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Light-Induced Hydrogen Abstraction from Isobutanol by Thienyl Phenyl, Dithienyl, and Thienyl Pyridyl Ketones

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In this paper the bi-molecular interactions of some heteroaromatic (thienyl phenyl, dithienyl, and thienyl pyridyl) ketones with isobutanol were studied by using nanosecond laser flash photolysis in trifluoroethanol at room temperature. The absorption spectra of the triplets and ketyl radicals and their decay dynamics were investigated. Depending on the thienyl ring position (2 or 3), two types of photobehavior were found: (1) the 2-thienyl ketones, which have lowest triplets of π,π^* character, abstract hydrogen at a slow rate ($k_H < 2 \times 10^4$ dm^3 mol^{-1} s^{-1}) and (2) the 3-thienyl ketones, which have lowest triplets of n,π^* character, abstract hydrogen at a faster rate ($k_H \sim 3 \times 10^5$ dm^3 mol^{-1} s^{-1}). For most of the latter compounds, both n,π^* and π,π^* triplets are spectrally and kinetically observed. While in 2-thienyl ketones the upper reactive n,π^* triplet is thermally populated by the lowest π,π^* one, in 3-thienyl ketones the two states are independent populated from the singlet state and vibronic mixing between them is not efficient.

Introduction

Hydrogen abstraction from a suitable donor is a typical photoreaction of carbonyl compounds and was one of the first photoreactions to be studied.[1,2] The wide interest in this process is demonstrated by the many papers published on this subject which deal with several classes of ketones and different types of hydrogen donors. The interaction of the triplet state ketone with the ground state hydrogen donor produces a hydroxy radical which may dimerize to give pinacols or further abstract hydrogen from the donor, forming adducts. The diphenylhydroxymethyl radical (ketyl) from benzophenone was first detected in the early 1960s by Porter using flash photolysis.[3]

Ketones are often used as photosensitizers and photoinitiators. In the first case, hydrogen abstraction is undesirable, because it competes with the energy transfer, while in the second case, it should be highly efficient.

The rate constant of the reaction depends on the C−H bond energy of the donor, as well as on the energy and configuration of the excited state of the carbonyl compound. Ketones having the lowest triplet states of n,π^* configuration easily abstract hydrogen, due to their similarity to alkoxy radicals; ketones having low lying π,π^* triplets are less reactive and their reactivity decreases as the energy gap between π,π^* and n,π^* triplets increases.[4,5] For many aromatic ketones, the two triplet states are very close in energy and substituent or solvent effects can lead to an inversion of states. By investigating the effect of substituents on a large number of valerophenones, Wagner and collaborators[5] have shown that when the two lowest n,π^* and π,π^* states lie very close together, being therefore quite substituent and solvent sensitive, the reaction may take place from the equilibrium populations of both states; the reactivity of ketones with π,π^* lowest triplets decreases as the energy gap between the π,π^* and n,π^* upper triplets increases. A charge-transfer contribution to the photoreduction of aryl ketones was also demonstrated.[6] In the 1980s, Formoshino developed a theory, based on the tunnel effect, to model the photochemistry of the carbonyl group and, in particular, to explain radical-like and CT interactions in H abstraction.[7]

In this study we are concerned with intermolecular hydrogen-abstraction by the nine thienyl ketones (thienyl phenyl ketones, *n*-TPhKs; dithienyl ketones, *n,n′*-DTKs; and thienyl pyridyl ketones, *n,n′*-TPK) shown in Chart 1. Some of them are newly synthesized molecules. The photochemical behavior of the nine molecules is compared with benzophenone and with some substituted benzophenones bearing electron-withdrawing and electron-donating substituents.

The position of sulfur affects the charge density to the carbonyl in thienyl ketones, thus determining the characteristics of the lowest triplet state and therefore the efficiency in the hydrogen-abstraction process. The attractive interaction of charge-transfer character from the sulfur to the oxygen should cause a reduced activity toward hydrogen abstraction compared to the parent aryl ketone benzophenone. Up to now, sparse and limited information is reported in the literature for TPhKs and DTKs, while no investigation concerning hydrogen-abstraction has ever been carried out on TPKs. Traynard and Blanchi[8] have shown, by PP calculations, that the decreased photoreduction yield of TPhKs by propan-2-ol (compared with benzophenone) is due to the increased negative charge on the oxygen. Pinacol formation through photoreaction with an alkene has been reported for 2,2′-DTK,[9] while 2-TPhK was found to react at the ring position with olefins to give an unstable photoadduct.[10]

Recently, we investigated the photophysical behavior of the six *n,n′*-TPK isomers,[11,12] 2,2′-DTK and 2-TPhK.[13] The lowest $S_0 \rightarrow S_1$ transitions of all these molecules were assigned to n,π^* excitation, based on several pieces of evidence (spectral region, vibronic structure, a low molar absorption coefficient, and solvent effect). Intersystem crossing yields are close to unity. The orbital character of the triplet was shown by the lifetime and vibronic structure of the phosphorescence spectra in a rigid matrix at 77 K.[12] The triplet configuration, n,π^* or π,π^*, is dictated by the position (2 or 3) of the thienyl sulfur atom relative to the carbonyl. Generally, when the thienyl group is in the 3 position, the lowest triplet state is of n,π^* character

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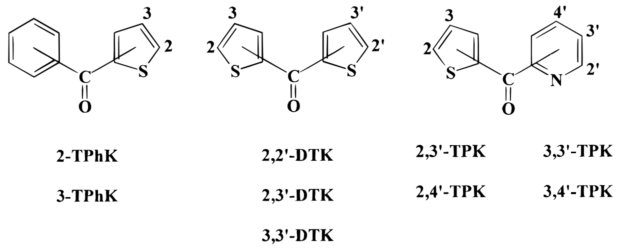
CHART 1



and exhibits benzophenone-like behavior, while when it is in the 2 position, the lowest triplet state is of π,π^* configuration. Laser flash photolysis experiments gave further information on the triplet properties and triplet dynamic behavior in mono- and bi-molecular interactions.[12,13] A matter of great significance from our earlier studies is the dependence of the photophysics of these molecules on the close proximity of states of different configuration. Even though the energy difference between the lowest triplets is small enough to allow thermal equilibration at room temperature, we proposed that, in some cases, the lowest triplets are independently populated by singlet states.[12]

In this work, we carried out a laser flash photolysis study (nanosecond time resolution) aimed at determining the effect of structure on hydrogen-abstraction photoreactivity. Photoreactivity depends on the properties of both the ketone and the hydrogen donor as well as on the solvent properties. To deal with only one of these effects, the same solvent, trifluoroethanol, where the carbonyl compounds are thermally and photochemically stable, and the same hydrogen donor, isobutanol, were used with all ketones. The results obtained indicate that the most important factor in determining photoreactivity is the thienyl ring position (2 or 3) since it determines the nature, n,π^* or π,π^*, of the lowest triplet state.

