Solvent effects on the quenching of the equilibrating n,π* and π,π* triplet states of 9,10-phenanthrenequinone by 2-propanol

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Abstract

Quenching of the triplet state of 9,10-phenanthrenequinone (PQ) by 2-propanol was studied using laser flash photolysis. The room temperature rate constant is solvent dependent and is $3.3(\pm1.1) \times 10^8 \, M^{-1} \, s^{-1}$ in carbon tetrachloride (CCl_4), $1.2(\pm0.3) \times 10^8 \, M^{-1} \, s^{-1}$ in chlorobenzene (CB), and $2.5(\pm0.8) \times 10^7 \, M^{-1} \, s^{-1}$ in acetonitrile (MeCN). The rate constant in CCl_4 is the largest known for abstraction of hydrogen from 2-propanol by an excited ketone. An activation energy of $0.017(\pm0.006) \, kcal/mol$ and a pre-exponential A factor of the Arrhenius equation of $4.45 \times 10^8 \, M^{-1} \, s^{-1}$ was found in CCl_4; an activation energy of $2.14(\pm0.006) \, kcal/mol$ and an A factor of 4.5×10^8 was found in MeCN. These results are consistent with a mechanism involving a reactive n,π* triplet in thermal equilibrium with a non-reactive π,π* triplet, and are in agreement with a previous study of the room temperature phosphorescence of PQ showing that the lowest energy triplet is n,π* in CCl_4 but π,π* in MeCN.
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1. Introduction

We recently studied the fluid solution phosphorescence emission of 9,10-phenanthrenequinone (PQ) in both a polar solvent, acetonitrile (MeCN), and a non-polar solvent, carbon tetrachloride (CCl_4), and were able to measure the energies of both the n,π* and π,π* triplets [1]. It was shown that these two states are close in energy and there is an inversion of the configuration with this change in solvent, the lowest energy triplet, T_1, being n,π* in CCl_4 and π,π* in MeCN. This is demonstrated in the energy diagram shown in Fig. 1.

It is known that PQ is photochemically reactive and that the excited triplet abstracts hydrogen atoms from a large range of donors [2–6]. When alcohols such as 2-propanol are used 9,10-dihydroxyphenanthrene (PQH_2) is formed (Scheme 1) [7].

For aromatic ketones which have n,π* and π,π* triplets close in energy, the observed reactivity for hydrogen abstraction from suitable donors such as 2-propanol is considered to be due to the population of the n,π* state in the thermal equilibrium [8]. The measured reactivity is the product of the intrinsic reactivity and the relative population of each state in thermal equilibrium, given by Eq. (1), where k_{obs} is the observed rate constant for hydrogen abstraction, $\chi_{n,\pi*}$ and $\chi_{\pi,\pi*}$ are respectively the molar fractions of the n,π* and π,π* states, and $k_{n,\pi*}$ and $k_{\pi,\pi*}$ are the intrinsic rate constants for each state [8]. The n,π* state provides most or all of the reactivity when $\Delta E \, (E_{n,\pi*} - E_{\pi,\pi*}) < 5 \, kcal/mol$ [8].

$$k_{obs} = \chi_{n,\pi*}k_{n,\pi*} + \chi_{\pi,\pi*}k_{\pi,\pi*} \qquad (1)$$

The knowledge of the energies of both triplet states in polar and non-polar solvents permits the calculation of the relative population of both states at a given temperature, according to Eq. (2) [8], and the analysis of the intrinsic reactivity of each

