex showing a significant increase in the electron density on the α-dicarbonyl compound and a reduction in the electron density of the phenoxyl fragment. Then, a complete electron transfer followed by ultra-rapid proton transfer leads to a triplet radical pair, ultimately resulting in the ground state ketyl-aryloxyl radical pair (Scheme 1) [4,42–45].

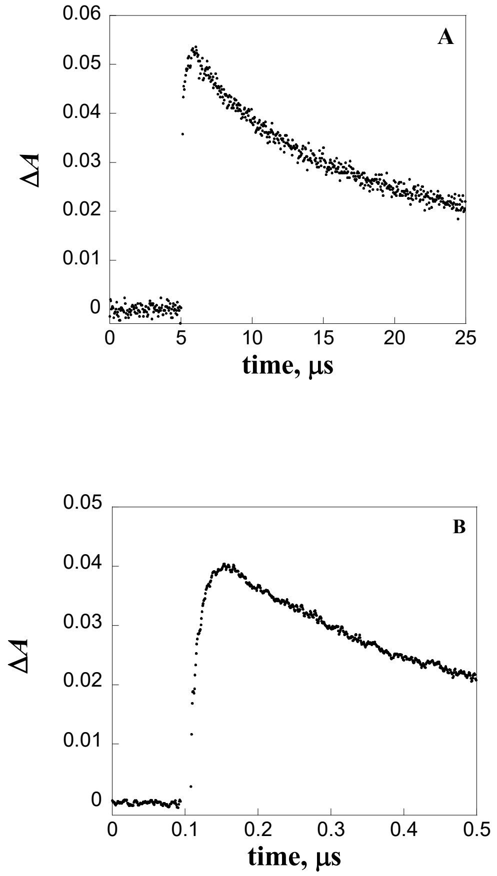
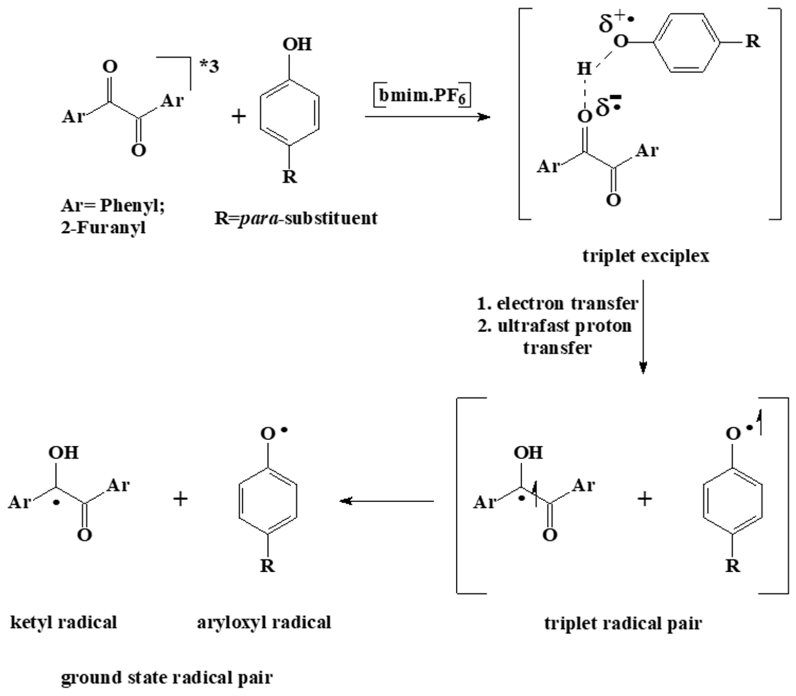


Figure 11. (**A**): decay trace due to the 2,2′-furil triplet state monitored at 650 nm and generated upon excitation (l = 355 nm) of 2,2′-furil in the presence of *para*-chlorophenol (1.0×10^{-4} mol L^{-1}) in [bmim.PF_6]. (**B**): growth and decay of the absorption at 380 nm due to formation of the 2,2′-furil ketyl radical generated as above.



Scheme 1. Mechanistic proposal for the phenolic hydrogen abstraction by the triplet excited state of benzil or 2,2′-furil in [bmim.PF_6].

4. Conclusions

The photoreactivity of α-diketones in organic solvents is influenced by the conformation of the carbonyl groups, which, naturally, affects the degree of conjugation among them, being a critical factor in modulating their photoreactivity. This difference in photoreactivity can be verified by comparing, for example, the rate of hydrogen abstraction towards phenol between benzil (k_q = 3.6 × 10^6 L mol^{-1} s^{-1}, in ACN) with a triplet excited state showing a *transoid* conformation and acenaphthoquinone (k_q = 7.1 × 10^7 L mol^{-1} s^{-1}, in ACN), of *cisoid* conformation, in which the latter is two orders of magnitude more reactive [46].

As stated above, the angle between the two carbonyl groups in ground-state benzil is 72°. In contrast, the lower triplet excited state benzil, of np* configuration, has a *transoid* conformation (dihedral angle = 180°). On the other hand, ground and excited state (np*) 2,2′-furil are almost *trans*-planar. Literature results indicate that the hydrogen abstraction rate constant for 2,2′-furil from 2-propanol (k_q = 5.1 × 10^5 L mol^{-1} s^{-1}, in ACN [19], is at least one order of magnitude greater when compared to that for benzil (k_q < 1.7 × 10^4 L mol^{-1} s^{-1}) in the same solvent [46]. Nanosecond laser flash photolysis studies demonstrated that the irradiation (l = 355 nm) of benzil and 2,2′-furil in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [bmim.PF_6] leads to the formation of the corresponding triplet excited state, which was characterized by energy transfer experiments employing *trans*-stilbene as a quencher. Surprisingly, using the ionic liquid [bmim.PF6] as a solvent, the values obtained in the present work for the phenolic hydrogen abstraction rate constants for both benzil and 2,2′-furil were the same and close to diffusion-control in all cases, with formation of their corresponding ketyl radical. These results indicate that using this ionic liquid as a solvent not only causes the conformational influence on the reactivity of benzyl and 2,2′-furil to cease to exist but, more importantly, the hydrogen abstraction rate constants become controlled by diffusion in all cases. Thus, the low solubility of oxygen in [bmim.PF_6] and, mainly, the diffusional control in hydrogen transfer reactions indicate that this ionic liquid is an excellent solvent for studying the reactivity of triplet excited states and future applications, especially those involving photopolymerization reactions initiated by free radicals.

Author Contributions: A.R.B.: formal analysis, data curation. J.C.N.-F.: writing—review and editing, writing—original draft, supervision, funding acquisition, conceptualization. All authors have read and agreed to the published version of the manuscript.

Funding: The authors very much appreciate grants from the Brazilian funding agencies Fundação de Amparo à Pesquisa do Estado da Bahia (FAPESB), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), and Financiadora de Estudos e Projetos (FINEP).

Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

Acknowledgments: The authors acknowledge Cristina Quintella from the Universidade Federal da Bahia, Brazil, for making the laser flash photolysis facilities available.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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