Experimental Section

Materials. The thienyl ketones were synthesized according to a literature method[14] and carefully purified,[11] with the exception of 2-thienyl phenyl ketone (2-TPhK) and di-2-thienyl ketone (2,2′-DTK) which were synthesized at the University of Gröningen and kindly supplied to us for a previous work.[13] The 2-TPhK was used without further purification, while 2,2′-DTK was purified by sublimation in vacuo. Aryl ketones, benzophenone (B), Carlo Erba, 4-fluoro-benzophenone (4-FB), 4-COOH-benzophenone (4-COOHB), and 4-phenyl-benzophenone (4-PhB), Aldrich products, were carefully crystallized before using. The solvent, trifluoroethanol (TFE), Fluka product, and the hydrogen donor, isobutanol (*i*-ButOH), Carlo Erba product, were used without further purification.

Equipment and Experimental Conditions. For laser flash photolysis measurements, the 347 nm line from a ruby laser (J. K. Lasers) or the third harmonic (355 nm) from a Continuum Surelite Nd:YAG laser were used. The laser energy was less than 10 mJ per pulse; the time resolution was about 20 ns. The expected accuracy in lifetime was within 10%. Neutral filters were employed to reduce the laser intensity and to avoid contributions to lifetime from triplet−triplet annihilation. Transient absorption spectra were recorded in point-by-point fashion. Ketone concentrations were on the order of 1.5×10^{-3} mol dm^{-3}, corresponding to an absorbance of ca. 0.6−0.8 at the exciting wavelength. Computerized graphical software programs, FIG.P or ORIGIN, were used to calculate mono- and biexponential decay and rise-time rate constants. Even when there was significant overlap of absorption spectra of different transients (biexponential decay), decay rate determinations at different wavelengths were in agreement within 10%. A somewhat larger error (≤20%) was found in the rise-time measurements.

Rate constants for the quenching of transients by oxygen k_{ox} were determined using oxygen-free, air-saturated, and oxygen-saturated solutions. To determine the hydrogen-abstraction rate constants k_H, the donor concentrations ranged from 10^{-3} to 7 mol dm^{-3}, which depended on both the triplet lifetime of the ketone and its efficiency in abstracting hydrogen. In both determinations (k_{ox} and k_H), the linear correlations, based on Stern−Volmer type equations, were very good (correlation coefficient, $\rho \geq 0.9$).

All measurements were carried out at room temperature (20 ± 2 °C).

Results

The thienyl ketones investigated were 2,3′-, 2,4′-, 3,3′-, and 3,4′-TPKs; 2,2′-, 2,3′-, and 3,3′-DTKs; 2- and 3-TPhKs (see Chart 1). For the purpose of comparison, some aryl ketones, having n,π^* (benzophenone, B; 4-F-benzophenone, 4-FB; and 4-COOH-benzophenone, 4-COOHB) and π,π^* (4-phenyl-benzophenone, 4-PhB) lowest triplet states were also investigated under the same conditions.

The triplets of all molecules were characterized by their absorption spectra, lifetimes and quenching by oxygen in TFE. The hydrogen-abstraction process from *i*-ButOH was kinetically followed in TFE at room temperature by measuring the triplet lifetime of the $T_1 \rightarrow T_n$ absorption band in the absence of *i*-ButOH (τ_o) and in the presence of varying *i*-ButOH concentrations (τ). The rate constant for the hydrogen-abstraction process k_H was obtained from the equation:

$$1/\tau = 1/\tau_o + k_H[i\text{-ButOH}] \qquad (1)$$

The hydroxy radical produced (ketyl) was characterized with its doublet−doublet absorption in neat *i*-ButOH and, when experimentally feasible (the radicals are often too long-lived for the laser setup used), by its recombination kinetics and quenching by oxygen.

Aryl Ketones. *4-Phenyl Benzophenone (4-PhB).* For this molecule, which is characterized by a π,π^* lowest triplet state[15] and does not exhibit room temperature phosphorescence emission, hydrogen abstraction was undetectable. Upon laser excitation in TFE, it showed a quite long-lived triplet ($\tau = 21$ μs), which was efficiently quenched by oxygen ($k_{ox} = 8.4 \times 10^8$ dm^3 mol^{-1} s^{-1}). Addition of *i*-ButOH to the TFE solution did not affect the absorption spectrum ($\lambda_{max} = 490$ nm) or lifetime of the triplet transient. Excitation in neat *i*-ButOH produced a substantially identical triplet absorption and lengthened the lifetime ($\tau = 41$ μs). In the literature, 4-PhB has been reported to abstract-hydrogen from propan-2-ol, which is a more efficient donor than *i*-ButOH, at a rate of 1×10^3 dm^3 mol^{-1} s^{-1}.[16]

Benzophenone (B), 4-F-benzophenone (4-FB), and 4-COOH-benzophenone (4-COOHB). These molecules exhibit a clear n,π^* triplet behavior and also show quite intense room-temperature phosphorescence emissions. The $T_1 \rightarrow T_n$ absorption spectra are very similar, showing two maxima at 350−355 nm and 520−565 nm and triplet lifetimes of 10 μs (B), 3 μs (4-FB), and 16 μs (4-COOHB). Interaction with *i*-ButOH was followed by the quenching of the $T_1 \rightarrow T_n$ absorption. Linear least-squares analysis (correlation coefficient ≥ 0.99) of a plot of the triplet decay rate ($k = 1/\tau$) as a function of *i*-ButOH concentration yielded the rate constant k_H as slope, according to eq 1. The k_H values determined ($k_H = (4.4-5.3) \times 10^5$ dm^3 mol^{-1} s^{-1}) were

TABLE 1: Spectral Characteristics (λ_{max}) and Triplet Lifetimes (τ) of Thienyl Ketones in TFE[a]

compound	λ_{max}/nm	$\tau/\mu s$	k_{ox}/ $dm^3\ mol^{-1}\ s^{-1}$	k_H/ $dm^3\ mol^{-1}\ s^{-1}$
2,4′-TPK	400	9.7	9.9×10^8	2.2×10^4
	640			
2,3′-TPK	370	10.6	9.2×10^8	9.9×10^3
	620			
2-TPhK	375	5.2	11×10^8	$\sim 10^3$
	600			
2,3′-DTK	370	3.9	8.5×10^8	$\leq 10^3$
	590			
2,2′-DTK	395	7.2	7.9×10^8	$\leq 10^3$
	650			
3,4′-TPK	530 (T_1)	0.35 (T_1)	2.0×10^9 (T_1)	3.0×10^5 (T_1)
	740 (T_1)			
	400 (T_2)	6.5 (T_2)	1.4×10^9 (T_2)	not linear (T_2)
	640 (T_2)			
3,3′-TPK	350 (T_1)	0.35	2.2×10^9	3.0×10^5
	500 (T_1)			
	720 (T_1)			
3-TPhK	460 (T_1)			
	690 (T_1)	0.25 (T_1)	2.3×10^9 (T_1)	$\sim 5 \times 10^4$ (T_1)
	370 (T_2)	7.1 (T_2)	3.3×10^8 (T_2)	
	520 (T_2)			
3,3′-DTK	480 (T_1)			
	730 (T_1)	0.08 (T_1)	2.2×10^9 (T_1)	unmeasurable
	370 (T_2)	1.6 (T_2)	6.9×10^8 (T_2)	
	575 (T_2)			

