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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 @-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 (l_{max}=355 nm) of benzil yields its triplet excited state with l_{max} at 480 nm and t_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 t_T=1.4 µs. Quenching rate constants (k_q) of the reaction between benzil triplet and substituted phenols ranged from 1.4x10^7 L mol^{-1} s^{-1} (*para*-chlorophenol) to 1.8x10^8 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 1.9x10^8 L mol^{-1} s^{-1} (*para*-chlorophenol) to 2.2x10^8 L mol^{-1} s^{-1} (*para*-methoxyphenol). The 2,2′-furil ketyl radical was also observed in all cases (l_{max}=380 nm). The quenching rate constants are almost independent of the substituent and diffusion-controlled (k_q ~ 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: benzil; 2,2′-furil; nanosecond laser flash photolysis; triplet excited state; ionic liquids; phenolic hydrogen abstraction

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].

The first application of ILs in photochemistry reported in the literature consisted of the photooxidation of the iron II diimine complex in an ionic liquid formed by a mixture of aluminum chloride and ethylpyridinium bromide (2:1) [3]. A reaction mechanism was proposed where ethylpyridinium cations, when cooled, accept an electron to form the corresponding radical, with a subsequent dimerization of this species resulting in a colored component. The photolysis of anthracene results in its photodimerization in different ionic liquids through a [4+4] photocycloaddition via the singlet excited state, as in conventional solvents [4]. On the other hand, in irradiation of 9-methylanthracene [5], which is more easily oxidized, a series of neutral and charged intermediates are formed, regardless of whether threaction is conducted in acidic or basic ionic liquids or the presence of oxygen [3].

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≈10^8 L mol^{-1} s^{-1}) than those observed for conventional organic solvents such as benzene, methanol, and acetonitrile [3]. In the absence of quenchers, the hydrogen abstraction rate constant of ionic liquids based on 1,3-dialkylimidazole salts is lower than that observed for solvents such as toluene or 1-butanol. Furthermore, the activation energy for the hydrogen abstraction process is similar for all ionic liquids used (E_a≈6.0 kcal/mol) and about 2.4 kcal/mol higher than the values obtained for toluene or 1-butanol [3].

Xanthone has been widely employed as a triplet probe since its triplet-triplet absorption spectrum and reactivity are highly dependent on the polarity of the solvent. Laser flash photolysis of xanthone in a solution of the ionic liquid [bmim.PF_6] results in an absorption maximum for its triplet excited state at 622 nm and a relatively long lifetime compared to acetonitrile. 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}. The hydrogen abstraction rate constant towards phenols containing polar substituents in [bmim.PF_6] was independent of the substituent [6].

Triplet-triplet energy transfer studies using xanthone as donor and naphthalene as acceptor showed that, in the ionic liquid [bmim.PF_6], the energy transfer rate constant k_q, even in exergonic processes like this one (ΔE=14 kcal/mol), is about two orders of magnitude lower than that observed in conventional organic solvents, as already described above [1]. 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]. Thus, a quenching rate constant of 6.8x10^6 L mol^{-1} s^{-1} was determined using diphenylmethane as a hydrogen donor. Furthermore, the formation of the ketyl radical derived from xanthone could be observed at 530 nm [1].

A laser flash photolysis study of 2,4,6-triphenylthiapyrylium chloride, both in a solution of the ionic liquid [bmim.PF_6] and adsorbed on zeolite Y resulted in observing the triplet excited state of the thiapyrylium salt. When quenched by dicyclopentadiene, which behaves as an electron donor, this triplet forms the corresponding radical ion. The polarity of the environment can stabilize this species, which increases its lifetime [7].

Ionic liquids are excellent solvents for generating radical ions. Thus, the photoinduced transformation of functional groups that goes through an electron transfer process has been used in the photoreduction of ketones, the photosensitized nucleophilic addition to alkenes, and aromatic nucleophilic photosubstitution reactions. In most cases, the distribution of products observed when using ionic liquids as solvents differs entirely from that in conventional organic solvents.

The photoreduction of benzophenone by amines in ionic liquids at room temperature mainly provides benzhydrol, unlike what occurs with organic solvents, in which the primary process corresponds to an electron transfer, followed by proton transfer and subsequent pinacolization or coupling between the ketyl radical derived from benzophenone and the α-aminyl radical [8]. The electron transfer reaction between photoexcited $[Ru(bpy)_3]^{2+}$ and the methylviologen dication (MV^{2+}) is diffusion controlled. However, the degree of escape from the solvent cage is much higher than that found in conventional organic solvents [9].