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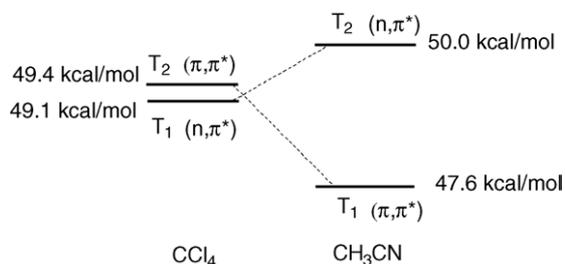
Fig. 1. State energy diagram of the two lowest triplet states of PQ in CCl$_4$ and in MeCN.
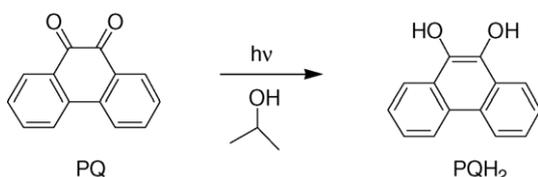
Scheme 1.

triplet. This had not been possible until now in fluid solution where ketone reactivity is studied, because the experimental measurement of the energies of both states and therefore the relative population of each state had not been reported before for other aromatic ketone. In those cases studied, the energy of the second state had only been estimated [9–11]. It was not possible to measure the intrinsic reactivity of the n,π^* state of aromatic ketones when this state is higher in energy than the π,π^* state or when the two triplets are close in energy.

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

This paper presents a study of the photochemical reactivity of PQ towards hydrogen abstraction from 2-propanol in CCl$_4$ and MeCN. Using laser flash photolysis the rate of quenching of the triplet of PQ by 2-propanol was measured as a function of temperature. The results are discussed in terms of the individual contributions of the n,π^* and π,π^* states to the observed reactivity.

2. Experimental

9,10-Phenanthrenequinone (PQ) (Aldrich 99+%) was used as received. Solvents were UV grade. Samples were deoxygenated by bubbling purified nitrogen for 5 min prior to analysis or through four freeze pump thaw cycles followed by sealing in 10 mm Pyrex ampules on a high vacuum line.

The laser flash photolysis system was 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 used as the excitation source of PQ had an average energy of 40 mJ and a lifetime of 5 ns. Triplet–triplet absorption and phosphorescence

emission were detected by a Hamamatsu R928 photomultiplier digitized by a Tektronix TDS520 oscilloscope.

The measured decays of PQ triplet as a function of PQ concentration, used in the self-quenching experiment, were from the emission at 580 nm using "front face" geometry between the laser pulse and the analysis train, obtained with a 45° rotated and inclined sample holder furnished by the system manufacturer. All other experiments used right angle geometry. The decays of PQ triplet as a function of 2-propanol concentration used in the Stern–Volmer plots were obtained from the emission at 580 nm in carbon tetrachloride or chlorobenzene (CB), and from absorption at 680 nm in acetonitrile. The rate constants in the Arrhenius plots were obtained from the emission at 580 nm in both carbon tetrachloride and acetonitrile. Temperature control was obtained by immersing the samples in a bath of heated or cooled ethanol within a Pyrex dewar. The concentrations of PQ were in the range $(1–10) \times 10^{-4}$ M in MeCN in the experiment of self-quenching, and were 3×10^{-4} M in CB and MeCN, and 4.3×10^{-4} M in CCl$_4$ in the other experiments.

3. Results

The transient T–T absorption spectra of PQ were obtained in CCl$_4$, CB and MeCN (Fig. 2). The spectra in CCl$_4$ and CB show an absorption band with λ_{max} 460 nm. In MeCN there is a corresponding band with λ_{max} 470 nm and an additional band with λ_{max} 680 nm and a shoulder in the 600–650 nm region. The lifetimes of the absorptions in CCl$_4$ and MeCN were the same as the lifetimes of decay of the emission shown to be due to phosphorescence [1]. The decay of the PQ triplet in MeCN at 470 nm is shown in Fig. 3 and at 680 nm in Fig. 4. Data of the T–T absorption of PQ in MeCN have been previously reported [12–14].