[a] Bimolecular rate constants for oxygen quenching (k_{ox}) and hydrogen-abstraction (k_H) from *i*-ButOH obtained by laser flash photolysis measurements.

similar for the three compounds. From earlier works, in the case of B, the kinetic constant for hydrogen-abstraction ranged from 4.3×10 $dm^3\ mol^{-1}\ s^{-1}$ (from neat acetonitrile)[17] to 1.4×10^9 $dm^3\ mol^{-1}\ s^{-1}$ (from *N*-methyl-2-butylamine in benzene).[18] The k_H value, determined for B under the experimental conditions used here, is of the order of magnitude of that reported for hydrogen abstraction from ethanol (5.6×10^5 $dm^3\ mol^{-1}\ s^{-1}$)[19] and is slightly smaller than that of propan-2-ol (1.9×10^6 $dm^3\ mol^{-1}\ s^{-1}$).[20] This finding is in line with expectations, based on the characteristics of the donors. For all three molecules in *i*-ButOH, the ketyl radicals showed two absorption maxima in the UV (330−335 nm) and visible (550−590 nm) regions; their rates of formation (rise time, 0.06−0.09 μs) matched those of triplet consumption (lifetime, 0.06−0.12 μs).

Thienyl Ketones. From earlier works we have found that features of phosphorescence emission in a rigid matrix at 77 K and $T_1 - T_n$ absorption in acetonitrile solution of thienyl ketones were strongly dependent on structural factors (mainly the position of the thienyl group), while room-temperature phosphorescence emissions, detected in oxygen-free solutions, were similar for all thienyl derivatives.[11−13] The characteristics of the transients observed upon nanosecond laser excitation are critically dependent on the position of the heteroatom sulfur.

To describe the results obtained, the nine thienyl ketones investigated have been divided into two groups: (1) molecules which have the lowest triplet with π,π^* characteristics and (2) molecules which give spectral and kinetic evidence for two nearby triplet states (n,π^* and π,π^*), the lowest of which is the n,π^* one. Spectral features of the transients obtained upon flashing TFE and *i*-ButOH solutions of thienyl ketones are reported in Tables 1 and 2, respectively, along with monomolecular and bimolecular kinetic parameters.

TABLE 2: Spectral Characteristics (λ_{max}) of the Ketyl Radicals, Obtained by Flashing Thienyl Ketones in *i*-ButOH at Room Temperature; Dynamic Parameters (τ) for the Radical Formation (rise time) and Triplet Decay in *i*-ButOH

compound	λ_{max}/nm	$\tau/\mu s$ (rise time)	$\tau/\mu s$ (triplet decay)
2,4′-TPK	390	2.0	2.2
	580		
2,3′-TPK	350		4.2
	600		
2-TPhK	355		4.5
	580		
2,3′-DTK	350		4.0
2,2′-DTK	370		6.7
3,4′-TPK	350	0.10	0.09
	530		
3,3′-TPK	330		
	410	0.14	0.16
	540		
3-TPhK	350	0.10	0.22
	400		
	520		
3,3′-DTK	400	0.11	0.12

(1) 2-Thienyl Ketones (2-Thienyl-4′-pyridyl Ketone, 2,4′-TPK; 2-Thienyl-3′-pyridyl Ketone, 2,3′-TPK; Di-2,2′-thienyl Ketone, 2,2′-DTK; Di-2,3′-thienyl Ketone, 2,3′-DTK and 2-Thienyl Phenyl Ketone, 2-TPhK). These molecules are structurally characterized by having at least one thienyl group in the 2 position. At low temperature (77 K), the phosphorescence spectra did not exhibit the typical five-fingered carbonylic emission and their lifetimes were rather long (about 100 ms). Thus, the transitions were assigned to π,π^* lowest triplets.[12] In TFE solution, all these molecules exhibited triplet−triplet absorptions characterized by two bands with maxima in the 370−400 nm region and in the visible region (590−650 nm), Figures 1a (2,4′-TPK) and 2a (2,2′-DPK). Triplet lifetimes were on the microsecond time scale (4−10 μs, Table 1). Efficient oxygen quenching was found; the rate constants k_{ox} were in the range $(8-10) \times 10^8$ $dm^3\ mol^{-1}\ s^{-1}$, Table 1. Hydrogen-abstraction rate constants were obtained (eq 1) from linear plots of the triplet decay rate as a function of *i*-ButOH concentration for only 2,4′-TPK (Figure 1a, inset) and 2,3′-TPK. The rate constants k_H were on the order of 10^4 $dm^3\ mol^{-1}\ s^{-1}$ (Table 1). Due to the lower hydrogen-abstraction efficiency of the other three molecules in this group, 2,2′-DTK, 2,3′-DTK, and 2-TPhK, it was impossible to use eq 1 to obtain k_H, which was only qualitatively estimated to be equal to or less than 10^3 $dm^3\ mol^{-1}\ s^{-1}$, which was the sensitivity limit under the experimental conditions used. In fact, the triplet lifetimes of 2,2′-DTK, 2,3′-DTK, and 2-TPhK in neat *i*-ButOH (Table 2) were as long as those in TFE, within the experimental error. However, even for these molecules, hydrogen abstraction in the donor solvent was demonstrated by radical formation which followed triplet appearance (Figures 1b and 2b). In *i*-ButOH, the absorption spectra of the ketyl radicals are characterized by maxima located in the 350−390 nm (more intense) and 580−600 nm regions (Table 2); for some compounds the latter absorption was hardly detectable (2,2′-DTK and 2,3′-TPK). Matching of triplet decay (2.2 μs at 680 nm) to rise time of ketyl formation (2.0 μs at 410 nm) was observed only for 2,4′-TPK (Figure 1b, inset), while for the other molecules it could not be detected due to the intensity and overlap of the triplet and ketyl absorptions (see, e. g., Figure 2b for 2,2′-DTK). The radicals formed were rather stable ($t_{1/2} \sim 500$ μs), except for that of 2,4′-TPK which decayed at a faster rate ($t_{1/2} \sim 80$ μs) due to formation of a photoproduct or a longer lived transient (Figure 1b, spectrum after 160 μs).

