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Journal of Photochemistry and Photobiology A: Chemistry 162 (2004) 231–238

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Solvent and temperature effects on the phosphorescence of 9,10-phenanthrenequinone in fluid solution

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Received 21 April 2003; received in revised form 13 August 2003; accepted 23 August 2003

Abstract

The phosphorescence of 9,10-phenanthrenequinone (PQ) was observed and studied in carbon tetrachloride (CCl_4) and acetonitrile (MeCN) using steady-state and time-resolved emission spectroscopy. From the estimated phosphorescence quantum yields and the measured triplet lifetimes at room temperature the natural radiative lifetime of the PQ triplet was calculated to be 10 ± 4 ms in CCl_4 and 39 ± 8 ms in MeCN. The emission showed vibrational fine structure in both solvents and a hypsochromic shift when going to the more polar solvent. Both are typical of the n,π^* state. Examination of the temperature effect on the intensity of the initial emission in time-resolved experiments indicated an activation energy of 2.38 ± 0.39 kcal/mol in MeCN, and a negative activation energy of -0.25 ± 0.04 kcal/mol in CCl_4. It was concluded that the emissive state is n,π^* in nature and is in thermal equilibrium with a nearby non-emissive π,π^* state in these solvents. In CCl_4 the lowest triplet state is n,π^* with an energy of 49.1 kcal/mol, and the second excited triplet is π,π^* and is almost isoenergetic with an energy that is only 0.25 kcal/mol higher. In MeCN there is an inversion of these states, the lowest state is π,π^* with an energy of 47.6 kcal/mol, and is in equilibrium with a higher n,π^* state of 50.0 kcal/mol. This is the first time that it has been possible to show an inversion of states due to changes in the solvent at room temperature and measure the energies of both the lowest n,π^* and π,π^* triplet states.

Keywords: Triplet state inversion; 9,10-Phenanthrenequinone; Phosphorescence; Time-resolved emission

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1. Introduction

Photochemical hydrogen abstraction by ketones is fast and efficient when the nature of the lowest energy triplet excited state is n,π^* [1]. The reactivity toward hydrogen abstraction of n,π^* ketone triplets is comparable and parallels that of alkoxy radicals [2–5]. When the ketone excited state is of π,π^* character, the rate of reaction from the same donors is normally much slower or not observed [1]. In most cases where the lowest excited state is π,π^* in nature and hydrogen abstraction is still observed, this reactivity has been attributed to a slightly higher energy n,π^* triplet which is thermally accessible [1]. Although it was initially proposed that this proximity could induce state mixing, and increase the reactivity of the lowest π,π^* state [6], Wagner and co-workers [7] found that this reactivity was due to reaction from the higher n,π^* state in thermal equilibrium with the lower π,π^* state in the systems they studied, and this mechanism is now generally accepted. This conclusion is indirectly based on data obtained for ketones with lowest π,π^* triplets in which the energy gap can only be estimated, and the verification of the concept depends on a knowledge of the energy of both the lowest excited n,π^* and π,π^* states [7b]. Wagner et al. [7b] pointed out in 1976 that "unfortunately, it is impossible to measure the precise energy levels of both triplets under reaction conditions." This state of affairs persists until now [8], and we could not find any measurements of the energy of both triplets in fluid solution under conditions where reactions are observed. The necessary data are normally obtained by the observation of phosphorescence emission, and the majority of the ketones studied do not phosphoresce sufficiently in solution at room temperature [9].

The states are differently affected by solvation. The energy of the π,π^* state is lowered upon going to solvents of increasing polarity while the n,π^* state energy increases. This could, in principle, affect state ordering, the nature of the lowest excited state and consequently ketone photoreactivity. Inversion of the n,π^* and π,π^* triplet states with changing solvent polarity has been invoked to explain xanthone photoreactivity [10], and acetophenone triplet absorption spectra

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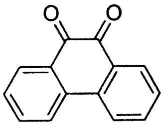
doi:10.1016/j.nainr.2003.08.008

[11], and the general concept is discussed and exemplified in basic organic photochemistry texts [9,12]. While the concept is reasonable, the examples used do not in fact support the argument. They do not in fact show state inversion as a result of increasing solvent polarity in fluid solution. They start with the premise that the state inversion observed in phosphorescence spectra at low temperature in glass equally applies to room temperature in fluid solution and use the presumed state inversion to explain experimental results such as chemical reactivity and triplet absorption spectra. In both cases other explanations could equally well be invoked. In the case of xanthone, the low temperature state inversion has been questioned and it was concluded that this compound has a lowest π,π* triplet in all low temperature matrixes [13]. Both studies do not consider the effect of solvation on the ordering of states when going from rigid low temperature matrixes to room temperature fluid solutions. This is understandable since even today these effects are unknown. In the case of xanthone the changes in reactivity on going from a non-polar to a polar solvent are equally well explained by an increasing separation between the states in polar solvents with reaction from the upper n,π* state. In the case of acetophenone, state inversion is presumed and used to explain other data [11]. Solvent effects on the relative position of n,π* and π,π* states have been known for many years [14], however solvent induced inversion of these states in fluid solution has never actually been shown. Considering the general acceptance and use of this concept to explain photochemical reactivity, a convincing example showing state inversion with changing solvent polarity would be very welcome.