The lifetime of the PQ triplet in MeCN decreased with an increase in the PQ concentration (Fig. 5), indicating self-quenching in this solvent. The self-quenching rate constant k_{sq} was obtained from the linear relationship found when the
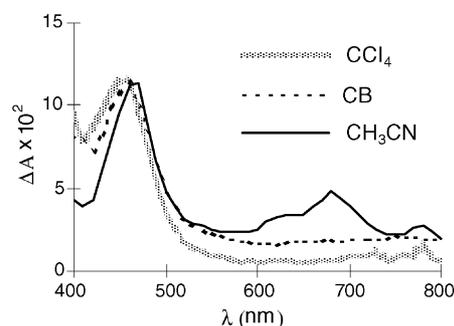
Fig. 2. Triplet–triplet transient absorption spectra of PQ in carbon tetrachloride (CCl$_4$), chlorobenzene (CB), and acetonitrile (MeCN) were recorded respectively 0.7, 0.4 and 0.43 µs following laser excitation at 355 nm. The Y axis values of ΔA refers to the spectrum in CCl$_4$; the spectra in CB and MeCN were reduced respectively 1.5 and 1.3 times.
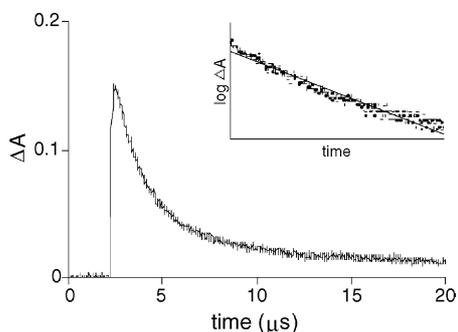
Fig. 3. T–T absorption decay of PQ in MeCN monitored at 470 nm. (Inset) Fit for first-order decay, $k_d = 4.44(\pm 0.29) \times 10^5\,\mathrm{s}^{-1}$, $r^2 = 0.79$.
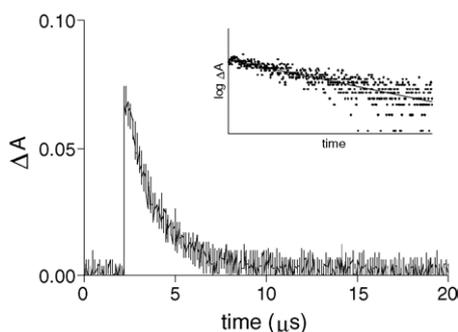
Fig. 4. T–T absorption decay of PQ in MeCN monitored at 680 nm. (Inset) Fit for first-order decay, $k_d = 4.77(\pm 0.15) \times 10^5\,\mathrm{s}^{-1}$, $r^2 = 0.66$.

first-order triplet decay constants were plotted against the PQ concentration (Fig. 5). A value of $2.0(\pm 0.2) \times 10^8\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ was found.

The rates of quenching of the PQ triplet by 2-propanol in these three solvents of differing polarity were measured. These solvents were chosen because they are poor hydrogen donors (CB and MeCN) or non-donor (CCl$_4$). The respective rate constants were found by measuring the rate of triplet decay as a function of the 2-propanol concentration using emission at 580 nm in the case of CCl$_4$ and CB, and T–T absorption at 680 nm when MeCN was studied because the emission intensity of PQ in MeCN was much less intense. The triplet decay fit to a single mono-exponential decay in all cases. Fig. 6 shows the Stern–Volmer plots of the triplet decay versus the 2-propanol concentration for all three solvents. The
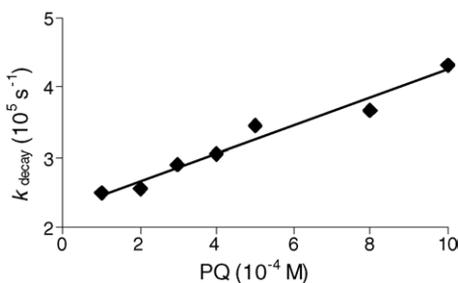
Fig. 5. Plot of the pseudo-first-order rate constant for triplet decay vs. the concentration of PQ in acetonitrile observed from emission at 580 nm.
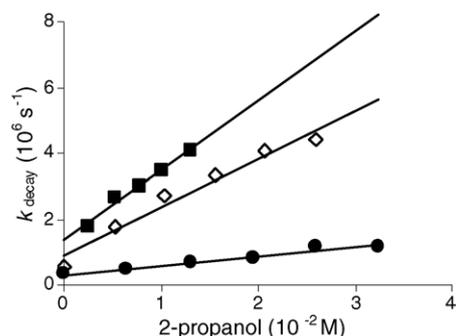
Fig. 6. Stern–Volmer plots of the rate of PQ triplet decay as a function of 2-propanol concentration in (■) CCl$_4$, (◇) CB and (●) MeCN.