Other examples of electron transfer reactions in ionic liquids include the quenching of the singlet excited state of the 2,4,6-triphenylpyrylium ion and its triplet excited state (biphenyl: k_q=1.1x10^9 L mol^{-1} s^{-1}; ferrocene: k_q=1.8x10^8 L mol^{-1} s^{-1}; tetrabutylammonium: k_q=1.1x10^8 L mol^{-1} s^{-1}), as well as the quenching of the anthracene triplet by the methylviologen dication (MV^{+2}), for which a rate constant of 1.1x10^8 L mol^{-1} s^{-1} was found [1]. Finally, the photoisomerization of *trans* to *cis*-stilbene in the ionic liquid 1-ethyl-3-methylimidazole/$AlCl_3$ also occurs via an electron transfer mechanism through its singlet excited state [3].

Ionic liquids were used as a solvent for chiral induction in the photoisomerization of dibenzobicyclo [*2.2.2*] octatrienes, with an enantiomeric excess of 3 to 12% being obtained in the di-◎-methane rearrangement reaction. This chiral induction process is derived from the interaction of deprotonated diacids' ion pair with the ionic liquid's cation. [10].

Triplet excited state photosensitizers soluble in ionic liquids at room temperature can be prepared through the covalent linkage of 1-methylimidazole to aryl ketones. These sensitizers have the advantage of remaining soluble in the ionic liquid after extraction of the reaction product by organic solvents. Thus, the isomerization of *trans*-◎-ionol to *cis*-◎-ionol was efficiently carried out by employing such a procedure [4]

The triplet-triplet absorption spectrum for the carbonyl compounds thioxanthone and benzil in the ionic liquid [bmim.PF_6] is like those observed in organic solvents [11]. However, the lifetimes for the triplet excited state in both cases depend on the solvent type. Thus, thioxanthone has a triplet lifetime of 178 ◎s in [bmim.PF_6] and 14 ◎s in acetonitrile were measured, while the lifetime obtained for benzil was 10 ◎s in [bmim.PF_6] and 3.8 ◎s in acetonitrile. It is worth noting that thioxanthone triplet lifetime varies dramatically, depending on whether the solution is degassed or not. Thus, although the triplet excited state of thioxanthone in deoxygenated [bmim.PF_6] solution was 178 ◎s, in an oxygen-saturated solution a surprising value of 500 ns was observed. For comparison, in an oxygen-saturated acetonitrile solution, triplet thioxanthone is totally quenched ($t_T <$ 10 ns) [11]. Since it is possible to observe the thioxanthone triplet decay even in oxygen-saturated solvents unequivocally demonstrates the very low oxygen solubility in ionic liquids. This agrees with previous studies showing that oxygen and argon are poorly soluble in ionic liquids [12].

◎-Diketones are used in several applications in photochemical reactions and, among the most important, are the epoxidation reaction of olefins in the presence of oxygen [13–15] and photopolymerization by free radicals when in the presence of hydrogen donors [16,17]. Due to their importance, many studies on their electronic and spectroscopic properties have been dedicated to ◎◎diketones [18–27].

Similarly to monoketones, the photoreduction of the triplet excited state of ◎-diketones is governed by several factors, such as the energy of the triplet excited state, the n◎* or ◎◎* character of the lowest energy triplet excited state, the geometry of the triplet excited state conformation, and the presence of heteroatoms in the ◎ position relative to the dicarbonyl group, which can considerably reduce the electrophilicity of the excited carbonyl group [28,29].

Several groups have demonstrated that the n◎* nature of the lowest energy excited state strongly depends on the dihedral angle between the carbonyl groups [30–32]. Benzil (E_T=54.0 kcal/mol) is a ◎-dicarbonyl compound that presents different conformations due to possible rotation of the ◎$_{C\text{-}C}$ bond in the ground state and in the excited state [33–38].

In the ground state, the angle between the two carbonyl groups is 72º, and, after excitation, the first triplet excited state acquires a *transoid* conformation in which the carbonyl groups are at 180º [37]. The lowest energy triplet excited state for benzil has an n◎* 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. In a fluid medium, after excitation, benzil undergoes conformational relaxation, going from a twisted structure in the ground state to a planar conformation in the triplet excited state [37].