It is known that the *ortho*-quinone 9,10-phenanthrenequinone (PQ) is efficiently photoreduced by hydrogen donors [15]. Time-resolved triplet ESR and CIDEP studies by Shimoishi et al. indicated a small energy separation between the lowest n,π* and π,π* triplets of PQ [16], indicated that the lowest energy triplet is dominantly of π,π* character in an ethanol matrix while it is an n,π* state in non-polar matrices [16a], and assigned π,π* character to the T_1 state associated with the reaction of PQ with triethylamine in acetonitrile [16b].



PQ

We have observed that PQ phosphoresces at room temperature in carbon tetrachloride (CCl_4) and acetonitrile (MeCN), thus it was a good candidate for the study of equilibrating triplet states. This paper describes the study of this phosphorescence using time-resolved and steady-state emission spectroscopy. The effects of solvent and temperature were determined. It was possible, for the first time, to directly determine the energy of both the n,π* and π,π* triplets and observe the inversion of these states due to changing solvent polarity in fluid solution.

2. Experimental

9,10-Phenanthrenequinone (PQ)(Aldrich >99%) was used as received. Solvents were UV grade. Samples were deoxygenated by bubbling purified nitrogen for five minutes prior to analysis or through four freeze pump thaw cycles followed by sealing in 10 mm Pyrex ampules on a high vacuum line. Temperature control in emission experiments was obtained by immersing the sample in a bath within a Pyrex dewar fitted with windows. For very low temperature liquid nitrogen was used. For other temperatures heated or cooled ethanol was used.

Steady-state luminescence spectra were obtained on 1.0×10^{-4} M solutions of PQ. A SPEX-Fluorolog 2-Model F111X1 fluorimeter with photo-counting was used in the right angle configuration and spectra were corrected for the instrument response. An excitation wavelength of 412 nm was used for the majority of the spectra but excitation at 346 nm gave the same emission spectra. The band width was ± 1 nm which corresponds to an energy variation of ± 0.1 kcal/mol in the range where PQ first starts emitting. Excitation spectra were in agreement with the absorption spectra of PQ, and emission was only observed from carefully deoxygenated solutions. All emissions were quenched by the addition of air. Emission quantum yields were estimated using quinine sulfate as the reference emitter [17], with application of standard corrections for differences in refractive index [18]. Due to the considerable intensity difference between sample and reference, the excitation and emission slits were opened when analyzing PQ phosphorescence. It was found experimentally that the emission intensity varied with the square of the slit width for both monochromators, as expected [18], and this relation was used to correct the reference intensity to that of the sample.

The time-resolved emission experiments were performed using an Edinburgh Analytical Instruments LP900 time-resolved spectrometer. The third harmonic of a Continuum Surelite II-19 Nd/YAG laser was used for excitation. The 355 nm pulses had an average energy of 40 mJ and a lifetime of 5 ns. The emission was detected by a Hamamatsu R928 photomultiplier and digitalized by a Tektronix TDS520 oscilloscope. The concentrations of PQ in these experiments were between 3×10^{-4} and 4.3×10^{-4} M and no attempt was made to match absorption or laser power. Spectra taken with this instrument were not corrected for the photomultiplier response. The initial intensity of emission was measured at 580 nm using a time resolution of 2 ns per canal and taking the signal from 560 to 960 ns. This signal decay was extrapolated back to time zero. The initial intensities were corrected for the variation in the density and refractive index with temperature using literature values [19].