(2) 3-Thienyl Ketones (3-Thienyl-4′-pyridyl Ketone, 3,4′-TPK; 3-Thienyl-3′-pyridyl Ketone, 3,3′-TPK; Di-3,3′-thienyl Ketone, 3,3′-DTK; and 3-Thienyl Phenyl Ketone, 3-TPhK). All these molecules have a thienyl group in the 3 position with respect

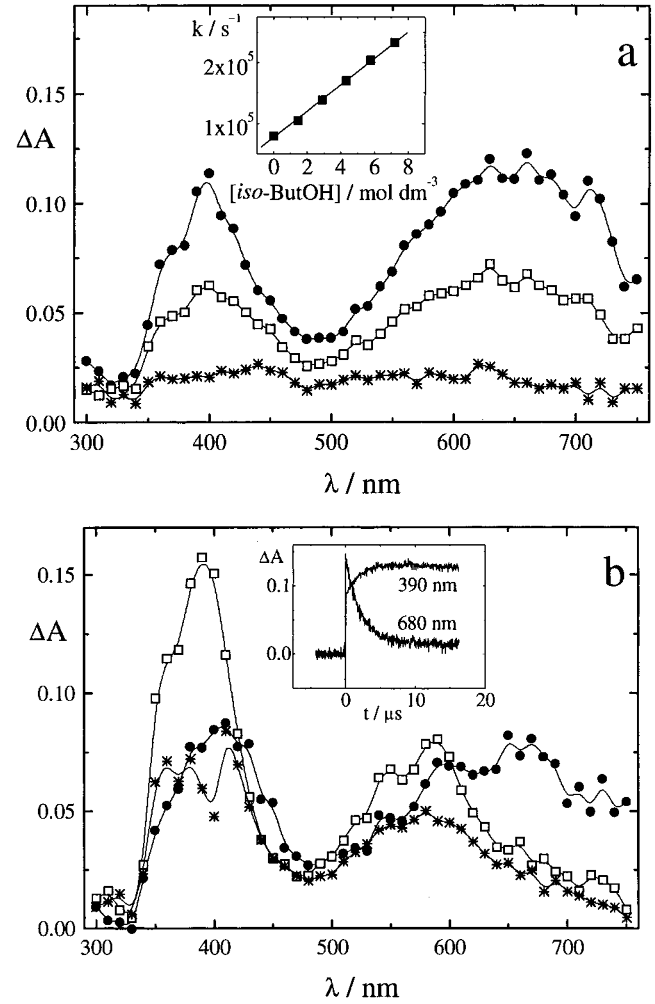


Figure 1. (a) Time-resolved spectra of triplet 2,4′-TPK in TFE: (●) 1 μs, (□) 6.5 μs, (*) 80 μs. Inset: triplet quenching by *i*-ButOH (eq 1). (b) Time-resolved spectra obtained upon flashing an *i*-ButOH solution of 2,4′-TPK: (●) 0.8 μs, prevalent triplet absorption; (□) 5.6 μs, prevalent ketyl absorption; (*) 160 μs, photoproduct absorption (+ ketyl). Inset: kinetics of triplet decay (680 nm) and radical formation (390 nm).

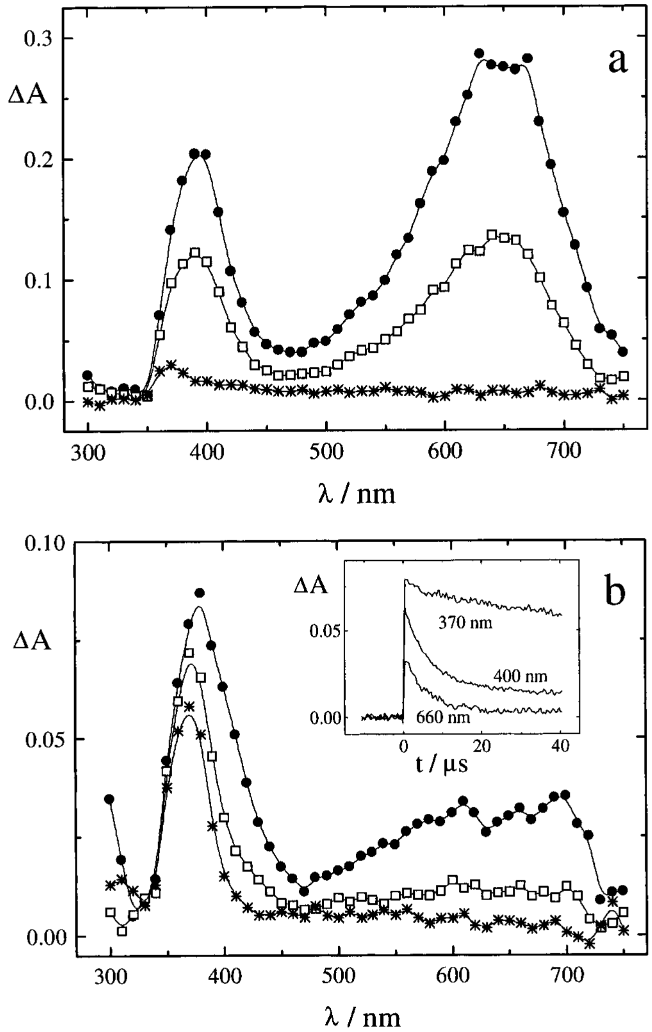


Figure 2. (a) Time-resolved spectra of triplet 2,2′-DTK in TFE: (●) 1 μs, (□) 5.8 μs, (*) 81 μs. (b) Time-resolved spectra obtained upon flashing an *i*-ButOH solution of 2,2-TPK: (●) 0.5 μs, prevalent triplet absorption; (□) 8.0 μs; (*) 40 μs, doublet−doublet radical absorption. Inset: kinetics of triplet decay (400 and 660 nm), at 370 nm triplet decay overlaps to radical formation.

to the carbonyl. Some of them exhibit a benzophenone-like behavior from phosphorescence measurements in EPA at 77 K (well-developed vibronic carbonyl progression and a lifetime of a few milliseconds).[12,21] Under laser excitation in TFE, all the molecules, except 3,3′-TPK, exhibited the peculiar behavior of showing absorptions from two triplet states. For 3,3′-TPK, the triplet transient in TFE shows bands at 350, 500, and 720 nm (Figure 3a) and monoexponential decay over all the absorption spectrum ($\tau = 0.35$ μs). The triplet is efficiently quenched by oxygen ($k_{ox} = 2.2 \times 10^9$ dm^3 mol^{-1} s^{-1}). The triplet lifetime decreased when *i*-ButOH was added to the TFE solution of 3,3′-TPK. The hydrogen-abstraction rate constant, $k_H = 3 \times 10^5$ dm^3 mol^{-1} s^{-1}, obtained from eq 1 (Figure 3a, inset), is close to the values for B, 4-FB, and 4-COOHB. This confirms the *n*,π* nature of the lowest triplet state. In neat *i*-ButOH, the ketyl radical formation could be followed from the triplet decay (0.16 μs at 740 nm) and ketyl rise time (0.14 μs at 410 nm), as shown in Figure 3b, inset. The final doublet−doublet absorption of the radical exhibits fairly intense peaks at 330 and 410 nm and a weaker, broader band in the visible (Figure 3b).