As the behavior of the benzil triplet excited state presents a significant dependence 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 solution [33–36,38] and organized systems such as microcrystalline cellulose, ◎◎cyclodextrin [39], 4-*tert*-butylcalix[*n*]arenes (*n* = 4, 6 and 8) and silicalite [40].

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 ◎$_{C\text{-}C}$ bond [41,42]. Furthermore, the interaction 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 131º [43], whereas, in the triplet excited state, only over long periods of time, a completely planar conformation is achieved.

In this work, kinetic and spectroscopic data are presented, using the nanosecond laser flash photolysis technique, on the triplet excited state reaction of benzil and 2,2'-furil with phenols containing polar substituents, using the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [bmim.PF$_6$] as solvent.

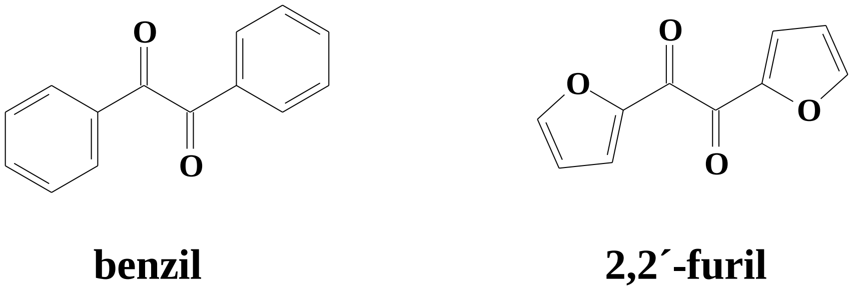


Figure 1. Structures for benzil and 2,2’-furil.

2. Materials and Methods

Materials. HPLC-grade acetonitrile was purchased from J. T. Baker. 1-*n*-Butyl-3-methylimidazolium hexafluorophosphate [bmim.PF$_6$] was purchased from Fundação Universidade Federal do Rio Grande do Sul, Brazil, and used as received. Benzil and 2,2'-furil from Aldrich 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 and used as received.

Methods. Spectra in the ultraviolet-visible region were obtained on a Hewlett Packard 8453 spectrophotometer equipped with a diode array detector and interfaced with a PC containing a Windows Workstation 4.0 software.

Nanosecond laser flash photolysis experiments were performed using a Luzchem model mlfp 112 system employing a 175 W CERMAX xenon lamp, a CUI laser Corporation Digikröm CM 110 monochromator, a Hamamatsu photomultiplier, and a Tektronix model TDS 2012 oscilloscope where the photomultiplier signals are digitized. The oscilloscope can make acquisitions every two nanoseconds and its memory can store up to 15000 points. The data read by the oscilloscope is transmitted to a personal computer (Dell, Pentium IV, 3.4 GHz) through a GPIB interface. The computer controls the acquisition, processing, frequency of the laser pulse and the shutters through the Kinetic Processor program, which uses the Labview software 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 ($\lambda = 355$ nm, 10 ns pulse, ~ 40 mJ/pulse) of a Surelite II model, Continuum Nd/YAG laser. 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 a-diketones 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 x 10 mm was used containing 1 mL of ketone solution in the ionic liquid 1-*n*-butyl-3-methyl imidazolium hexafluorophosphate [bmim.PF], deaerated for 30 minutes 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 [44].

$$k_{obs} = k_o + k_q[Q] \qquad \text{(eq. 1)}$$

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 ⊚s, in a similar way to what was previously described by our group [11]. The triplet characteristic of this transient was confirmed by quenching studies using *trans*-stilbene (E_T=49 kcal/mol) as a quencher [45]. 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 [45]. 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, consequence of the low diffusion rate constant for [bmim.PF_6].

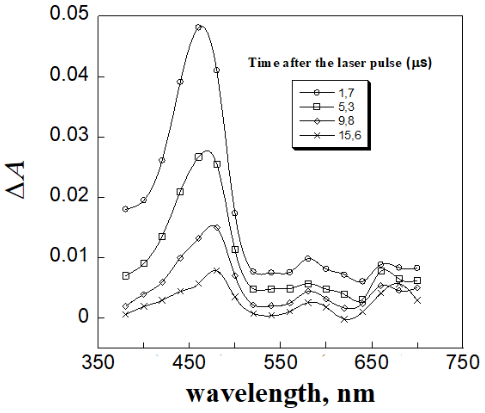


Figure 2. Absorption spectra for the transient generated in the photolysis (⊚=355 nm) of benzil in [bmim.PF_6].