3. Results

3.1. Steady-state phosphorescence spectroscopy

Room temperature emission was observed from rigorously degassed solutions of 9,10-phenanthrenequinone (PQ) in acetonitrile (MeCN) or carbon tetrachloride (CCl_4). As shown in Fig. 1, the spectrum in MeCN shows two maxima, respectively, at 572 (17 480 cm^{-1}) and 628 nm (15 920 cm^{-1}), the higher energy band corresponds to an energy of 50.0 kcal/mol. In CCl_4 the emission is stronger (the spectra are scaled to allow direct comparison), the bands are better defined and the spectra is slightly shifted to lower energy with maxima at 582 (17 180 cm^{-1}) and 645 nm (15 500 cm^{-1}). The 582 nm band corresponds to an energy of 49.1 kcal/mol. These energies are consistent with PQ triplet energies measured by phosphorescence emission in glassy matrixes at 77 K. A value of 48.8 kcal/mol was found in aliphatic hydrocarbons [20,21], and 51.3 kcal/mol in alcohol [20]. The separation between the bands is 1680 ± 60 cm^{-1} in CCl_4. This is in excellent agreement with the measured IR ground state carbonyl stretching vibration of 1684 cm^{-1} [22]. In MeCN a similar progression is observed, but is poorly resolved. When mixtures of MeCN in CCl_4 are used, there is a linear increase in the energy of the first emission band as a function of the molar fraction of MeCN ($R^2 = 0.991$, Table 1).

Quantum yields of phosphorescence were estimated by comparison with the emission of quinine sulfate. A value of 4.8×10^{-4} was found in CCl_4, while 8.5×10^{-5} was found in MeCN.

It was found that a one to one mixture by volume (at room temperature) of MeCN and CCl_4 (molar fraction of MeCN of 0.65) formed a glass at 77 K. Emission spectra in this mixture at room temperature and 77 K are compared in Fig. 2. The low temperature spectrum is about 15 times more intense and at 0.4 kcal/mol higher energy, the first emission band is at 576 nm at room temperature compared to 569 nm in the glass. Perhaps due to the stronger signal and higher resolution a third vibrational band is observed in the low temperature glass. This third band around 701 nm leads to a progression of 1650 ± 30 cm^{-1} (569, 628, 701 nm) which within experimental error is the same as the room temperature progression. All the data is consistent with the observation of PQ phosphorescence.

Table 1
Wavelength maxima of phosphorescence of PQ as a function of the molar fraction of MeCN in mixtures with CCl_4

Molar fraction of MeCN	0,0 emission (nm)
0	582
0.02	582
0.09	581
0.14	580
0.65	576
0.88	574
1	572

In the room temperature spectra, a weak emission is observed at about 550 nm (Fig. 1), in both CH_3CN and CCl_4. This same band is not observed in the low temperature spectrum (Fig. 2). Similar room temperature bands have been observed previously for other aromatic ketones [23]. They were attributed to delayed fluorescence generated by thermally activated reverse intersystem crossing. In these cases there is a linear relationship between the log of the ratio of thermal fluorescence to phosphorescence intensities and the inverse of the absolute temperature. The slope of the plotted line is a function of the difference between the energies of the lowest singlet and triplet states. In the case of PQ, the relationship between the intensities of the bands as a function of temperature was measured by taking emission spectra at two different temperatures in both CCl_4 and MeCN (Figs. 3 and 4).

In CCl_4 the lower temperature spectrum (−15 °C versus +30 °C, Fig. 3) is about nine times more intense while an even larger temperature differential (−30 °C versus +31 °C, Fig. 4) produces little change in intensity when the solvent

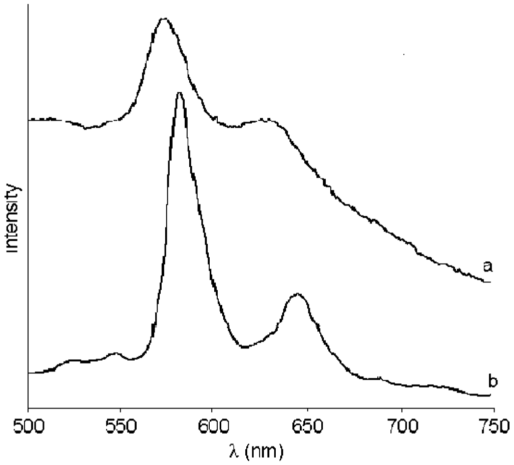


Fig. 1. Phosphorescence spectra of PQ at 298 K in (a) MeCN and (b) CCl_4. The spectrum in MeCN is amplified.

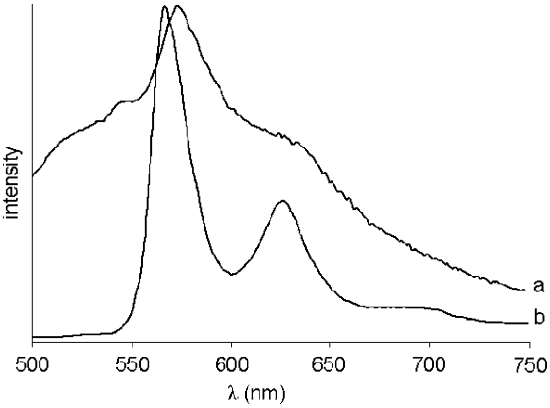


Fig. 2. Phosphorescence spectra of PQ in MeCN/CCl_4 (MeCN molar fraction of 0.65) at (a) 298 K (amplified) and (b) in glass at 77 K.