For the other molecules, the presence of two triplets was revealed by different decay rates determined at wavelengths where either one or the other triplet absorbs, as for 3,4′-TPK (at 500 and 740 nm for T_1 and at 600 nm for T_2, see Figure 4a) and 3,3′-DTK (at 740 nm for T_1, Figure 5a, inset), or from biexponential decay at a wavelength where both triplets absorb, as shown in Figures 5a (at 370 nm for 3,3′-DTK) and 6a, inset (at 370 nm for the 3-TPhK). Since one of the triplets T_1 is shorter-lived ($\tau_1 = 0.35$, 0.08 and 0.25 μs for 3,4′-TPK, 3,3′-DTK and 3-TPhK, respectively) than the other ($\tau_2 = 6.5$, 1.6, and 7.1 μs for 3,4′-TPK, 3,3′-DTK, and 3-TPhK), the spectra recorded a few microseconds after the laser pulse substantially represent the neat absorptions of the longer-lived triplets, T_2 (Figures 4a−6a). For 3,4′-TPK (Figure 4a), the spectrum of T_1 is characterized by maxima at 530 and 740 nm, that are no longer present after 2.1 μs, while the residual absorption due to T_2 consists of two bands around 400 and 640 nm (similar to the molecules of the first group). For the 3,3′-DPK, T_1 is even shorter lived ($t_1 = 0.08$ μs) and its absorption spectrum is no longer present after 0.23 μs, as shown in Figure 5a; the spectrum of T_2 is characterized by bands at 370 and 575 nm. In the same figure (inset), fast monoexponential decay is shown at 740 nm, where only T_1 absorbs, while a biexponential curve is monitored at 370 nm. The spectral features of the 3-TPhK (Figure 6a) are similar. Both T_1 ($k_{ox} \gg 2.2 \times 10^9$ dm^3 mol^{-1} s^{-1} for all three compounds) and T_2 ($k_{ox} = 1.4 \times 10^9$ to 3.3×10^8 dm^3 mol^{-1}

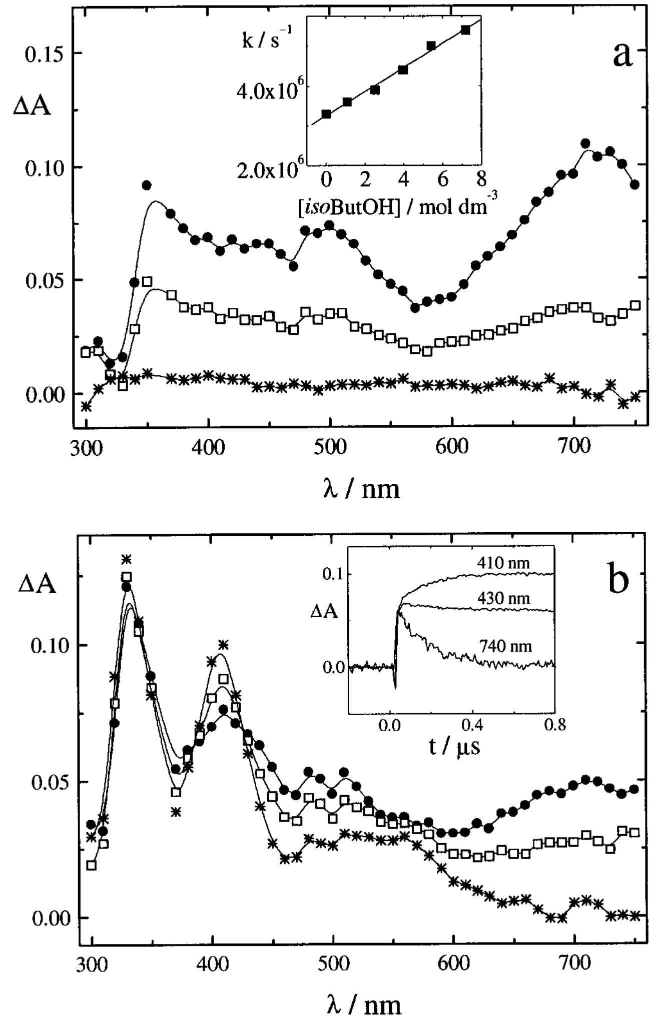


Figure 3. (a) Time-resolved spectra of triplet 3,3′-TPK in TFE: (●) 0.08 μs, (□) 0.38 μs, (*) 4.0 μs. Inset: triplet quenching by *i*-ButOH (eq 1). (b) Time-resolved spectra obtained upon flashing an *i*-ButOH solution of 3,3′-TPK: (●) 0.08 μs, prevalent triplet absorption; (□) 0.14 μs; (*) 0.8 μs, doublet−doublet radical absorption. Inset: kinetics of triplet decay (740 nm) and radical formation (410 nm); 430 nm, isobestic point.

s^{-1}) were sensitive to oxygen (Table 1). Spectral features and dynamic behavior (τ and k_{ox}) indicate that T_1 has n,π^* character, while T_2 has π,π^* character.

The effect of adding *i*-ButOH was investigated in the spectral regions typical of one or the other triplet. For the 3,4′-TPK, where the spectral situation is more favorable, measurements of triplet quenching by *i*-ButOH at 500 and 750 nm (prominent T_1 absorption) yielded the same k_H value, $3.0 \pm 0.2 \times 10^5$ dm^3 mol^{-1} s^{-1}, with a fairly good correlation (correlation coefficient 0.996, see Figure 4a, inset). Measurements at 600 nm for the same compound (prominent T_2 absorption), treated according to eq 1, yielded a nonlinear plot showing an upward curvature (Figure 4a, inset). This trend fitted a quadratic function. Such dependence of $1/\tau_2$ on the alcohol concentration might be justified by assuming that T_2 reversibly interacts with isobutanol yielding an encounter complex which back-dissociates or further interacts with the alcohol giving a photoproduct. However, this point deserves further investigation.

The absorption spectra of the ketyl radicals (Figures 4b, 5b, and 6b), recorded in neat *i*-ButOH a few microseconds after the laser pulse, are characterized by an intense absorption at 350−400 nm and a weaker absorption in the visible region which was almost undetectable for the 3,3′-DTK and 3-TPhK (Figures 5b and 6b). For these three molecules, matching of triplet (T_1) decay (0.09 μs for 3,4′-TPK, 0.12 μs for 3,3′-DTK and 0.22 μs for 3-TPhK) and radical rise-time (0.10 μs, 0.11 μs, and 0.10 μs for 3,4′-TPK, 3.3′-DTK, and 3-TPhK, respectively) demonstrates that T_1 is the precursor of the ketyl radical (see Figures 4b, 5b, and 6b, insets, and Table 2). The second-order decay kinetics of the ketyl, divided by its unknown molar extinction coefficient ϵ_K, could be evaluated for the 3,4′-TPK ($k_2/\epsilon_K = 2 \times 10^4$ dm^3 mol^{-1} s^{-1}), due to fast radical recombination which gives a detectable photoproduct ($\lambda_{max} = 390$ nm, Figure 4b). Measurements of k_2/ϵ_K in oxygen-free, air-saturated, and oxygen-saturated solutions allowed the rate constant for radical quenching by oxygen to be determined ($k_{ox} = 9.1 \times 10^5$ dm^3 mol^{-1} s^{-1}). The radicals of the other isomers were more stable and recombination kinetics and oxygen quenching could not be measured with our experimental setup.