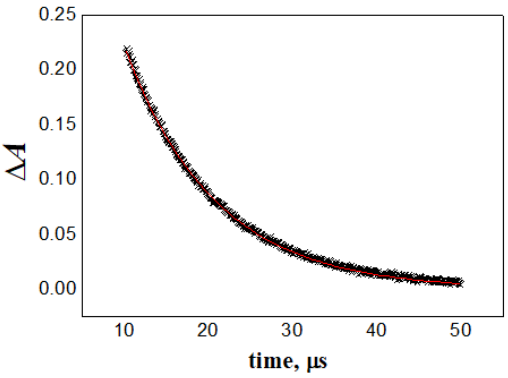


Figure 3. Kinetic decay trace for benzil in [bmim.PF_6], monitored at 480 nm. (x) Expermental data; (-) fitting trace.

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 (eq. 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.

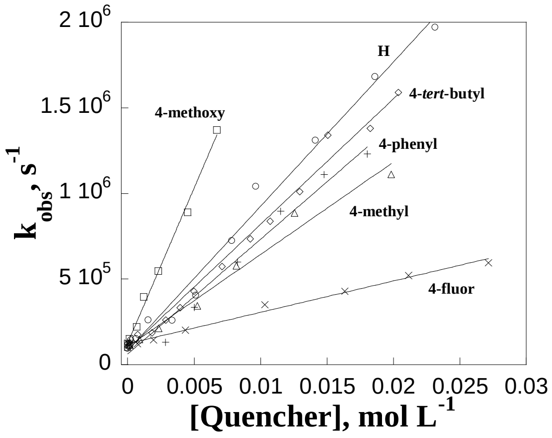


Figure 4. Stern-Volmer plots for the quenching of benzil triplet by several phenols in [bmim.PF$_6$].

Photolysis (◎$_{exc}$=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 [40,46,47].

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$_6$].

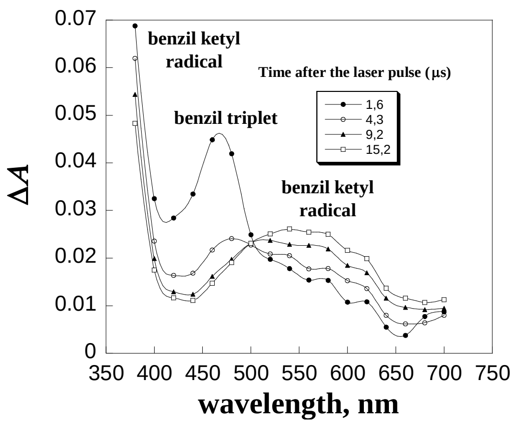


Figure 5. Transient absorption spectra for the photolysis (l=355 nm) of benzil in the presence of excess *para*-fluorophenol in [bmim.PF$_6$].

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}**
phenol	$(8.4\pm0.3)\times10^7$
para-methoxyphenol	$(1.8\pm0.1)\times10^8$
para-terc-butilphenol	$(7.3\pm0.2)\times10^7$
para-phenylphenol	$(6.7\pm0.5)\times10^7$
para-methylphenol	$(5.4\pm0.3)\times10^7$
para-chlorophenol	$(1.4\pm0.1)\times10^7$
para-fluorophenol	$(1.8\pm0.1)\times10^7$

The absorption spectrum for the transient generated upon irradiation (l_{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 [41]. The lifetime for this transient monitored at these maxima was 1.4 ◎s and its characterization as the triplet excited state of 2,2′-furil was confirmed by quenching studies using *trans*-stilbene (E_T=49 kcal/mol). The purely first-order decay being obtained for this this transient (Figure 7) indicates that its deactivation does not involve a triplet-triplet annihilation process.

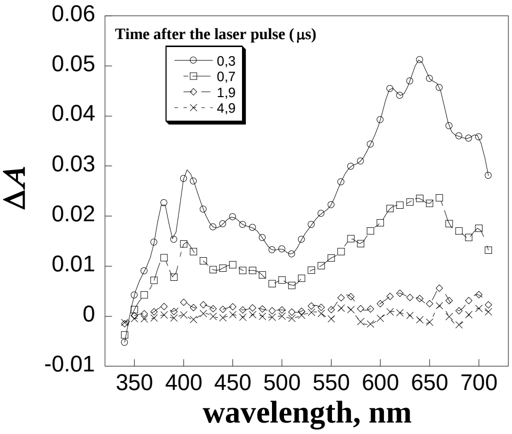


Figure 6. Absorption spectra for the transient generated in the photolysis (l=355 nm) of 2,2′-furil in [bmim.PF_6].