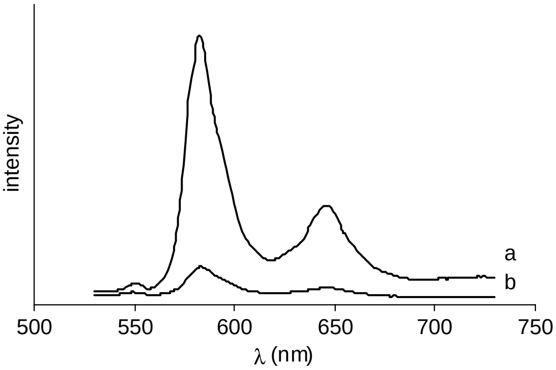


Fig. 3. Phosphorescence spectra of PQ in CCl_4 at (a) 258 K and (b) 313 K.

is MeCN. The spectra in MeCN are not sufficiently resolved to allow analysis of the ratios of the intensities of the bands. The spectra in CCl_4 (Fig. 3) did allow this analysis, and the ratio of the high energy band to the low energy bands increases 3.6 times in the higher temperature spectrum relative to the low temperature spectrum. Using these values an activation energy of 3.7 kcal/mol can be estimated. If we consider that the 550 nm emission corresponds to the lowest singlet state, and 582 nm is the 0,0 band of the lowest triplet state, then the difference between the energies of the lowest singlet and triplet states would be 3.0 kcal/mol. This value is in reasonable agreement with the estimated value of 3.7 kcal/mol obtained using the activation energy, and the evidence indicates that the 550 nm band is indeed due to delayed fluorescence. Considering that the lowest n,π* absorption is at around 500 nm [24], there is a 50 nm Stokes shift between absorption and emission. This corresponds to a singlet state relaxation of about 4 kcal/mol.

3.2. Time-resolved phosphorescence spectroscopy

Time-resolved emission spectra were obtained in CCl_4 (Fig. 5) and MeCN (Fig. 6) using pulsed laser excitation at 355 nm. The spectra are of lower wavelength resolution than the steady-state spectra (Figs. 1–4) but show the same features. In the MeCN spectrum (Fig. 6), the 400–550 nm region does not show the emission seen in the steady-state spectrum (Fig. 1a). The steady-state emission in this region is likely due to the formation of fluorescent products whose fast emission does not appear in the scale of the time-resolved spectrum. In CCl_4 the emission maxima is at 585 nm while in MeCN it is in 575 nm. The weak band at higher energy (550 nm) is observed in both solvents, however at much lower spectral resolution. The 550 nm emission decays at the same rate as the rest of the spectrum for both solvents, as expected for thermally activated delayed fluorescence.

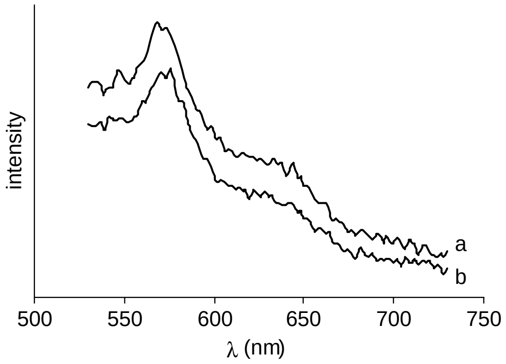


Fig. 4. Phosphorescence spectra of PQ in MeCN at (a) 243 K and (b) 314 K.

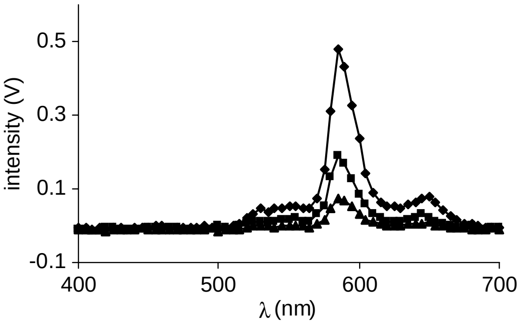


Fig. 5. Transient phosphorescence spectra of PQ in CCl_4 recorded 2, 5 and 8 μs following laser excitation at 355 nm.