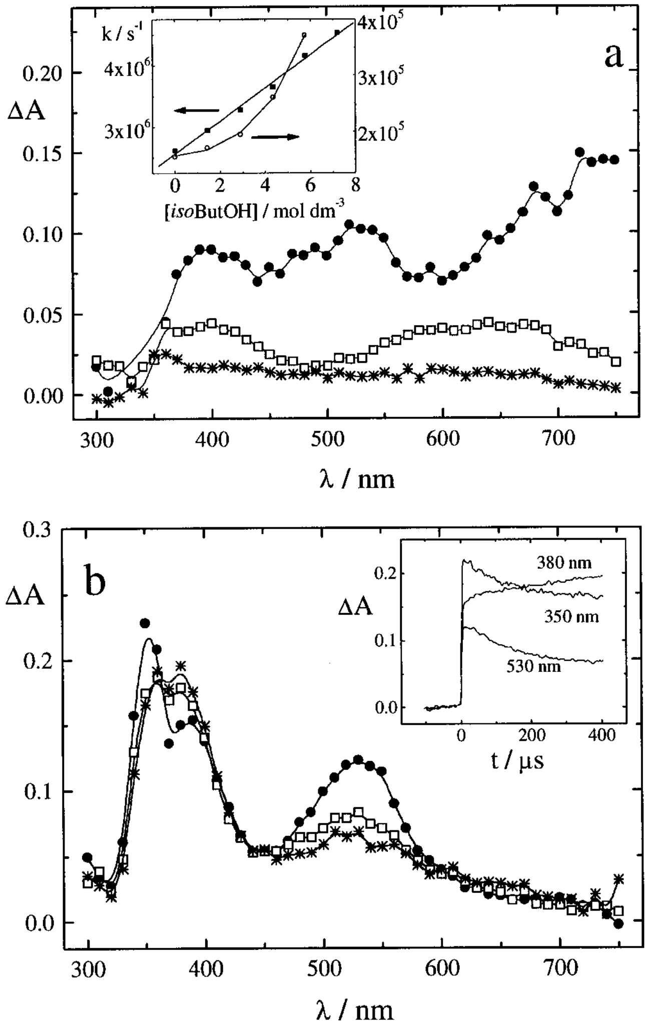


Figure 4. (a) Time-resolved spectra of triplet 3,4′-TPK in TFE: (●) 0.08 μs, (□) 2.1 μs, spectrum of T_2; (*) 16 μs. Inset: triplet quenching by *i*-ButOH (eq 1) determined at 750 nm, (■) (T_1) and 600 nm, (○) (T_2). (b) Time-resolved spectra (long-time scale) obtained upon flashing an *i*-ButOH solution of 3,4-TPK: (●) 5 μs, prevalent ketyl absorption; (□) 173 μs, (*) 400 μs, photoproduct absorption. Inset: kinetics of ketyl decay (350 and 530 nm) and photoproduct formation (380 nm).

Discussion

In this paper, hydrogen abstraction from *i*-ButOH by a number of thienyl ketones (and some aryl ketones for the purpose of comparison) was investigated under the same fixed experimental conditions. The solvent used, TFE, was especially chosen

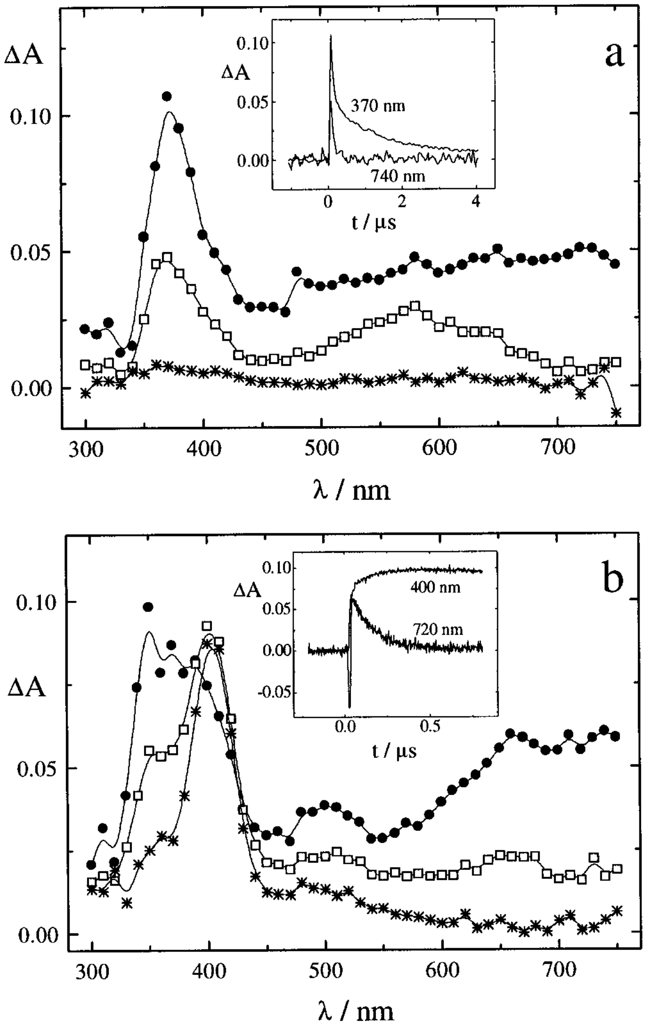


Figure 5. (a) Time-resolved spectra of triplet 3,3′-DTK in TFE: (●) 0.08 *μ*s, (□) 0.23 *μ*s, spectrum of T_2; (*) 4 *μ*s. Inset: decay kinetics of T_1 at 740 nm and $T_1 + T_2$ at 370 nm (biexponential). (b) Time-resolved spectra obtained upon flashing an *i*-ButOH solution of 3,3′-DTK: (●) 0.08 *μ*s, prevalent triplet absorption; (□) 0.26 *μ*s, (*) 4 *μ*s, doublet–doublet absorption of ketyl radical. Inset: kinetics of triplet decay (720 nm) and ketyl formation (400 nm).

because of its inertness toward ground- and excited-state ketones. However, it is rather acidic and has a strong H-bonding ability.[22] Its $E_T(30)$[23] value ($E_T(30) = 81$), determined on a relative scale built with pyridyl ketones,[24] is even greater than water ($E_T(30) = 63$), and here, it is greater than the $E_T(30)$ of *i*-ButOH ($E_T(30) = 51$, based on the same scale). This implies that TFE, compared with other, even polar, solvents, such as *i*-ButOH, should stabilize *π,π** states of ketones compared to *n,π** ones. Consequently, by changing the solvent from neat TFE to neat *i*-ButOH, the energy difference between *π,π** and *n,π** triplets should increase for compounds having the lowest triplet of *n,π** character, and vice versa, the energy difference should decrease (and a solvent induced inversion may possibly occur)[25] for compounds having the lowest triplet of *π,π** character.