Table 1
Quenching rate constants and Arrhenius parameters for the reaction of the PQ triplet with 2-propanol

Solvent	k_r (M^{-1} s^{-1})	E_a (kcal/mol)	A (M^{-1} s^{-1})
CCl$_4$	$3.3(\pm 1.1) \times 10^8$	$0.017(\pm 0.006)$	$4.45(\pm 0.04) \times 10^8$
CB	$1.2(\pm 0.3) \times 10^8$		
MeCN	$2.5(\pm 0.8) \times 10^7$	$2.14(\pm 0.06)$	$4.5(\pm 0.5) \times 10^8$
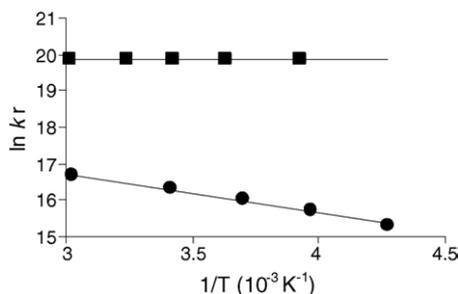
Fig. 7. Arrhenius plots for the reaction of PQ triplet with 2-propanol in (■) CCl$_4$ and (●) MeCN.

second order rate constants shown in Table 1 are the result of four measurements in CCl$_4$ and MeCN, and three in CB.

Considering that the quenching of the PQ triplet by 2-propanol is due to hydrogen abstraction, the rate constant observed in the non-polar solvent CCl$_4$ is very large but decreases with increasing solvent polarity (Table 1).

The activation energies for this reaction in CCl$_4$ and MeCN were found by measuring the rate of the reaction as a function of temperature in the range from -20 to $60\,^{\circ}$C for CCl$_4$ and from -42 to $60\,^{\circ}$C for MeCN. The Arrhenius plots are shown in Fig. 7. The activation energies and pre-exponential values are given in Table 1.

4. Discussion

The spectra in Fig. 2 were assigned as PQ triplet–triplet absorption spectra. They showed mono-exponential decays

in MeCN, CB and CCl_4 (Figs. 3 and 4) with the same lifetimes observed when phosphorescence emission was used [1]. The longest wavelength band observed in MeCN (Fig. 2) has been seen for PQ in benzene [15].

It appears that π,π^* excited states are more prone to self-quenching (quenching of the excited triplet state by the ground state) than n,π^* triplets [16]. Benzophenone which is clearly n,π^* has a self-quenching rate constant of $7.5 \times 10^5\,M^{-1}\,s^{-1}$ in MeCN [17] while xanthone, which has a lowest π,π^* triplet, is self-quenched with a rate of $7.5 \times 10^8\,M^{-1}\,s^{-1}$ in MeCN [9]. The value of $2 \times 10^8\,M^{-1}\,s^{-1}$ found here for the rate of self-quenching of PQ in MeCN (Fig. 5) is only slightly smaller than the literature value for xanthone and is indicative of a π,π^* excited state. This is in agreement with time-resolved phosphorescence studies [1] which indicate that in MeCN the n,π^* triplet is 2.4 kcal/mol above the lowest π,π^* triplet. At room temperature the π,π^* triplet would be 98% of the triplet population calculated by Eq. (2). It would be interesting to measure the self-quenching rate constant in CCl_4 where PQ has a lowest n,π^* triplet with the n,π^* and π,π^* triplets very close in energy [1] but this was not possible due to the limited solubility of PQ in CCl_4. Self-quenching did not affect the other quenching experiments reported here because low concentrations of PQ were used and short lifetimes were observed.