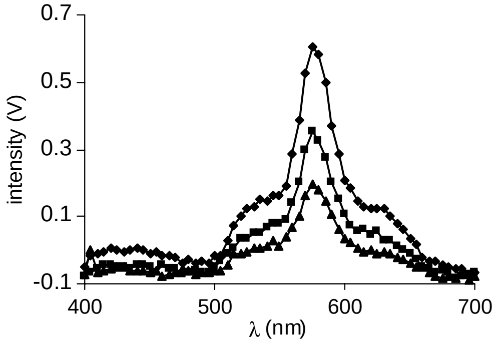


Fig. 6. Transient phosphorescence spectra of PQ in MeCN recorded 1.6, 2.8 and 6.0 μs following laser excitation at 355 nm.

Figs. 7 and 8 show representative emission decays in the two solvents. The emission decay is well represented by a single exponential in both solvents. In MeCN a lifetime of

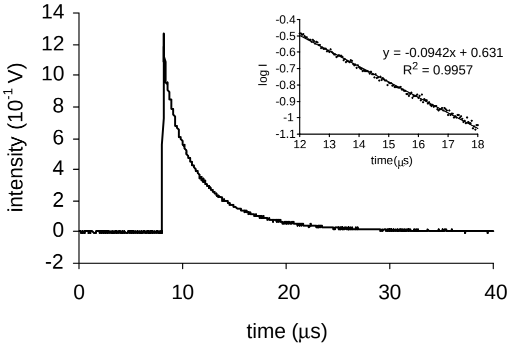


Fig. 7. Phosphorescence decay of PQ in CCl_4 observed at 585 nm.

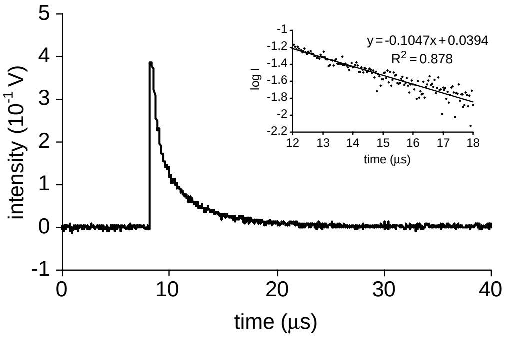


Fig. 8. Phosphorescence decay of PQ in MeCN observed at 580 nm.

3.1 ± 0.6 µs was found (15 observations), it is compared with literature values of 2.2 µs [25], 7.1 µs [26] and 9.6 µs [27] obtained from triplet–triplet absorption time-resolved spectra. The lifetime in CCl_4 was found to be 5.0±2.1 µs (16 observations), a value considerably shorter than the reported lifetime of 62 µs [28]. The lifetimes are typical of room temperature phosphorescence [9], and corroborate the other spectral data.

Using laser induced emission, the intensity of the initial signal was studied as a function of temperature in the range from −2 to 56 °C in CCl_4 (Fig. 9), and from −35 to 52 °C in MeCN (Fig. 10). Since there is the possibility of some PQ consumption in MeCN with consequent diminution of signal, in this solvent (Fig. 10) the experiments were not performed in order of temperature with the intention to minimize the introduction of systematic errors. After correction for changes in density and refractive index due to the temperature changes, the ln of the initial intensity was plotted against the inverse of the absolute temperature. Linear plots were obtained in both CCl_4 (Fig. 9) and MeCN (Fig. 10). An activation energy of 2.38 ± 0.39 kcal/mol was obtained in MeCN, while a negative activation energy of −0.25 ± 0.04 kcal/mol was found in CCl_4.

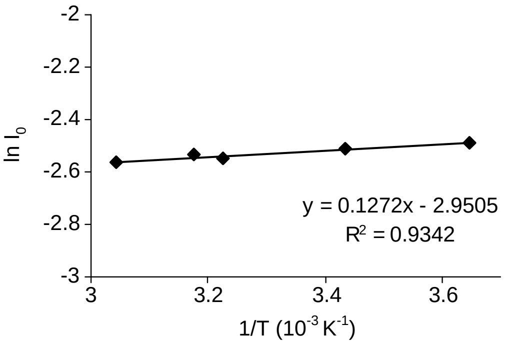


Fig. 9. Temperature dependence of the initial emission at 580 nm (I_0) of PQ in CCl_4 following laser excitation at 355 nm.