The results indicate that the position of the sulfur atom with respect to the carbonyl determines whether the lowest triplet is of *π,π** or *n,π** character. The effect of the heteroatom on the triplet state can be considered to be like that of a substituent at a ring position. Thus, the sulfur in 2 position has a stronger electron-donating power, compared with 3 position, and, therefore, causes an inversion of triplets such that the unreactive *π,π** state has the least energy in the 2-thienyl ketones. However, these compounds also abstract hydrogen from *i*-ButOH, even if with lower efficiency. We believe that this is due to the reaction of the equilibrium population of the upper *n,π** triplet, as proposed and widely accepted for aryl ketones bearing strong electron-donor substituents.[5] Recently, similar compounds, tiaprofenic acid and 2-benzoyl-5-ethylthiophene, both with a thienyl group in 2 position, were investigated.[26] Even in these cases, the lowest state of triplet manifold T_1 was found to be of *π,π** character, while calculations and photochemistry demonstrated that T_2 (*n,π**), which is the reactive state, is located at a thermally accessible distance (about 30–40 kJ mol^{-1}). Our earlier experimental findings (from phosphorescence excitation spectra at 77 K) showed that the energy difference between the lowest (*π,π**) and the upper (*n,π**) triplet states is approximately 13 kJ mol^{-1} for the 2,3′- and 2,4′-TPK.[12] This means that the *n,π** state may well be responsible for hydrogen abstraction. The reaction efficiency of the 2-thienyl ketones is also affected by the other ring (phenyl, pyridyl or thienyl). Considering the electron-withdrawing properties of pyridine and electron-donating characteristics of the thienyl group, the energy difference between the two triplets is expected to decrease in the sequence:

$$\text{2,2}'\text{-DTK} > \text{2,3}'\text{-DTK} > \text{2-TPhK} > \text{2,3}'\text{-TPK} > \text{2,4}'\text{-TPK}$$

which corresponds well to the increasing magnitude of the k_H value (Table 1). The process is favored in neat *i*-ButOH, where, due to the solvent properties, the energy gap is smaller than in TFE, and this effect, in addition to the effect of donor-solvent cage, allows the photoproduced ketyls to be also detected for the less reactive molecules (2,2′-DTK, 2,3′-DTK and 2-TPhK). For the *π,π** triplet aryl ketone investigated, 4-PhB, the upper *n,π** triplet state is too far from the lowest *π,π** triplet to be thermally populated by it even in a hydrogen-donating solvent, such as *i*-ButOH, which is less polar than TFE.

Considering that the ground-state σ_+ constants for the sulfur heteroatom are −0.79 and −0.52 for the 2 and 3 positions, respectively,[27] the electron-donating effect of the sulfur toward the carbonyl is attenuated in 3-thienyl ketones and, therefore, the lowest triplet is of *n,π** character. When a pyridyl ring is present (3,n′-TPKs), its electron-attracting effect far outweighs the opposite effect of the thienyl ring. However, even where two thienyls are in 3 (and 3′) position (3,3′-DTK), the *n,π** character of the lowest triplet is maintained. Therefore, considering the effect of the second ring, the energy difference between the two lowest triplets (*n,π** and *π,π**) is expected to increase in the sequence:

$$\text{3,3}'\text{-DTK} < \text{3-TPhK} < \text{3,3}'\text{-TPK} < \text{3,4}'\text{-TPK}$$

As the energy difference increases, the lowest triplet state increases in *n,π** character and, therefore, the k_H should also increase. This was what we observed (Table 1). The reactivity toward hydrogen-abstraction exhibited by T_1 of 3,3′- and 3,4′-TPK is similar to that of aryl ketones having the lowest triplet of *n,π** character (B, 4-FB, and 4-COOHB). The rate constant $k_H = 3 \times 10^5$ dm^3 mol^{-1} s^{-1} is substantially independent of structure, indicating that the solvent (TFE) stabilization of *π,π** states is not large enough to alter the *n,π** reactivity, which, therefore, is mostly determined by the C–H bond strength of the donor. Except for 3,3′-TPK, absorptions from *n,π** and *π,π** triplets were observed for the 3-thienyl ketones; no spectral or kinetic features indicated that one triplet was the precursor of the other. This implies that the two states are independently populated from the (*n,π**) singlet state and vibronic mixing between them is not efficient, that is, internal conversion is low enough to allow both states to be excited and to decay inde-

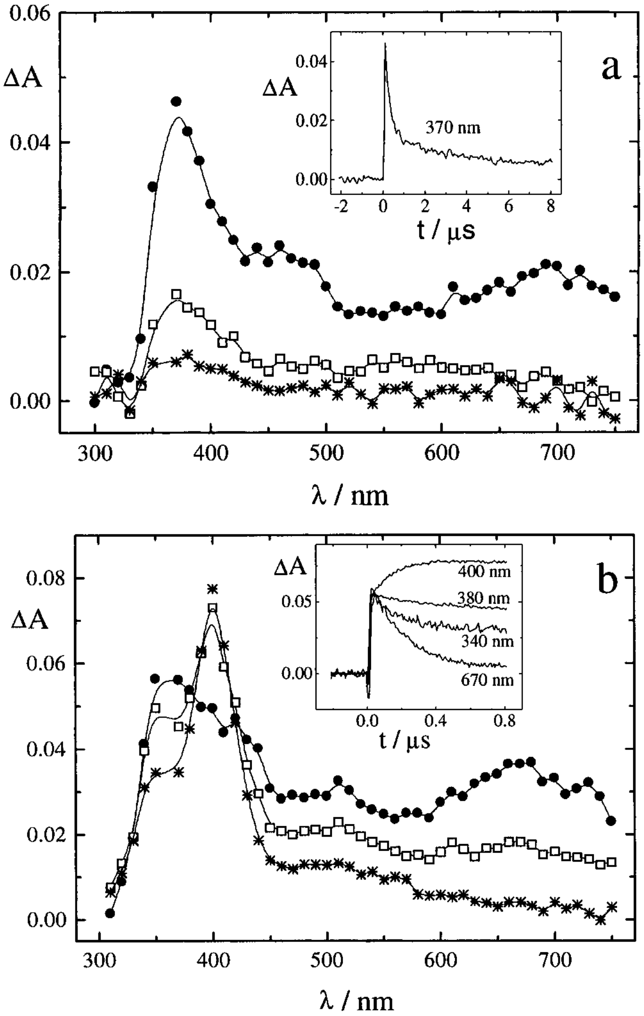


Figure 6. (a) Time-resolved spectra of triplet 3-TPhK in TFE: (●) 0.1 μs, (□) 0.7 μs, spectrum of T_2; (*) 8.0 μs. Inset: biexponential decay kinetics ($T_1 + T_2$) at 370 nm. (b) Time-resolved spectra obtained upon flashing an *i*-ButOH solution of 3-TPhK: (●) 0.04 μs, prevalent triplet absorption; (□) 0.18 μs, (*) 0.8 μs, doublet−doublet radical absorption. Inset: kinetics of triplet decay (340 and 670 nm) and radical formation (400 nm). 380: quasi-isobestic point.

pendently of each other, as well as to be independently quenched by oxygen. This does not happen in aryl ketones having the lowest triplet of n,π^* character.