The rate constants for the quenching of PQ triplets by 2-propanol are large in the three solvents studied here. Considering that the quenching of the excited triplet of PQ by 2-propanol is due to hydrogen abstraction, it was found that the rate of this reaction decreased with an increase in solvent polarity (Fig. 6 and Table 1). This tendency had previously been reported using benzene and MeCN [12]. The value found in benzene of $1.6 \times 10^8\,M^{-1}\,s^{-1}$ is close to that found here ($1.2 \times 10^8\,M^{-1}\,s^{-1}$) in chlorobenzene. However the value of $7.6 \times 10^6\,M^{-1}\,s^{-1}$ found by Barra et al. in MeCN is lower than that found here ($2.5 \times 10^7\,M^{-1}\,s^{-1}$).

We know of no ketone with a rate of hydrogen abstraction from 2-propanol as large as that measured here (Table 1). The xanthone triplet, which is considered to be very reactive in non-polar solvents, has a rate constant of abstraction from 2-propanol in CCl_4 of $1.1 \times 10^8\,M^{-1}\,s^{-1}$ [9]. This value is about three times less than the rate of the reaction of the PQ triplet with 2-propanol in the same solvent. It was found, using phosphorescence, that in CCl_4 the n,π^* triplet is 0.25 kcal/mol lower in energy than the π,π^* state [1]. Using this value and Eq. (2), the population of the reactive PQ n,π^* triplet is then about 60% in the equilibrium mixture at room temperature. Considering that reaction is from the n,π^* state, then the intrinsic rate is even larger and is calculated to be $5.5(\pm2.0) \times 10^8\,M^{-1}\,s^{-1}$.

The PQ triplet is 10 times less reactive towards hydrogen abstraction from 2-propanol in MeCN (Table 1). In MeCN the n,π^* triplet was found to be 2.4 kcal/mol higher in energy than the π,π^* state [1]. At room temperature the equilibrium mixture would then contain about 2% of the n,π^* triplet,

calculated from Eq. (2), which explains the lower reactivity observed in this solvent. The calculated intrinsic rate constant in MeCN is then $2.1(\pm1.6) \times 10^9\,M^{-1}\,s^{-1}$.

For ketones in which the lowest excited triplet is π,π^*, hydrogen abstraction from a thermally accessible higher energy n,π^* triplet is proposed to explain the observed reactivity. Since until now it has been impossible to measure the energy separation between the states, values of the activation energy for hydrogen abstraction have been used to estimate the energy separation, considering that this energy would be added to the normal activation energy of abstraction by the n,π^* triplet [8–10,18–20]. In the case of PQ, for the first time, the energies of both triplets are known in both CCl_4 and MeCN. The activation energy for hydrogen abstraction from 2-propanol in CCl_4, obtained here, is essentially zero (Table 1). The activation energy for hydrogen abstraction in MeCN of $2.14(\pm0.06)$ kcal/mol is the same as the previously measured [1] energy difference between the π,π^* and n,π^* triplets of $2.4(\pm0.4)$ kcal/mol within experimental error and all of the activation energy can be assigned to the energy cost of reaching the higher n,π^* state in this solvent. There is basically no activation energy for hydrogen abstraction from the n,π^* triplet in either solvent, which explains, in part, the high rates observed.