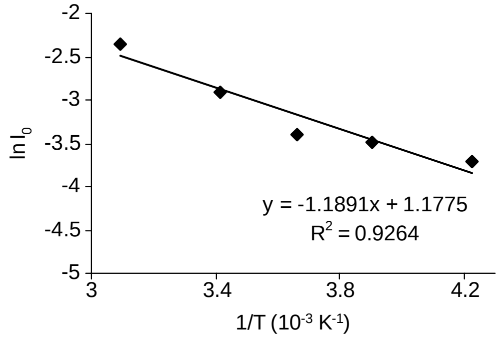


Fig. 10. Temperature dependence of the initial emission at 580 nm (I_0) of PQ in MeCN following laser excitation at 355 nm.

4. Discussion

Three papers have previously presented data on the room temperature phosphorescence of PQ, two in rigid poly(methylmethacrylate) [28–30]. In the first [29], the authors observed a non-exponential time-resolved emission of a single band with a maximum at 475 nm. This spectrum is completely different from the previously published low temperature spectra [20,21], and from the data presented here (Section 3.1). The second paper [30], presents an emission spectrum with bands at 394, 403, 546, and 574 nm. The majority of these bands are at wavelengths too short to be due to PQ phosphorescence. It has been reported that PQ is photoreduced in this polymer [31], and it is possible that the observed emission is in fact due to photochemical products. The third recent paper [28] reports the emission in CCl_4 with a spectrum comparable to that found here in CCl_4 (Section 3.1).

Various lines of evidence indicate that the observed phosphorescence is from an n,π* state. The quantum yield of phosphorescence, Φ_p, in the case for which triplet formation from S_1 is efficient, which is the case of PQ [32], is given by Eq. (1) [9], where k_p is the radiative rate of phosphorescence, k_d represents the sum of all unimolecular deactivations of T_1 and $k_q[Q]$ represents the sum of all bimolecular deactivations of T_1.

$$\Phi_p \sim \frac{k_p}{(k_d + k_q[Q] + k_p)} \qquad (1)$$

From Eq. (1), using the estimated phosphorescence quantum yields (4.8×10^{-4} in CCl_4 and 8.5×10^{-5} in MeCN) and the measured triplet lifetimes, $1/(k_d + k_q[Q] + k_p)$, (5.0 ± 2.1 µs in CCl_4 and 3.1 ± 0.6 µs in MeCN), the calculated radiative lifetimes ($1/k_p$) of PQ are 10 ± 4 ms in CCl_4 and 39 ± 8 ms in MeCN.

The value of 10 ± 4 ms in CCl_4 is within the normal range for n,π* ketones [9]. The vibrational structure [9], and the hypsochromic shift on going to the more polar solvent MeCN [6a,20,33], are also characteristic of n,π* emission (Fig. 1 and Table 1).

It has been observed that n,π* ketones emit at lower energies in non polar fluid solutions than they do in non-polar low temperature glasses [7b,23a,34]. Differences of 1–2 kcal/mol were found, although the same solvents were not used for the room temperature and low temperature studies. The commonly used solvent mixtures in low temperature glasses are not useable at room temperature due to hydrogen abstraction from the solvent by the triplet ketone, giving lowered lifetimes and emission quantum yields. On the other hand, the solvents normally employed for room temperature studies do not form useable low temperature glasses. In this context, the formation of a clear glass from a mixture of MeCN (molar fraction of 0.65) and CCl_4 at the temperature of liquid nitrogen was valuable as it allowed the comparison of room temperature and low temperature spectra in the same solvent (Fig. 2). The observed lowering of 0.4 kcal/mol of the emission of PQ at room temperature (576 nm) relative to the emission at 77 K (569 nm) is in agreement with emission from an n,π^* ketone.

Although the emission is no doubt n,π^* in CCl_4, the data in MeCN are not so clear (Fig. 1). The spectrum in MeCN is not as well defined, and the observed radiative lifetime is somewhat long for an n,π^* triplet (39 ± 8 ms). Broadening and loss of fine structure in phosphorescence spectra are commonly observed for π,π^* triplets in glassy matrices at low temperatures [9], but in the PQ room temperature spectrum in MeCN these may be due to the low quantum yield of emission observed. Phosphorescence from T_1 n,π^* states is commonly observed in fluid solutions, but phosphorescence from T_1 π,π^* states are rarely observed unless extraordinary care is taken to eliminate bimolecular quenching [9]. It was concluded that the emission observed is from an n,π^* state in both solvents.

The longer radiative lifetime, lower quantum yield, and less well-defined spectrum of this n,π^* state triplet in MeCN could be explained in two ways. This emission may be from an n,π^* state "mixed" with some π,π^* character, and in this case state mixing is important and the n,π^* and π,π^* states are expected to be closer in energy in MeCN than in CCl_4. Alternately, this emission could be from a higher n,π^* state in thermal equilibrium with a lower energy π,π^* state, and state mixing is not important. Under these conditions the spectral broadening may be due to the low quantum yield of emission observed.