As expected, within the two categories of molecules, the ketyl spectra are more similar to each other than the triplet absorption spectra, where the 500 and 700 nm regions are typical of n,π^* triplets, while the 400 and 600 nm regions characterize the π,π^* triplets. In *i*-ButOH, the T_2 triplet of 3-thienyl ketones is no longer detectable, due to solvent effect on excited-state energies.

Interestingly, the rate constant for oxygen quenching of 4-PhB ($k_{ox} = 8.0 \times 10^8$ dm^3 mol^{-1} s^{-1}) is close to those found for both T_1 (of π,π^* character) of the 2-thienyl ketones and for T_2 (π,π^*) of the 3-thienyl ketones. For n,π^* triplets, k_{ox} is always larger than 10^9; that is, π,π^* triplet states are less efficient oxygen quenchers than n,π^*ones. A similar behavior was reported by Redmond and Braslavsky,[28] who found that for triplet states with predominant n,π^* character, k_{ox} is higher (and increases with the triplet energy) than for π,π^* triplets.

Also of interest was the detection of photoproducts formed from ketyl radicals that was only observed for compounds with the pyridyl ring linked in 4 position (2,4′- and 3,4′-TPK). The spectral region of the photoproduct absorptions (380 nm, Figures 1b and 4b) corresponds to that reported as typical of LATs (light absorbing transients).[17,29] These species, which are air sensitive, are derived from ortho or para coupling of a ketyl radical with another radical. They form more easily when the para-position (here the pyridyl nitrogen) is electron rich.[30]

Conclusions

The results described here show that all thienyl ketones abstract hydrogen from *i*-ButOH; the rate constant for the process strongly depends on the position of the thienyl ring which plays a role analogous to that of an electron-donating substituent. When the thienyl ring is in the 3 position and the other group is a pyridyl (3,3′-TPK and 3,4′-TPK), the rate constant is fairly high ($k_H \sim 3 \times 10^5$ dm^3 mol^{-1} s^{-1}), close to that found for n,π^* triplet aryl ketones (B, 4-FB, 4-COOHB). When it is in the 2 position, thus increasing the charge density to the carbonyl, the reactivity is reduced ($k_H \le 10^4$ dm^3 mol^{-1} s^{-1}), but not as much as is found for 4-Ph-B, where hydrogen abstraction was undetectable under our experimental conditions. This reduced reactivity of 2-thienyl ketones is due to the occurrence of reaction in an upper n,π^* triplet state, thermally accessible from the lowest π,π^* one. In 3-thienyl ketones, the upper triplet state of π,π^* character behaves independent of the lowest n,π^* one.

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References and Notes

(1) Scaiano, J. C. *J. Photochem.* **1973/1974**, *2*, 81.
(2) Wagner, P. J.; Park, B. S. *Org. Photochem.* **1991**, *11*, 227.
(3) Porter, G. *Trans. Faraday Soc.* **1963**, *2*, 1686.
(4) Wagner, P. J.; Truman, R. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 7093. Wagner, P. J.; Nakahira, T. *J. Am. Chem. Soc.* **1973**, *95*, 8474.
(5) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604 and references cited therein. Wagner, P. J.; Siebert, E. J. *J. Am. Chem. Soc.* **1981**, *103*, 7329.
(6) Wagner, P. J.; Truman, R. J.; Puchalski, A. E.; Wake, R. *J. Am. Chem. Soc.* **1986**, *108*, 7727.
(7) Formosinho, S. J.; Arnaut, L. G. *Adv. Photochem.* **1991**, *16*, 67.
(8) Traynard, P.; Blanchi, J.-P. *J. Chim. Phys. Physicochim. Biol.* **1972**, *69*, 284.
(9) Cantrell, T. S. *J. Org. Chem.* **1977**, *42*, 3774.
(10) Cantrell, T. S. *J. Chem. Soc., Chem. Commun*, **1972**, 155.
(11) Romani, A.; Bigozzi, A.; Ortica, F.; Favaro, G. *Spectrochim. Acta, Part A* **1999**, *55*, 25.
(12) Romani, A.; Ortica, F.; Favaro, G. *Chem. Phys.* **1998**, *237*, 413.
(13) Becker, R.; Favaro, G.; Poggi G.; Romani, A. *J. Phys. Chem.* **1995**, *99*, 1410.
(14) Hardtmann, G.; Houlihan, W. J.; Takesue, E. I. *J. Med. Chem.* **1969**, *12*, 1093.
(15) Ermolaev, V. L.; Terenin, A. N. *J. Chim. Phys.* **1958**, *55*, 698.
(16) Turro N. J.; Lee, C.-G. *Mol. Photochem.* **1972**, *4*, 427.
(17) Naguib, Y. M. A.; Steel, C.; Cohen, S. G.; Yang, M. A. *J. Phys. Chem.* **1987**, *91*, 3033.
(18) Topp, M. R. *Chem. Phys. Lett.* **1975**, *32*, 144. Cohen, S. G.; Litt, A. D. *Tetrahedron Lett.* **1970**, 837.
(19) Porter, G.; Topp, M. R. *Proc. R. Soc. A* **1970**, *315*, 163.
(20) Okamoto, D. R.; Teranishi, H. *J. Am. Chem. Soc.* **1986**, *108*, 6370.
(21) Arnold, D. R.; Birtwell, R. J. *J. Am. Chem. Soc.* **1973**, *95*, 4599.
(22) Mukherjee, L. M.; Grumvald, E. *J. Phys. Chem.* **1958**, *62*, 1311. Figueros, J. *J. Am. Chem. Soc.* **1971**, *93*, 3255.
(23) Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlmann, F. *Liebigs Ann. Chem.* **1963**, *661*, 1.
(24) Favaro G.; Ortica, F. *Spectrochim. Acta, Part A*, **1991**, *47*, 1721.
(25) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.
(26) Encinas, S.; Miranda, M. A.; Marconi, G.; Monti, S. *Photochem. Photobiol.* **1998**, *67*, 420.
(27) Marino, G. *Int. J. Sulfur Chem.* **1972**, *7*, 61.
(28) Redmond, R. W.; Braslavsky, S. E. *Chem. Phys. Lett.* **1988**, *148*, 523.
(29) Demeter, A.; Bérces, T. *J. Photochem. Photobiol.* **1989**, *46*, 27.
(30) Minn, F. L.; Trichilo, C. L.; Hurt, C. R.; Filipescu, N. *J. Am. Chem Soc.* **1970**, *92*, 3600.