The benzophenone triplet abstracts a hydrogen atom from 2-propanol in benzene with a rate constant of $1.8 \times 10^6\,M^{-1}\,s^{-1}$ [21]. The activation energy is 2.6 kcal/mol and the pre-exponential factor A is $1.5 \times 10^8\,M^{-1}\,s^{-1}$ (dividing $2.0 \times 10^9\,s^{-1}$ by 13 M) with 2-propanol as the solvent [22]. Benzophenone is a 100-fold less reactive than PQ and this is mostly due to the difference in activation energy as the pre-exponential factors are not that different. The pre-exponential factors for PQ for this reaction are slightly higher ($4.5 \times 10^8\,M^{-1}\,s^{-1}$ in MeCN) and, within experimental error, the same in both solvents (Table 1). The pre-exponential factor found for PQ is a clear indication that reaction occurs from the n,π^* state in both solvents. It would be expected that n,π^* states would have larger pre-exponential values than π,π^* states and that orbital mixing due to vibronic coupling would lower the pre-exponential factors of n,π^* states with some π,π^* character relative to "pure" n,π^* states [17,18]. In the present case, considering the closeness of the two states in CCl_4 some vibronic coupling might be expected. The high reactivity and the large value of the pre-exponential value indicate that this is not occurring. All the evidence points to reactivity from "pure" n,π^* states in both solvents.

Three factors which influence the rate of hydrogen abstraction of n,π^* excited ketone triplets are, the nature of the H–X bond being broken (here H–C in 2-propanol), the triplet energy, and the reduction potential of the ground state ketone [21]. Wagner and coworkers have found that substituted benzophenones with lowest n,π^* triplet states show a good correlation between the log of k_r and the reduction potential of the triplet state E_{red}^* [23,24], where k_r is the rate of hydrogen abstraction of the ketone triplet from cyclopentane and E_{red}^*

is obtained from Eq. (3).

$$E_{red}^* = E_T + E(A^-/A) \qquad (3)$$

Here E_T is the triplet energy and $E(A^-/A)$ is the half-wave reduction potential of benzophenone in the ground state [23]. The more easily reduced benzophenones abstract from cyclopentane more rapidly. A small degree of stabilization of the transition state due to charge transfer was suggested [24]. When 2-propanol is the hydrogen donor this type of stabilization of the transition state would be expected to be even more important in lowering the activation energy. The reduction potential of the triplet state of PQ calculated from Eq. (3) using the triplet energy in CCl_4 and the ground state reduction potential of $E(A^-/A)$ of 15.4 kcal/mol [25] is $E_{red}^* = 33.6$ kcal/mol. This value is greater than that calculated for benzophenone which is $E_{red}^* = 27.1$ kcal/mol. The high reactivity of PQ would then be related to the high reduction potential of the excited n,π^* triplet state.

5. Conclusions

The reactivity of the PQ triplet towards hydrogen abstraction from 2-propanol is consistent with reaction from an n,π^* excited state in thermal equilibrium with a non-reactive π,π^* triplet. The energies of both triplets in both MeCN and CCl_4 have previously been measured using PQ phosphorescence [1]. In that study, it was found that the two triplets are almost iso-energetic in CCl_4 with the n,π^* triplet at slightly lower energy. In MeCN the lowest triplet is π,π^*. The rate of hydrogen abstraction is proportional to the population of the n,π^* triplet in equilibrium with the π,π^* triplet in both solvents. No reactivity of the π,π^* triplet was observed even in MeCN where the π,π^* state is the lowest triplet. The intrinsic rate (correcting for the n,π^* population) is the same in both solvents and is essentially the same as the pre-exponential rate factor, A, of the Arrhenius equation. There is basically no activation energy for this reaction. The lower rate of reaction observed in MeCN is entirely due to the lower equilibrium population of the n,π^* triplet in this solvent. Further there is no evidence of reduced reactivity of the n,π^* triplet in CCl_4 due to vibronic coupling of states even though they are very close in energy in this solvent.

Acknowledgments

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