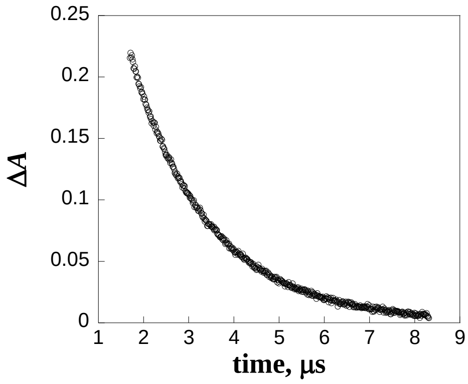


Figure 7. Decay for the transient generated in the photolysis (◎=355 nm) of 2,2′-furil in [bmim.PF$_6$], monitored at 650 nm.

Representative plots for 4-fluorophenol, 4-methoxyphenol and 4-methylphenol are shown in Figure 8, 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}).

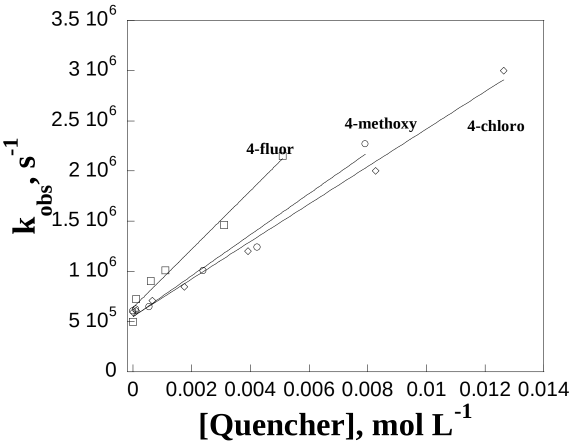


Figure 8. Representative Stern-Volmer plots for the quenching of 2,2′-furil triplet by several phenols (4-fluor-; 4-methoxy-; 4-chloro-) in [bmim.PF$_6$].

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}**
phenol	(2.2±0.4)x10^8
para-methoxyphenol	(2.9±0.2)x10^8
para-methylphenol	(3.5±0.2)x10^8
para-chlorophenol	(1.9±0.2)x10^8

para-fluorophenol	(2.1±0.2)x10^8

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 9), which can be associated with the 2,2'-furil ketyl radical according to previous literature results [41]. This transient decays with a lifetime over 25 ms when data acquisition was set at a 10 ms timescale (Figure 10A), 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 10B).

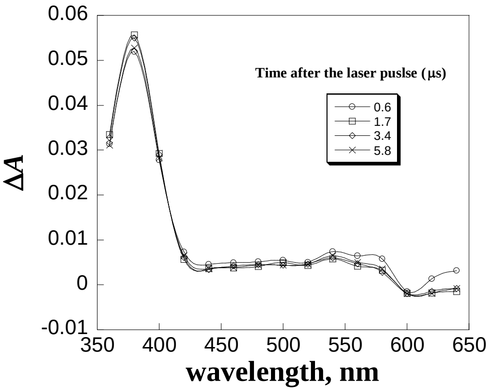
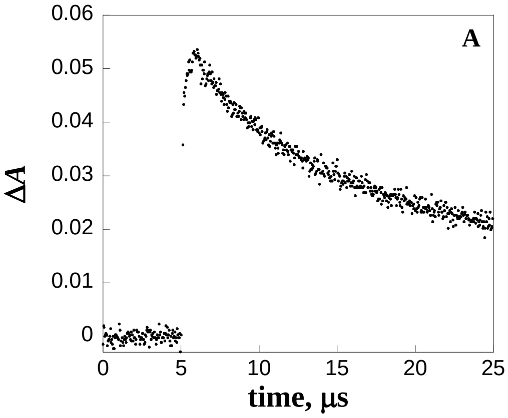


Figure 9. Transient absorption spectra for the photolysis (l=355 nm) of 2,2’-furil in the presence of excess *para*-chlorophenol in [bmim.PF$_6$].