The second possibility can be verified experimentally. Considering Shimoishi et al.'s indication of a small energy separation between the lowest n,π^* and π,π^* triplets of PQ [16], there is a thermal equilibrium between these two states, and this is reflected in the phosphorescence spectra. The population of each state is a function of the energy gap between them and the temperature, and is described by Eq. (2) [1], where χ_{n,π^*} and χ_{π,π^*} are, respectively, the molar fractions of the n,π^* and π,π^* triplets.

$$\chi_{n,\pi^*} = 1 - \chi_{\pi,\pi^*} = \frac{e^{-\Delta E/RT}}{[1 + e^{-\Delta E/RT}]} \quad (2)$$

The observed phosphorescence quantum yields as a function of the molar fraction of the two triplets are described by Eq. (3), where ϕ_{obs} is the observed phosphorescence quantum yield, ϕ_{n,π^*} is the contribution of the n,π^* triplet, and ϕ_{π,π^*} is the contribution of the π,π^* triplet to the overall emission.

$$\phi_{obs} = \chi_{n,\pi^*}\phi_{n,\pi^*} + \chi_{\pi,\pi^*}\phi_{\pi,\pi^*} \quad (3)$$

Considering that the π,π^* triplet is much less emissive [9], the majority of the emission is due to the n,π^* triplet and the observed phosphorescence quantum yields depend only on the molar fraction of the n,π^* triplet according to Eq. (4).

$$\phi_{obs} = \chi_{n,\pi^*}\phi_{n,\pi^*} \quad (4)$$

The estimated phosphorescence quantum yield of PQ in CCl_4 is 4.8×10^{-4}, while in MeCN it is 8.5×10^{-5}. The lower quantum yield observed in MeCN compared with CCl_4 may be related to a lower population of the n,π^* triplet in this solvent. The observed emission quantum yield may well be higher than the actual phosphorescence quantum yield in MeCN due to the superposition of fluorescence from photoproducts formed by reaction of PQ with this solvent. According to Shimoishi et al. [16b], in MeCN the T_1 state of PQ has π,π^* character, and in this case the observed emission is from the T_2 state. The emission of a n,π^* T_2 state thermally populated, in spite of the lower population, had been observed from some ketones and aldehydes in rigid solutions and in crystal systems at low temperatures [13,35–38]. Thus, in fluid solution at room temperature the emission of a n,π^* T_2 state thermally populated is more probable.

The longer PQ radiative lifetime in MeCN (39 ± 8 ms) may be related to the higher population of the π,π^* state in MeCN, considering that the radiative decay rates of the π,π^* states are expected to be much lower than those of the n,π^* states [9]. The observed radiative lifetime of the two states in equilibrium is given by Eq. (5), where τ_{obs}, τ_{n,π^*} and τ_{π,π^*} are, respectively, the observed "radiative lifetime", the radiative lifetime of the n,π^* triplet and the radiative lifetime of the π,π^* triplet.

$$\frac{1}{\tau_{obs}} = \frac{\chi_{n,\pi^*}}{\tau_{n,\pi^*}} + \frac{\chi_{\pi,\pi^*}}{\tau_{\pi,\pi^*}} \quad (5)$$

To demonstrate that the two lower triplet states of PQ are in thermal equilibrium and to determine if a solvent induced state inversion occurs it is necessary to obtain the energy gap between the two states in both solvents. The latter is related to the molar fraction of the states, see Eq. (2).

Mao and Hirota [38], studying the thermal equilibrium between the lowest π,π^* and the nearby n,π^* triplet states of some aromatic carbonyl molecules, proposed Eq. (6), where I_1 and I_2 are the relative intensities of the emissions, to be applicable to the temperature dependence of the phosphorescence spectra assuming that the emission decay constants from the T_1 and T_2 states, k_1 and k_2, do not depend much on vibrational states.

$$\frac{I_2}{I_1} = \frac{k_2}{k_1}\exp\left(-\frac{\Delta E_T}{RT}\right) \quad (6)$$

A plot of $\log I_2/I_1$ versus $1/T$ should be linear, and should provide from its slope the activation energy, which corresponds to the energy gap between the two states, ΔE_T, if k_1 and k_2 are temperature-independent. Mao and Hirota [38] measured the ratios of the intensities of the peaks (I_2/I_1) corresponding to the 0,0 bands, respectively, of the n,π^* T_2 and π,π^* T_1 states, in the phosphorescence spectra of mixed crystals of 4-chlorobenzaldehyde over the temperature range from 77 to 210 K, and of 4-methoxy-benzaldehyde over the temperature range from 77 to 163 K. In both cases the plots of $\log I_2/I_1$ versus $1/T$ gave satisfactory straight lines. The activation energy determined for 4-chlorobenzaldehyde was very close to ΔE_T determined spectroscopically.