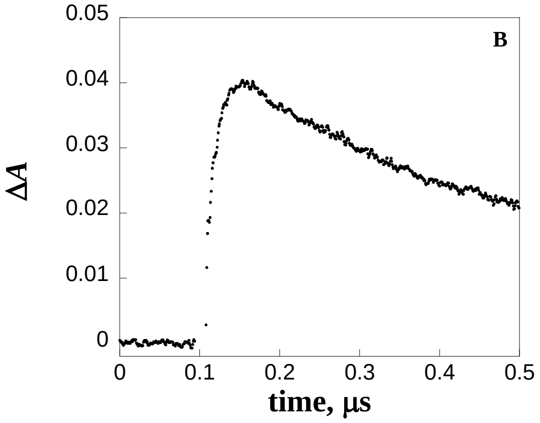
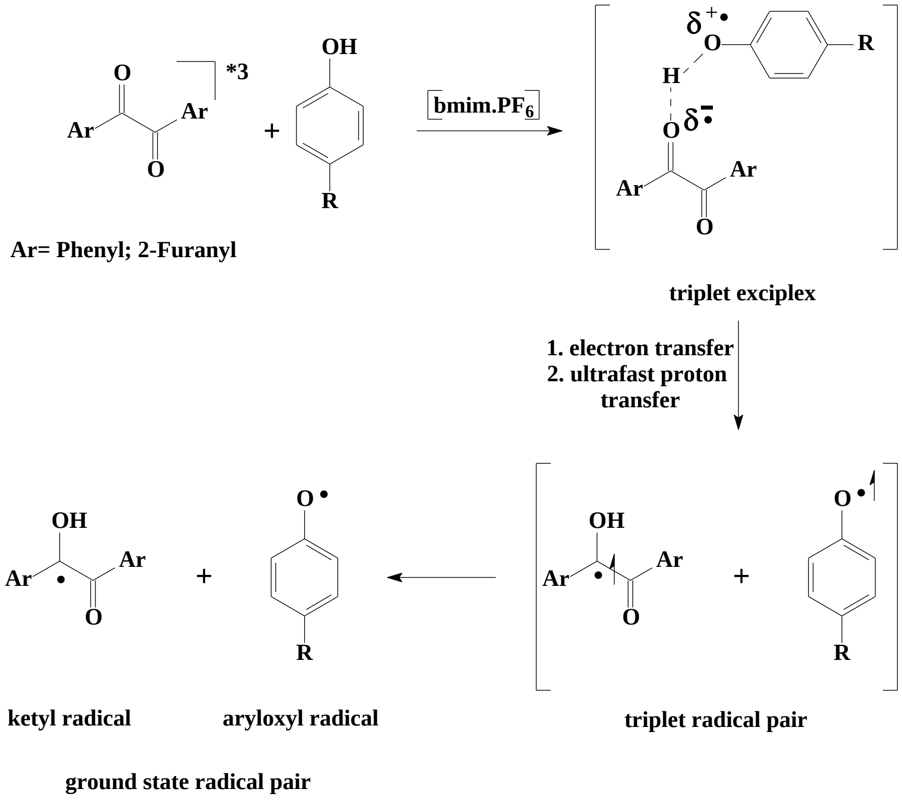


Figure 10. **A**: decay trace due to the 2,2′-furil triplet state monitored at 650 nm and generated upon excitation (l = 355 nm) of 2,2′-furil in the presence of *para*-chlorophenol (1.0×10^{-4} mol L^{-1}) in [bmim.PF$_6$]. **B**: growth of absorption at 380 nm due to formation of the 2,2′-furil ketyl radical generated as above.

Phenolic hydrogen abstraction reaction is a well know process in the photochemistry of the triplet excited state of carbonyl compounds [48–59]. This reaction is usually described by a proton-coupled electron transfer (PCET) mechanism [60–70], 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 [64,71], with the triplet exciplex showing a significant increase in the electron density on the ◎-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) [6,57–59,64,72–81].



Scheme 1. Mechanistic proposal for the phenolic hydrogen abstraction by the triplet excited state of benzil or 2,2′-furil in [bmim.PF$_6$].

Conclusions

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. Phenolic absolute rate constants were measured, and the resulting quenching rate constants were close to diffusion-controlled in all cases. Photolysis of benzil or 2,2′-furil in the presence of phenols also shows the formation of their corresponding ketyl radical.

CRediT authorship contribution statement Ada Ruth Bertoti: Formal analysis, Data curation. **José Carlos Netto- Ferreira:** Writing – review & editing, Writing – original draft, Supervision, Funding acquisition, Conceptualization.

Data availability No data was used for the research described in the article.

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Declaration of competing 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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