We expect only the n,π^* triplet state of PQ to appreciably emit in fluid solution, as already discussed, and the emission intensity of the π,π^* state can be considered constant. The phosphorescence spectra of PQ in fluid solution are only due to the n,π^* triplet state emission, irrespective of it being the first or the second triplet state. Hence, Eq. (6) is simplified. However, it is known that non-radiative transitions are temperature dependent, principally in fluid solution at temperatures close to room temperature, and a plot of the log (or ln) of the overall emission intensity (or peak intensity) versus $1/T$ would not be a linear function under these conditions. Consequently the interpretation of the temperature effects on the PQ steady-state phosphorescence spectra (Figs. 3 and 4) is not simple. This problem can be resolved using time-resolved emission and measuring the initial intensity (extrapolated to time zero) [39][1] as a function of temperature. In this way k_2/k_1 represents the ratio between the radiative decay rate constants that are not supposed to vary with temperature [40], and a plot of the $\ln I_0$ versus $1/T$ is expected to be a linear function. Consequently the value of the energy gap between the two states, ΔE_T, can be obtained from these plots for each solvent.

The plots of $\ln I_0$ versus $1/T$ gave satisfactory straight lines over the temperature ranges studied for both solvents (Figs. 9 and 10). An activation energy of 2.38 ± 0.39 kcal/mol was determined in MeCN (Fig. 10), while a negative activation energy of -0.25 ± 0.04 kcal/mol was found in CCl_4 (Fig. 9). The activation energies found correspond to the energy gaps between the two lowest triplet states of PQ. The low negative activation energy to emission in CCl_4 indicates that the two triplet states are very close in energy and the emissive n,π^* state is the first triplet state, T_1, in this solvent. The positive value of the activation energy to emission in MeCN indicates that the emissive n,π^* state is the second triplet state, T_2, in this solvent. These results are in accordance to the second mechanism proposed and indicate that state mixing is not important for PQ.

With the values of the activation energies and knowing the energy of the n,π^* state in both solvents (the 0,0 band in the room temperature spectra, Fig. 1) the energy of the π,π^* state is also known. In CCl_4, the n,π^* is the first triplet state with an energy of 49.1 kcal/mol, and the π,π^* state is very close (as it was previously proposed [16]) with an energy of 49.4 kcal/mol. In MeCN there is an inversion of configuration, the lowest state is π,π^* (as it was previously proposed [16b]) with an energy of 47.6 kcal/mol, and the n,π^* state is higher with an energy of 50.0 kcal/mol. These results are summarized in Fig. 11.

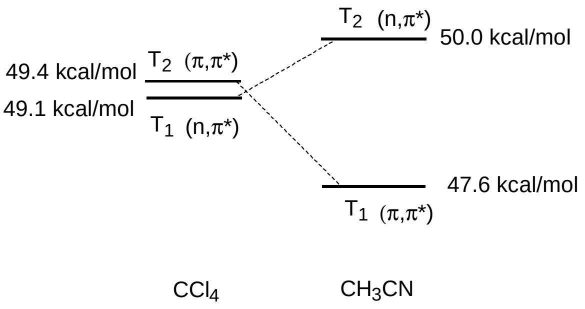


Fig. 11. State energy diagram of the two lowest triplet states of PQ in CCl_4 and in MeCN.

5. Conclusions

The results obtained in this work clearly show that for excited PQ in the solvents and temperatures studied there is an equilibrium mixture of two triplet states very different in nature: an emissive n,π^* state and a non-emissive π,π^* state. In spite of the close proximity of the two states in CCl_4 (almost degenerate with $\Delta E = 87 \pm 14\ \text{cm}^{-1}$) it is clear from the negative activation energy to emission that mixing is not important and the two states are “pure” or “almost pure” in nature. Because it is possible to determine the energy of both states in both solvents it is possible for the first time to determine the effect of solvent on the energy of the first two triplet states in the same molecule in fluid solution. The n,π^* state energy of PQ increases 0.9 kcal/mol, while the π,π^* state energy decreases 1.8 kcal/mol, in changing the solvent from CCl_4 to MeCN at room temperature, causing an inversion of configuration. This is the first time it has been possible to show an inversion of states as a result of a change in solvent in fluid solution.

Acknowledgements

This work was supported by grants from Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação Universitária José Bonifácio (FUJB), and Empresa Brasileira Financiadora de Projetos (FINEP).

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